USING NANOFLOUIDS FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) COOLING IN AUTOMOTIVE APPLICATIONS

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy (PhD)

Mohammad Rafiqul Islam
M.Eng.Sc

School of Engineering
College of Science, Engineering and Health
RMIT University
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DEDICATION

Dedicated to my beloved brother, late Dr Sofiqul Alam, for his unconditional support and inspiration
DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Mohammad Rafiqul Islam
August 2016
ACKNOWLEDGEMENT

In the last three and half years, it was fascinating for me to be engaged with a good number of academics and students in different research fields at RMIT University. Now, I would like to take this opportunity to express my gratitude to all.

At first, I would like to express my utmost respect and gratitude to my senior supervisor Dr Bahman Shabani who at our first meeting introduces himself as a colleague in very friendly manner. That few words encouraged me a lot, and I always remember those throughout my life. This research work would have never been completed without his invaluable guidance, encouragement, extraordinary patience, perseverance, and insightful comments. I am particularly indebted and grateful to him for his valuable time and efforts spent in editing this thesis. I would also like to express my gratitude to my second supervisors Professor Gary Rosengarten and Professor John Andrews for their knowledgeable guidance throughout my PhD candidature.

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<tr>
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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cells</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BEVs</td>
<td>Battery Electric Vehicles</td>
</tr>
<tr>
<td>bMt</td>
<td>Billion Metric Tons</td>
</tr>
<tr>
<td>BMW</td>
<td>Bavarian Motor Works</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon Capture and Storage</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined heat and power</td>
</tr>
<tr>
<td>DAC</td>
<td>Direct Absorption Collector</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct Methanol Fuel Cells</td>
</tr>
<tr>
<td>DoE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>D-SWNT</td>
<td>Dispersed Single Walled Nano-Tubes</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>EVS</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>FCEV</td>
<td>Fuel Cell Electric Vehicle</td>
</tr>
<tr>
<td>FCV</td>
<td>Fuel Cell Vehicle</td>
</tr>
<tr>
<td>FCX</td>
<td>Fuel Cell Experimental</td>
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<tr>
<td>F-SWNT</td>
<td>Functionalized Single Walled Nano-Tubes</td>
</tr>
<tr>
<td>GFC</td>
<td>Regenerative Fuel Cells</td>
</tr>
<tr>
<td>GHG</td>
<td>Green House Gas</td>
</tr>
<tr>
<td>GW</td>
<td>Giga Watt</td>
</tr>
<tr>
<td>HE</td>
<td>Heat Exchanger</td>
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<td>Hybrid Electric Vehicles</td>
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<tr>
<td>HHV</td>
<td>Higher Heating Value</td>
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<tr>
<td>HOR</td>
<td>Hydrogen Oxidation Reaction</td>
</tr>
<tr>
<td>HT</td>
<td>High Temperature</td>
</tr>
<tr>
<td>ICEs</td>
<td>Internal Combustion Engines</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>IEO</td>
<td>Independent Evaluation Office</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>ITD</td>
<td>Initial Temperature Difference</td>
</tr>
<tr>
<td>LMTD</td>
<td>Logarithmic Mean Temperature Difference</td>
</tr>
<tr>
<td>LT</td>
<td>Low Temperature</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten Carbonate Fuel Cells</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
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<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro Electro-Mechanical Systems</td>
</tr>
<tr>
<td>MFC</td>
<td>Microbial Fuel Cells</td>
</tr>
<tr>
<td>Mtoe</td>
<td>Million Tonnes of Oil Equivalent</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi Walled Carbon Nano-Tubes</td>
</tr>
<tr>
<td>NTU*</td>
<td>Number of Transfer Unit</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation of Economic Co-operation and Development</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxidation reduction reaction</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric Acid Fuel Cells</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange or Polymer Electrolyte Membrane Fuel Cell</td>
</tr>
<tr>
<td>PGS</td>
<td>Pyrolytic graphite sheet</td>
</tr>
<tr>
<td>PHEV</td>
<td>Plug-In Hybrid Electric Vehicle</td>
</tr>
<tr>
<td>Pt/C</td>
<td>Platinum catalysts</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>PZC</td>
<td>Point Of Zero Charge</td>
</tr>
<tr>
<td>SBIR</td>
<td>Small Business Innovation Research</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cells</td>
</tr>
<tr>
<td>SUVs</td>
<td>Sport Utility Vehicles</td>
</tr>
<tr>
<td>TWh</td>
<td>Terra Watt hour</td>
</tr>
<tr>
<td>U.S.</td>
<td>United States</td>
</tr>
<tr>
<td>ULEV</td>
<td>Ultra Low Emission Vehicles</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change</td>
</tr>
<tr>
<td>ZAFC</td>
<td>Zinc Air Fuel Cells</td>
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NOMENCLATURE

Q  Generated Heat from PEMFC
U  Overall heat transfer coefficient
A  Heat transfer area
ΔT  Temperature difference between coolants and ambient
H₃O⁺  Hydronium ions
Pt  Platinum
Wₑ  Maximum electric work
ΔG  Gibb’s free energy
n  Number of electrons participating in the reaction
h  Hour
F  Faraday’s constant
E  Ideal open circuit potential
ΔH  Difference between the heats of formation of products and reactants
ΔS  Difference between entropies of products and reactants
pH  The acidity or alkalinity of an aqueous solution
K  Thermal conductivity of nano-fluids
Re  Reynolds number
Pr  Prandtl number
v  Mean velocity of the object relative to the fluid
L  The characteristic linear dimension
h  Convection heat transfer co-efficient
Nu  Nusselt number
Pe  Peclet number
Cₚ  Specific heat
m  Mass of fluid
Vₑ  Output voltage
E_{Nernst}  Nernst energy
ΔV_{ohm}  Ohmic overpotential
ΔV_{act}  Activation overpotential
ΔV_{trans}  Concentration overpotential
E₀  EMF at standard pressure and temperature
R  Universal gas constants
P_H₂  Partial pressures of hydrogen
$P_{O_2}$ Partial pressures of oxygen

$P_{H_2O}$ Partial pressures of water

$P_{air}$ Cathode pressure

$i_0$ Exchange current density

$i$ Current density

$r$ Area-specific resistance including contact, ionic and electronic

$k$ The mass transport constant

$i_L$ The limiting current density

$A$ The active area of a single cell

$N$ The number of cells in a PEMFC stack

$m_{H_2, out}$ The unused mass of hydrogen

$T_s$ The stack temperature

$T_{in}$ The atmospheric temperature

$m_{air, out}$ The unused mass of hydrogen

$S_{O_2}$ The oxygen stoichiometric ratio

$M_{O_2}$ Molecular weight of oxygen

$M_{N_2}$ Molecular weight of nitrogen

$r_{O_2, in}$ Mole fraction of oxygen in air

$m_{H_2O, out}$ The generated water from hydrogen oxygen reaction

$h_{fg}$ Enthalpy of water at gas phase

$M_{H_2O}$ Molecular weight of water

$P_{H_2O, s}$ Saturation pressure of water at stack temperature

$P_{ca}$ Cathode pressure

$\Delta P_{ca}$ The pressure difference between cathode and atmosphere

$C_{min}$ The minimum heat capacity rate

$C_{max}$ The maximum heat capacity rate

$C^*$ The ratio of the minimum heat capacity rate to the maximum heat capacity rate

$G_{air}$ The core mass velocities of air

$G_c$ The core mass velocities of coolant

$\Delta P^*_i$ The target pressure drop at air and coolant sides

$r_{ha}$ The air side flow passage hydraulic radius
GREEK SYMBOLS

\[ \eta_p \] Pump efficiency
\[ \mu \] Dynamic viscosity of the fluid
\[ \rho \] Density of the fluid
\[ \varepsilon \] The target effectiveness.
\[ \alpha \] Thermal diffusivity
\[ \alpha_1 \] The amplification constant
\[ \alpha_e \] Charge transfer coefficient
\[ \nu \] Kinematic viscosity
\[ \Phi \] Volume fraction of nanoparticle in the nanofluids
### SUBSCRIPTS AND SUPERSCRIPTS

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<td>Activation</td>
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<tr>
<td>air</td>
<td>Air</td>
</tr>
<tr>
<td>b</td>
<td>Base fluid</td>
</tr>
<tr>
<td>ca</td>
<td>Cathode</td>
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<td>Electric load</td>
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EXECUTIVE SUMMARY

Globally, the transportation sector is one of the highest energy consuming sectors, while the light duty vehicles alone consumes more than that of all other modes of transportation. Moreover, transportation is the fastest growing sector in terms of energy consumption, forecasting an increase in energy demand of 50% in this sector by 2020. Apart from the energy consumption, the transport sector contributes to GHG emissions production significantly all over the world. With the present situation of increasing energy demand, rising energy prices, climate change, and shortage of oil supply, it is critical to find out an alternative to fossil fuels, especially for petroleum fuels, from economic, environmental, and social perspectives. In order to cope with the increasing demand of fuel and to slow down the current trend of climate change, several alternatives are being considered. This includes, but not limited to biofuels driven vehicles, battery electric vehicles, plug-in electric vehicles, plug-in hybrid electric vehicles, and hydrogen fuel cell cars. However, while these technologies offer opportunities to address the above-mentioned problems, each come with their own technological shortfalls and/or challenges. Hydrogen fuel cell technology, that is the focus of this study, is seen to be a strong alternative to play a significant role as part of this technological mix.

Due to the combination of climate change and health concerns, the hydrogen fuel cell technology is considered to be an important sustainable technology since the fuel cell generates electricity through an electrochemical oxidation of hydrogen without emitting any GHG. Hence, the combination of this technology with renewables such as wind and photovoltaic (i.e. to generate hydrogen) can clear the entire chain of hydrogen production and consumption off GHG emissions. Highly efficient, intrinsically clean converters such as fuel cells are adaptable to a wide range of energy-consuming applications including vehicles. For such applications high power density and high dynamic response in combination with short start-up times are essentials. Proton Exchange Membrane Fuel Cells (PEMFCs) are considered as a potential replacement for Internal Combustion Engines (ICEs) in automotive applications due to the fact that they offers high volumetric power density, rapid start-up, low operating temperature, and high electrical energy conversion efficiency over the other types of fuel cells.

Considering the advantages of PEMFCs, some renowned automotive manufacturers (i.e. Toyota, Honda, Hyundai and BMW) have already started developing fuel cell driven vehicles, some of which are commercially produced. This is while the challenges associated
with this technology are still being addressed for further improvement and take full advantage of what can be offered by this technology. One of these challenges is the enlarged radiator required for fuel cell cooling that in turn restricted the manufacturer to employ higher power fuel cells in their products. Although PEMFCs have a relatively high electrical energy conversion efficiency (i.e. 30-50%), they still generate almost equal or more heat than that of the generated power. Main part of this heat, known as fuel cell cooling load, can be up to about 100 kW or more in medium size passenger cars running on PEMFCs. This heat must be effectively removed to avoid overheating of FC components, especially its membrane. Considering the operating temperature range of PEMFCs (60-80 °C), the temperature difference between the coolant and ambient is usually small. This temperature difference is obviously dictated by the type of the fuel cell and the ambient temperature and hence, cannot be controlled in favour of enhancing the heat transfer rate. Hence, due to such a small temperature difference, the area of the heat exchanger should be increased to ensure that the fuel cell cooling load rejected effectively. Increasing the heat transfer area (i.e. the radiator size) can then suggest packaging implication within the engine compartment while it is not favourable from the vehicle overall mass point of view.

Although today’s PEMFCs are offering superior power densities, highly competitive with those commonly seen in ICEs (i.e. 3.7 kW/l), the relatively larger PEMFC cooling system sizes (i.e. the radiator) has remained to be a key area that needs further attention.

A nanofluid is a suspension of nano-scaled (<100 nm) particles (e.g. Al₂O₃, TiO₂ and ZnO) in a base fluid (e.g. water, ethylene glycol, mixture of water-ethylene glycol, engine oil, etc.) that are known for their improved heat transfer characteristics. Hence, they can be potential candidates to address the PEMFCs heat transfer challenge in automotive applications. A substantial increase in thermal conductivity and heat transfer coefficient are the unique features of nanofluids. The mechanism of improvement in the thermal properties of nanofluids is not limited to the effect of their enhanced thermal conductivity only (i.e. due to the presence of the nanoparticles). Complex intervention of the particles within the boundary layer of the fluid (moving close to the surface) plays an important role in enhancing their convection heat transfer factor. Using a coolant with enhanced overall heat transfer coefficient can offer a solution to the challenges associated with fuel cell cooling in vehicle application (i.e. large radiator). This can offset the negative effect of low temperature difference between the coolant and ambient.

Nanofluids also offer opportunities to eliminate the use of de-ionising filter in the cooling loop of PEMFCs. This advantage also helps reducing the size and weight of the cooling
system. When conventional fluids (e.g. water) are used as coolants, it is necessary to use a de-ionising filter in the fuel cell cooling loop though initially the coolant is de-ionised. However, when using nanofluids in the PEMFCs cooling system, some potential challenges such as stability of nanofluids and electricity leakage through the coolants also need to be addressed.

This present research studied the potential and challenges associated with using nanofluids as coolants in PEMFC cooling system with a view to addressing challenges with the cooling system design of PEMFCs in automotive applications. Following this aim the objectives of the study was to:

- study the electrical and thermo-physical characteristics of nanofluids with a view to identifying suitable nanofluids for use as PEMFC coolants;
- theoretically analyse the performance of nanofluids as coolants in PEMFCs cooling system by using a computer simulation model created as part of this research;
- investigate experimentally the feasibility of using nanofluids as coolants in PEMFCs and identify the potential and challenges associated with this cooling method;
- quantify the effect of using nanofluids as coolants on the thermal and electrical performances of PEMFCs;
- make recommendations for future research on using nanofluids as PEMFC coolant in automotive applications.

Based on these research objectives, the following research questions were addressed:

- What role the volume fraction, and type of the nanoparticles play in determining the electrical and thermal properties of nanofluids in the context of them being used as PEMFC coolant?
- What potentials and challenges nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performance of PEMFCs?
- How much the electrical and thermal performances of PEMFCs are affected by using nanofluids as coolants in PEMFCs?
- What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?
For achieving these objectives and addressing the questions, the research program has conducted systematically and led to the following original outcomes:

- **A comprehensive steady state, one dimensional and semi-analytical computer model, able to simulate the performance of PEMFCs cooling system when using nanofluids (and other conventional liquids) as coolants**

As part of this research project, a steady state one-dimensional semi-analytical computer simulation model has been developed using MATLAB to simulate the behaviour of PEMFC cooling systems while using different coolants (i.e. 50/50 water-EG, nanofluids). All the components of the cooling system including fuel cell stack, heat exchanger (i.e. radiator), coolant pump, and the coolants physical properties were modelled separately and combined together to investigate the thermal performance of the PEMFC cooling systems with different types of coolants being employed in the system. This computer simulation model can simulate the system in steady state condition. The FC stack model is capable of calculating the fuel cell cooling load and develop its polarisation (V-I) curve. The model that has been developed as part of this study was then used to simulate and investigate the effects of different types of coolants (i.e. conventional coolants and nanofluids) on the heat exchanger (i.e. radiator) size and the pumping power required by the system. A 2.4 kW liquid-cooled PEMFC was selected as a case study for this theoretical analysis. The simulation model was capable of simulating the electrical and thermal performances of this PEMFC and specially used to investigate the performance of its cooling systems with different coolants (i.e. 50/50 water-ethylene glycol mixture and selected nanofluids).

- **Theoretical study conducted on a 2.4 kW PEMFC stack using the computer simulation model developed for this study**

A case study based on a 2.4 kW PEMFCs has been conducted to investigate the performances of different coolants (i.e. selected nanofluids and 50/50 water-EG) in its cooling system. Though the developed computer simulation model was customised to analyse this 2.4 kW PEMFC, it can easily be scaled up for larger sizes, including those used in automotive applications (i.e. ~100 kW power). To fit the theoretical V-I curve of this stack with the manufacturer curve, unknown parameters such as charge transfer coefficient and exchange current density have been calculated by applying Tafel equation, whereas the ohmic resistance has been estimated by analysing the slope of the V-I curve provided by the manufacturer. The maximum cooling load of this 2.4 stack was calculated to be just over 2.1 kW (i.e. at 2.4 kW operating point) by the model. The computer model that has been
developed to estimate the size of the fuel cell’s heat exchanger used this cooling load (i.e. 2.1 kW) as one of the key design inputs to complete the fuel cell cooling system sizing task. All the necessary parameters for PEMFCs polarisation curves have been worked out by using the V-I curve provided by the manufacturer. The 50/50 water-EG has been taken as the base fluid for the nanofluids used in the study. All the temperature dependent thermo-physical properties of the base fluid has been taken from 2001 ASHRAE HVAC fundamental hand book. The thermo-physical properties of nanoparticles were assumed to be equal to the respective thermo-physical properties of the particle material in bulk form. The properties of nanofluids were predicted by using most reliable and widely used correlations in the literature.

Theoretically, the effects of using nanofluids as PEMFCs coolants on the convection heat transfer coefficient, size of the heat exchanger (i.e. radiator) and pumping power were evaluated and compared with those obtained by using 50/50 water-EG in the system as coolant. It was found that the suspended nanoparticles increase the convection heat transfer coefficient of the base fluid significantly. Compared with the base fluid, the convection heat transfer coefficient was found to be increased by about ~60% with the concentration of 0.05 vol% nanoparticles. With 0.5 vol% concentration, the convection heat transfer coefficient enhancement was obtained to be 70% for TiO$_2$ and Al$_2$O$_3$ nanofluids, and around ~74% for ZnO nanofluids compared to those calculated for the base fluid (i.e 50/50 water-EG).

The model was used to study the effect of different types of nanofluid-based coolants, with various concentrations (i.e. 0.05-0.5 vol%), on the frontal area of the fuel cell radiator while keeping the coolant mass flow rate constant. A significant augmentation of heat transfer was observed by suspending a small amount of nanoparticles in water-EG mixture. By adding only 0.05 vol% nanoparticles with 50/50 water/EG mixture, ~26% reduction in the frontal area of fuel cell heat exchanger (HE) was obtained compared to when the base fluid of 50/50 water/EG mixture was used as a coolant. With increasing the concentration of nanoparticles up to 0.5 vol%, no significant further reduction in the frontal area was estimated. Moreover, the effects of different nanofluids on the frontal area of heat exchanger were found to be almost identical.

As the viscosity of nanofluids increases with concentration, more pumping power is required compared with that needed with the base fluid. The simulation results showed that for 0.05 vol% concentrations of nanoparticles the required pumping power increased by ~5% whereas increasing the concentration to 0.5 vol% did not show a further significant increase in the pumping power.
An experimental study was conducted on a 2.4 kW PEMFCs cooling system with different coolants used in the system. The first step of this experimental investigation included preparation of nanofluids, and measuring their electrical and thermo-physical properties. The study was then followed by measuring the electrical and thermal performance of the fuel cell with using selected nanofluids and 50/50 water-EG.

It was found that most of the theoretically-predicted thermo-physical properties of nanofluids (i.e. thermal conductivity, viscosity, specific heat and density) were slightly different from the experimentally measured thermo-physical ones by maximum ~10%. These experimentally measured values of thermo-physical properties of nanofluids were provided as inputs into the computer simulation model and variations in outputs were compared with those obtained when theoretically predicted thermo-physical data were used in the model.

By using the experimentally obtained thermo-physical characteristics of nanofluids (0.05 vol% concentration) in the model the reduction in the size of the radiator for the 2.4 kW fuel cell (used as the case study) was calculated to be almost the same as that predicted by using theoretical data (i.e. ~ 27%). For 0.5 vol% concentration this reduction was showed no more than a couple of percent of further improvement (i.e. ~ 29%).

Next part of the experimental study included investigating the electrical and thermal performances of a PEMFC in which 50/50 water-EG and also selected 50/50 water-EG based nanofluids were used as coolants. The pressure drops along the coolant flow circuit was also measured by using pressure gauges installed on the rig while using different coolants (i.e. 50/50 water-EG and selected nanofluids).

The polarisation and power curves of the stack extracted and compared together with using 50/50 water-EG based 0.05 vol% ZnO, 0.5 vol% ZnO, 0.5 vol% TiO2 and 0.5 vol% Al2O3 nanofluids and 50/50 water-EG as coolants. The electrical performance of the stack remained almost the same with different coolants used in this study. However, all the nanoparticles investigated in this study were insulating materials and the electrical conductivities in the investigated nanoparticles concentrations (i.e. 0.05 vol% to 0.5 vol%) were below the threshold (i.e. 100 μS/cm).
The validation of theoretically obtained results was conducted by using the 2.4 kW PEMFCs experimental results. This has been done by varying the radiator outlet temperature and keeping the radiator size, coolant mass flow rate and radiator inlet temperature constant. The maximum difference between the output temperatures predicted by the model and those measured experimentally was measured to be ~10%.

The pressure drops along the closed cooling loop was measured for different coolants (i.e. 50/50 water-EG, 50/50 water-EG based 0.05 vol% ZnO nanofluids and 50/50 water-EG based 0.5 vol% ZnO nanofluids) for the required coolants flow rate to extract heat at different operating points (i.e. 30 A, 40 A, 50 A and 60A) of the PEMFCs. The pressure drops were found to be ~10% and ~7% higher for 50/50 water-EG based 0.5 vol% and 0.05 vol% ZnO nanofluid respectively compared with that for the 50/50 water-EG. Given that by using theoretical nanofluids thermo-physical data, the theoretical model suggested that the required pumping power can increase by ~5% for 0.05 vol% concentration and about 7-9% when the concentration was increased to 0.5 vol% (compare to when 50/50 water-EG is used as coolant).

Based on the results obtained by this study, the following recommendations were made for further studies:

- The developed computer simulation model in this study is capable of providing outputs for all range of cooling load concerning the PEMFCs application in automotive applications. However, the model did not include the effect of the electrical conductivity of nanofluids on the electrical performance of the fuel cell. This is while this effect was investigated experimentally. The model can further improved by including the effects of electrical conductivity of the coolants on the performance of PEMFCs.

- The developed computer simulation model was one dimensional and steady state. The transient behaviour of the fuel cell can be added as the fuel cells are expected to expose to a variable load or restarted after a period of being in operation in automotive applications.

- In this study, all the metal oxide nanoparticles (i.e. ZnO, TiO$_2$ and Al$_2$O$_3$) were intentionally selected with a view to using them in PEMFCs cooling system as coolants. Other types of nanoparticles (i.e. metallic, CNT, graphite, etc.) can be selected to study their effect on thermo-electrical performance of PEMFCs when used as coolants.
In both the theoretical and experimental studies conducted in this research, the concentrations of nanoparticles were considered to be varied in the range of 0.05 vol% to 0.5 vol%. Future studies can target a wider range of concentrations by (i.e. <0.05 vol% and >0.5 vol%).

Long term stability of nanofluids was excluded from the experimental investigation of this study. As the stability of nanofluids affects their properties, it is important to investigate the long term stability of nanofluids and to find out the ways to make them stable without affecting their electrical and thermal properties significantly.

The long term effects of using nanofluids as PEMFCs coolants on the PEMFC’s cooling channel as well as on the electrical performance of PEMFCs is an opportunity for further investigation. While de-ionising unit can be theoretically eliminated with nanofluids as coolants, the long-term effect of removing this part from the cooling loop is recommended to be further studied experimentally.


CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

1.1.1 Consumption of energy by transport sector

Across the globe, transport is one of the highest energy intensive sectors. The global transport sector consumed about 2200 million tons of oil equivalent (Mtoe), claiming about 19% of global energy supplies. About 96% of this amount comes from oil, and more than 60% of the oil, consumed globally (around 51 million barrels per day), goes to the transportation sector (WEC, 2015). The transportation of people and goods consumed almost 25% of world energy that consumed by all transports. As illustrated by Figure 1.1, among the transportation of people and goods, even light duty vehicles (LDV) alone (mainly including passenger cars) consume more than that of all transportation (EIA, 2016). In Europe, the transport sector accounts for about 20% of Europe’s primary energy consumption. The United States uses 28% of its energy for the transportation of people and goods. The transport sector in Australia accounts for 27% of total energy consumption, and the road transport accounts for nearly three-quarters of energy consumption in the sector (DIS, 2016). Moreover, in respect of energy use, transport is one of the fastest intensive sectors, forecasting an increase in demand of 50% for freight transport and 35% for passenger transport by 2020. Global oil demand is projected to increase from 90 million barrels per day in 2013 to 104 million barrels per day in 2040, an increase of over 15 per cent, due to increased oil use for transportation and petrochemicals. As a result, International Energy Agency (IEA) believes that US$900 billion per year is needed in upstream oil investment by the 2030s to meet global oil demand (IER, 2014).

Demand to fuel personal vehicles, which is mainly met through oil, has been projected to follow an increasing trend over the coming decades. Due to the development of technology that results in lowering vehicle price, people of 21st century are capable to afford private cars. As the world economy is expected to expand and evolve, demand to energy for commercial vehicles will grow significantly. Hence, around 70% increase in energy consumption is expected by 2040 due to the projected increase in economic activities. As a result, the transport demand is expected to still remain dominated by oil (87% in 2035, mostly for road use), while alternative cleaner technologies are likely to start making economic sense thereafter (BP, 2014). In fact the trend of moving toward such alternatives has already started but is moving slowly.
The transport sector is one of the most significant contributors to GHG emissions in the world which contributes almost 23% globally. In Australia, the transport sector produces around 91.5 million tonnes of direct CO₂ equivalent which is 48.1% above the emission level for 1990 (BITRE, 2016). 60-80% reductions in GHG by 2050 is also recommended by the climate change scientists compared to 1990 levels, with significant near-term reductions as well (Cynthia and Burbank, 2009). Achieving such radical levels of emission reduction (e.g. 60-80% by 2050 in Australia, or similar levels in many other countries) requires major changes starting from now, in many aspects of transportation throughout the world.

In order to cope with the increasing demand of fuel and also to reduce the emissions in transport sector, several alternatives to fossil fuel have been considered and tried over the last several decades. The main alternatives considered, are biofuels driven vehicles, plug-in electric vehicles, battery electric vehicles, hydrogen fuel cell cars, plug-in hybrid electric vehicles, etc. Although these technologies can be seen as part of the scenario for reducing emissions in the transportation sector, each of them still comes with its own drawbacks. In other words, none of these technologies can alone support a low emission transportation sector scenario, due to variety of reasons such as technological shortfalls, availability of resources, costs, availability of infrastructure, etc. (Andrews and Shabani, 2014).

Hydrogen fuel cell technology is seen to be a strong alternative to play a significant role as a part of this mix. A fuel cell vehicle (FCV) or a fuel cell electric vehicle (FCEV) uses hydrogen to power its on-board electric motor by using oxygen from air and hydrogen.
Advancements in fuel cell technology have reduced the size, weight and cost of fuel cell electric vehicles significantly in the past couple of decades. In 2010, the U.S. Department of Energy (DoE) reported that the cost of automobile fuel cells had fallen 80% since 2002 and they also estimated that such fuel cells can potentially be manufactured for $55/kW within a decade or so, assuming the fact that larger-volume productions can reduce the manufacturing costs considerably (Garbak, 2010, EERE, 2015). Fuel cell electric vehicles have been produced with driving ranges of 400 km between refuelling, and they can be refuelled in only around 3 to 5 minutes. These two can cover some main shortfalls of battery technology for electric vehicles. Recently developed Fuel Cell Technologies Program (FCTP) claims fuel cells achieved 55% (HHV of hydrogen) electrical energy efficiency at rated power, and a durability of ~ 120,000 km by only 10% voltage degradation (EERE, 2015).

1.1.2 PEMFC in automotive applications

The governmental agencies and environmental groups are continuously pressurising the car manufacturers to reduce the GHG gas emissions generated by vehicles. Hence, life on planet could be unsustainable without alternatives to fossil fuels. In principle, a hydrogen fuel cell produces electrical energy and heat as long as hydrogen fuel is supplied. Hydrogen can be generated through reforming hydrocarbon-based fuels such as natural gas, methanol, and even gasoline and diesel fuel. Since the fuel cell generates electricity through an electrochemical oxidation of hydrogen and not combustion, in-operation emissions from this type of a system would be zero, even if the hydrogen is sourced through fossil fuels (Johnston et al., 2005). However, this route of hydrogen generation is not a fully sustainable solution. The advantage of fuel cell technology for vehicle applications (i.e. in terms of reducing emissions) is firmly achieved when the hydrogen is manufactured through water electrolysis, powered by renewables. Some of the key advantages of fuel cell systems are as follows:

- Fuel cells produce almost zero or very low in-operation GHG emission (i.e. depending on the fuel or method used to produce hydrogen);
- Fuel cells produce power at efficiencies (e.g. ~40-50%) much higher than conventional internal combustion engines (e.g. an average of 20%);
- Fuel cells need minimal maintenance compared to ICEs;
- Fuel cells can operate efficiently both at part load as well as full load;
- Fuel cells can be used both for power and heat purposes; that further increase their energy efficiency.
The hydrogen fuel cell technology is considered as an important emerging sustainable technology even though it still needs further reduction in the cost to become fully viable economically (Hultman and Yaras, 2012). Among the various types of fuel cells Polymer Electrolyte or Proton Exchange Membrane (PEM) Fuel Cells (FCs) have emerged as a potential replacement for ICEs for automotive applications (Shabani and Andrews, 2015b, Meidanshahi and Karimi, 2012). This is due to the key advantages of this type of fuel cell such as high volumetric power density (e.g. 3.7 kW/l) (Bae et al., 2014), rapid start up (less than 30 seconds), low operating temperature (~ 60-80 °C) (Rabbani and Rokni, 2013, Park et al., 2016), high electrical energy conversion efficiency (over 50% based on the higher heating value of hydrogen) (Buonomano et al., 2015), compact size, low weight, long lifetime (close to ICEs), and the capacity to work in a discontinuous regime (Hosseinzadeh et al., 2013, Rakhshanpouri and Rowshanzamir, 2013, Nguyen et al., 2007b, Shabani et al., 2013, Anna, 2013, Nedstack, 2015, Andrews and Shabani, 2012, Kang and Min, 2016).

Due to the above mentioned advantages and continuous advancement of hydrogen FC technologies, the major global automotive companies believe that FC vehicles can play a significantly positive role in transport sector. For example, the Toyota Mirai that is a hydrogen fuel cell vehicle, was unveiled in November 2014 Los Angeles Auto Show, and also started selling in Japan from 15 December 2014. About 1500 of these fuel cell cars were sold in Japan during the first month that is almost triple of expected sales. The first production Toyota Mirai vehicles have officially been started selling in Europe (UK, Denmark and Germany) whereas about 2000 people have already raised their hand for a Toyota Mirai hydrogen fuel cell vehicle, which is now on sale in selected markets in California, USA (TheJapanTimes, 2015, AutoExpress, 2015b, Sarah, 2015). Hyundai iX35 (Tucson) hydrogen fuel cell car has also gone on mainstream sale in UK (AutoExpress, 2015a). Honda has also launched a fuel cell car “Clarity Fuel Cell vehicle” (Matthew, 2016) whereas BMW, at its 2015 Innovation Days, has shown off its first two cars that are powered by hydrogen fuel cells: a modified 5 Series GT (CarsTechnica, 2015).

Although significant progress has been made in the research area of PEMFCs, still certain matters can be addressed in order to improve the technology and speed up their commercialisation. Examples of these improvements are those related to, especially their durability, cost, and thermal management system (Zhang and Kandlikar, 2012).

Despite many proven advantages of PEMFC technology, transportation is a challenging application for taking this technology on board. The fuel cell must replace the traditional and
indeed well-established technology of ICEs. Although, the PEMFCs have a very high electrical energy conversion efficiency (up to over 50% based on HHV of hydrogen), there is still a significant amount of heat generated; i.e. even equal to or more than the power generated by the fuel cell (Barbir et al., 2005, Wai et al., 2007, Barbir and Yazici, 2008, Tekin et al., 2006) that can be up to 100 kW or more in a medium size passenger car running on hydrogen FC (Zhang and Kandlikar, 2012). This heat must be effectively removed to avoid overheating of FC components, especially the membrane. Though part of the generated heat (a few percentage of the total heat) is removed from the stack by the extra air and hydrogen, some is used to vaporise the product water (more or less about 30% depending on the FC operating point). The rest is referred to as the FC cooling load that has to be rejected by the fuel cell cooling system. It is noteworthy that only a small percentage of heat can be removed through convection heat transfer from the body of the fuel cell (Figure 1.2) (Shabani and Andrews, 2011).

![Sankey diagram](image)

Figure 1.2 Typical Sankey diagram for a PEMFC (Shabani and Andrews, 2011)

It is noteworthy that reducing the cost, weight, and volume of vehicle power–train systems (including their accessories) and improving their packaging flexibility have always been among the key concerns of the automotive manufacturers. Although today’s PEMFCs, with nearly 3.7 kW/l of volumetric power density, are offering superior power densities that are
competitive with those commonly seen in ICEs (~3 kW/l) (Anna, 2013), the relatively larger PEMFC cooling system sizes, used in automotive applications, are not seen as a desirable feature of this technology by the car manufacturers.

1.1.3 Challenges of PEMFC cooling system in automotive applications

Fundamentally the fuel cell cooling load to be rejected through the heat exchanger of the system (i.e. the radiator of the car) is calculated as follows:

\[ Q = UA \Delta T \] (1.1)

where \( Q \) is the heat need to be extracted in W (i.e. the fuel cell cooling load in this case), \( U \) is the overall heat transfer coefficient in W/m\(^2\)K, \( A \) is the heat transfer area of the radiator in m\(^2\), and \( \Delta T \) is the average temperature difference in K between the coolant and ambient that actually the driving force to reject the flow of heat (i.e. \( Q \)). The heat transfer can be increased by:

(i) increasing temperature difference, \( \Delta T \)
(ii) increasing heat transfer area, \( A \)
(iii) increasing overall heat transfer coefficient, \( U \)

In case of PEMFC cooling, \( \Delta T \) is usually small due to the fact that fuel cell operates at 50-60 °C that makes a small temperature difference with the ambient (especially in hot climates). That indeed limits the heat transfer rate and the cooling challenge of PEMFC starts from here. This \( \Delta T \) is dictated by the type of the fuel cell and the ambient temperature and hence cannot be controlled in favour of enhancing the heat transfer rate. Increasing heat transfer area \( A \) is a common to increase heat transfer for a given type of heat exchangers (e.g. in terms of material used or the overall shape and model) and a set coolant (e.g. conventional coolants such as water or ethylene glycol). That is why many radiators used in vehicle applications and also plate-and-frame heat exchangers are designed to maximise the heat transfer area. However, this strategy suggests enormous challenges for use in many applications such as aerospace, automotive, microprocessors and micro electro-mechanical system. Hence, in such applications, a practical solution for increasing the heat transfer rate is to increase the overall heat transfer coefficient, \( U \). Factors such as the radiator’s material, shape, and thickness (that affect the convection factor of the air side), the pattern of air flow passing over the radiator, the size and shape of the radiator’s tube on the coolant side, coolant’s type and flow rate, etc. directly affect the overall heat transfer coefficient.
Some automotive companies (i.e. Toyota, Honda, Hyundai and BMW) have already launched their FC driven vehicles, while they still welcome opportunities to reduce the size of the cooling system (i.e. radiator) of their product.

1.1.4 Nanotechnology to support PEMFC cooling system

Increase in thermal conductivity as well as heat transfer coefficient is the unique feature of nanofluids (Godson et al., 2010b, Murshed et al., 2008c, Choi, 1998). Nanofluids are defined as suspension of nano scaled (<100 nm) particles (e.g. Al₂O₃, TiO₂ and ZnO) in a base fluid (e.g. water, ethylene glycol, mixture of water-ethylene glycol, engine oil, etc.). These particles, generally a metal or metal oxide, increase the conductivity and the convection coefficients of the coolant, allowing for more heat to be transferred through the radiator without increasing its size (i.e. its surface area). This helps make the whole cooling system more compact, reduce the overall weight and obviously decrease the cost. The metallic solids possess higher thermal conductivity than that of fluids at any temperature as can be seen in Table 1.1. Hence, it is expected to increase the heat transfer rate significantly by suspending metallic or non-metallic materials into fluids (Murshed et al., 2008c). The mechanism of improvement in the thermal properties of nanofluids is not limited to the effect of their enhanced thermal conductivity only (i.e. due to the presence of the nanoparticles). Complex intervention of the particles within the boundary layer of the fluid (moving close to the surface) plays an important role in enhancing the convection factor of the fluid (Buongiorno, 2006).
Table 1.1 Thermal conductivity of some nanoparticles and base fluids at 300 °K (Leong et al., 2010, MEGlobal, 2016)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotube</td>
<td>3500 (Single wall), 3180 (multiwall)</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>429</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>401</td>
</tr>
<tr>
<td>Aluminium (Al)</td>
<td>237</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>148</td>
</tr>
<tr>
<td>Copper Oxide (CuO)</td>
<td>76.5</td>
</tr>
<tr>
<td>Aluminium Oxide (Al₂O₃)</td>
<td>40</td>
</tr>
<tr>
<td>Silicon Oxide (SiO₂)</td>
<td>1.38</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>0.628</td>
</tr>
<tr>
<td>Ethylene Glycol (EG)</td>
<td>0.258</td>
</tr>
<tr>
<td>Engine Oil</td>
<td>0.145</td>
</tr>
</tbody>
</table>

Nanofluids not only increase the heat transfer rate but also eliminate the necessity of using de-ionising filter in the cooling loop of PEMFCs. This advantage also helps improving the size and weight of system. When conventional fluids (e.g. water) are used as a coolant, it is necessary to use the de-ionising filters in the fuel cell cooling loop though initially the coolant is de-ionised (Figure 1.3. Deionisation is a chemical process of removing cations (i.e. calcium, iron, sodium, copper, etc.) and anions (i.e. chloride, sulphate, nitrate, etc.) from liquids. When the coolant (e.g. water) passes through the closed loop, it comes in contact with the metallic and non-metallic surface, picks different ions and gets contaminated with these ions. The coolant that is now ionised is considerably more electrically conductive than the deionised coolant. This electrical conductivity interrupts the electrical current collection throughout the fuel cell stack. That is why it is necessary to use a de-ionising filter when conventional coolants such as water or mixture of water-ethylene glycol (EG) are used in the system (APEC, 2014).
On the other hand, if nanoparticles are utilised as coolants, the nanoparticles can attract the free ions and immobilise them (Figure 1.4). Once the free ions are immobilised, their contribution towards increasing the electrical conductivity of the coolant can be suppressed. Nanoparticles can immobilise ions (i.e. both positive and negative) dissolved in the fluids, and they do that until they become saturated (DoE, 2011b).

As discussed, higher thermal conductivity of nanofluids and their enhanced thermal conductivity compared to conventional coolants such as water/EG mixture, offer potentials for reducing the size of the heat exchanger used in the fuel cell cooling systems. This is
considered to be a great advantage in terms of fuel cell system packaging as well as reducing the overall mass of the vehicle and obviously decrease the overall cost of the system. Preliminary back of envelope calculation that was conducted to pre-assess the viability of this idea, confirmed that by using nanofluids in a PEMFC cooling system (used in vehicle applications), the frontal area of the radiator can be potentially reduced by 10% of more (Singh et al., 2006). This could provide a great deal of flexibility for fuel cell system packaging in hydrogen fuel cell electric vehicles. While not within the scope of this study, it is important to mention that, smaller radiator frontal area would lead to decreasing aerodynamics drag that can be translated to fuel savings (Wong and De Leon, 2010). The benefit of enhanced thermal conductivity of nanofluids can be also captured by reducing the pumping power of the system (Choi and Eastman, 1995). The pumping power is proportional to the pressure drop of the coolant being circulated in the system and the fluid viscosity plays a key factor in determining this pressure drop (Murshed et al., 2008b). The presence of nanoparticles causes the viscosity to increase moderately; hence, pumping power is expected to moderately increase when nanofluids are used as coolants (i.e. compared to conventional base fluids). However, while eliminating the de-ionising unit offers opportunity of reducing the weight, size, and cost of the system, it also comes with the benefit of reducing the pumping power that can potentially offset the effect of increasing the pumping power through the increased viscosity of nanofluids. The de-ionising filter is a source of a considerable pressure drop within the cooling loop of a PEMFC that adds to the pumping load of the system.

For applications in extreme cold climate conditions (e.g. in Canada or north Europe), lowering the freezing point of the coolant is crucial; however, the fluids used for this purpose (i.e. usually ethylene-glycol) decrease the thermal conductivity of the coolant (Haiping and Walter, 2007). For example, the freezing point of water at close to atmospheric pressures is 0°C meaning it is not a suitable coolant in areas where ambient temperatures may drop well below 0°C. A mixture of 50% water and 50% EG can lower this freezing point to about -35.6 °C; however, the addition of EG into water reduces its thermal conductivity from 0.613 W/mK at 300K down to 0.3736 W/mK at the same temperature (Sundar et al., 2013). The reason of this decrease is mainly due to the fact that the thermal conductivity of EG is around 0.253 W/mK at 300K. The experimental results indicated that the nano-materials are very effective in lowering the freezing point of base fluids (e.g. Table 1.2). The measurements by Haiping and Walter (2007) (Table 1.2) showed that the effectiveness of adding nanoparticles with different concentrations (i.e. Single Walled nanotubes with a small amount of impurity (D-SWNT) and purified fluorinated (F-SWNT)) in lowering the freezing point of the base fluid.
Table 1.2 The effect of introducing nanoparticles to water coolant (i.e. making water-based nanofluids) on the freezing point of the coolant (Haiping and Walter, 2007)

<table>
<thead>
<tr>
<th>Nanofluid composition</th>
<th>Freezing point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0</td>
</tr>
<tr>
<td>Pure ethylene glycol (EG)</td>
<td>-12</td>
</tr>
<tr>
<td>50% water/50% EG</td>
<td>-35.6</td>
</tr>
<tr>
<td>0.05 wt% F-SWNT in 50% water/50% EG</td>
<td>-40.0</td>
</tr>
<tr>
<td>0.10 wt% F-SWNT in 50% water/50% EG</td>
<td>-41.1</td>
</tr>
<tr>
<td>0.20 wt% F-SWNT in 50% water/50% EG</td>
<td>-42.8</td>
</tr>
<tr>
<td>0.10 wt% D-SWNT in 50% water/50% EG</td>
<td>-40.6</td>
</tr>
<tr>
<td>0.20 wt% D-SWNT in 50% water/50% EG</td>
<td>-42.2</td>
</tr>
</tbody>
</table>

Strong van der Waals interactions between nanoparticles suggest a technical challenge for preparing a stable homogeneous suspension. To obtain stable nanofluids, some methods like physical and chemical treatment have been proposed and tested. They include using surfactant, surface modification of particles or applying powerful forces on the clustered nanoparticles (Ghadimi et al., 2011b). Xuan and Li (2000) also suggested that ultrasonic vibration of nanofluids and addition of surfactants enhance the stability of nanofluids.

In a PEMFC, the generated electricity creates an electrical field that causes the polarisation of the coolant and consequently the electricity leaks through the coolant flow. The electrical conductivity of a suspension can either increase or decrease depending on the background electrolyte, the particle size, the particle loading and the charge of the particle (Kole and Dey, 2013). This will be further investigated experimentally in chapter 5.

The suspended nanoparticles not only increase the thermal conductivity of the fluids, but they may also increase the electrical conductivity as well. However, for the applications of nanofluids as a coolant in PEMFCs, it is desirable to increase the thermal conductivity of the coolant while minimising the electrical conductivity. As a result it is very important to optimise both the thermal and electrical conductivity increment along with other properties of nanofluids.

Most of the studies on using nanofluids in cooling applications (e.g. heat exchanger, electronic cooling systems, solar collectors, etc.) have been reported for applications such as smart fluids, nuclear reactors, extraction of geothermal power and other energy sources.
Owing to the enhanced properties of nanofluids as heat transfer fluids, they are or can be used in a plethora of engineering applications ranging from automotive industry to the biomedical area. One of the potential applications of nanofluids is for use as fuel cell coolants to address the challenges associated with PEMFC cooling systems in automotive applications. The experimental and theoretical investigation of using nanofluids as fuel cell coolants has not been thoroughly investigated. Most research in the past decades or so has evaluated the thermal characteristics inside the FC stack channels, cells or electrodes based on the meso- or micro-scales approach. However, there have been very limited studies on thermal management of PEMFCs at a system level (Bao et al., 2006, Hu et al., 2010) and almost none on the optimisations of PEMFCs cooling systems by using nanofluids as coolants. The present research is an attempt to address this gap by theoretically and experimentally investigating the feasibility of using nanofluids as fuel cell coolants, and to identify suitable nanofluids (i.e. in term of both thermal and electrical properties) that can be used in such an application.

1.2 AIM, OBJECTIVES, AND SCOPE OF THESIS

1.2.1 Aim and Objectives

The main aim of the present thesis is to study the use of nanofluids as coolants in PEMFC cooling systems for automotive applications, with a view to enhancing the thermal performance and minimising the electrical conductivity (i.e. minimum impact on the FC electrical performance). The main challenge faced by PEMFC cooling system is the reducing in the size of the cooling system while maintaining the standard thermal and electrical performance of the PEMFC.

In view to addressing the cooling challenge, the objectives of the research project are to:

- study the electrical and thermo-physical characteristics of nanofluids with a view to identifying suitable nanofluids for use as PEMFC coolants;
- theoretically analyse the performance of nanofluids as coolants in PEMFCs cooling system by using a computer simulation model created as part of this research;
- investigate experimentally the feasibility of using nanofluids as coolants in PEMFCs and identify the potential and challenges associated with this cooling method;
- quantify the effect of using nanofluids as coolants on the thermal and electrical performances of PEMFCs;
- make recommendations for future research on using nanofluids as PEMFC coolant in automotive applications.
1.2.2 Scope of thesis

The scope of this project includes both theoretical and experimental investigations of the thermal and electrical performances of PEMFCs for which nanofluids are employed as coolants. The performance of individual PEMFC components such as cooling channels, Membrane Electrode Assembly (MEA), Gas Diffusion Layer (GDL), catalyst, etc. is not included in this study. The electrical performance of PEMFC will be investigated to observe the effects of using nanofluids as PEMFC coolants; however the parasitic energy losses will not be considered in this study.

Several nanoparticles (e.g. Al$_2$O$_3$, TiO$_2$ and ZnO) have been selected based on their electrical conductivities, and cost. 50/50 water-EG has been selected as base fluid considering its freezing point (~35.6 °C) is suitable for automotive applications. Ultra-sonication method is adopted to prepare nanofluids to be used as PEMFC coolants. Long term stability (>8 hours) is not considered in this study; hence no surfactant is used to prepare long term stable nanofluids.

The PEMFC cooling system computer simulation model created as part of this study is semi-analytical, one dimensional and steady state but a detailed CFD analysis or transient behaviour of the system is not part of this research project.

Commercially available PEMFC stack will be used in this study. The FC design, modification, and optimisation of the fuel cell cooling system components (e.g. the fuel cell cooling channels) for using nanofluids, are not considered to be within the scope of this project. Moreover, studying the long-term effect of nanofluids on the cooling channels is also not included in this project.

Commercially available radiators will be used in the experimental part of this research and, design of a new and dedicated radiator is not part of this research project.

1.3 RESEARCH QUESTIONS

The main research questions to be addressed by this research are:

- What role the volume fraction and type of the nanoparticles play in determining the electrical and thermal properties of nanofluids in the context of them being used as PEMFC coolant?
• What potentials and challenges nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performance of PEMFCs?
• How much the electrical and thermal performances of PEMFCs are affected by using nanofluids as coolants in PEMFCs?
• What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?

1.4 SIGNIFICANCE

Reducing the cost, weight, and volume of the vehicle power-train systems (including their accessories), and improving their packaging flexibility have always been among the key concerns of automotive manufacturers. As discussed before, although today’s PEMFC stacks, are very competitive to ICEs in terms of the volumetric power density (Anna, 2013), the relatively larger PEMFC cooling system sizes (in particular the radiator), are not seen as a desirable feature of this technology, particularly for use in automotive applications, in which the available space for packing the propulsion system is highly critical. Nanofluids as fuel cell coolants are studied in this thesis as a possible solution to this problem. Estimations made by Singh et al. (2006) showed a potential for reducing the radiator size (i.e. when using nanofluids instead of conventional coolants) by 10% when nanofluids are used as coolants. Nanofluids also offer opportunities to eliminate the coolant deionising unit (i.e. less pressure drop) and hence the use of a smaller pump (DoE, 2011a), although this can be offset by the fact that nanofluids have a higher viscosity than that of the normal based fluids used as coolants (e.g. water or the mixture of water and ethylene glycol). The proposed research investigates the feasibility of and the potential advantages and challenges associated with this idea; and also offer understanding to make informed decisions about suitable nanofluids that can be used as coolants in PEMFCs. Therefore, the project can potentially serve toward the PEMFC technology as an environmentally-friendly, technologically-advanced, and economically-attractive solution for vehicle applications.
1.5 ORIGINAL CONTRIBUTION TO KNOWLEDGE

This project was defined with the view to pushing forward the border of knowledge in the area of fuel cell electrical and thermal management by looking at the following innovative research lines:

- **Gaining understanding on the potentials and challenges of using nanofluids as a fuel cell coolant**
  
  Except some limited recent studies initiated by the U.S. department of Energy (DoE, 2012, DoE, 2011a), with not much results publically available, there is no data provided in the literature on the use of nanofluids as PEMFC coolants. This indicates that the option of using nanofluids as coolants in PEMFCs has not been thoroughly investigated before.

- **A novel computer model that simulates liquid-cooled PEMFC cooling systems used to study the performance of nanofluids as PEMFC coolants**
  
  A novel computer simulation model has been developed to study the cooling system of PEMFCs with different coolants, including nanofluids. This computer simulation model has been designed to support the experimental study that has been conducted as part of this project. The computer simulation model itself has validated by using the experimental data collected during this research. This computer model facilitates investigation around using nanofluids as coolants in PEMFCs.

- **Experimental data on the performance of different nanofluids as coolants in PEMFC cooling systems**
  
  A 2.4 kW liquid-cooled PEMFC rig with its balance of plant (BoP) have been designed, developed, and commissioned as part of this study to extract real-life experimental data on thermal and electrical performance of a PEMFC in which a nanofluid is used as a coolant. Such experimental data have not been reported in the literature before.

- **Gaining understanding on making informed selection of suitable nanofluids to be used as coolants in PEMFCs employed in automotive applications**
  
  Disregarding the type of application, it is widely accepted that the size, volume fraction, and type of the nanoparticles as well as the base fluid used in manufacturing nanofluids play key roles in determining their thermal, electrical, and fluidic properties. One of the objectives of this research is to study the effect of the above-mentioned properties nanofluids in the context of a fuel cell where narrow micro channels, within highly thermally and electrically conductive cooling plates, are used to carry the coolants (i.e. nanofluids) throughout the fuel
cell. The cooling plates are embedded within the electrical circuit of the fuel cell and should not be electrically isolated from the cathode and anode plates (i.e. this is to avoid any additional fuel cell over potentials). Therefore, it is very important to understand and consider all or some of the above-mentioned parameters for preparing suitable nanofluids that can be used in PEMFC cooling systems. The key challenge here is minimising the electrical conductivity of the coolant while increasing its thermal conductivity. Nanofluids with high thermal conductivity usually show high electrical conductivity (Madhusree and Dey, 2013, Steven et al., 2011b). While the high thermal conductivity of nanofluids is favourable, their high electrical conductivity is not considered to be a desirable feature of these coolants, since it negatively affects the electrical performance of the fuel cells (Sarojini et al., 2013b). An electrically conductive coolant can be easily polarised when passing through the electrically conductive cooling plates and this causes some fuel cell voltage drops.

1.6 RESEARCH OUTCOMES

The expected deliverables of the project are:

- A valid theoretical computer model that can simulate the behaviour of PEMFC cooling systems (with different coolants including nanofluids). This computer simulation model is capable of analysing, and sizing PEMFC cooling systems in which nanofluids used as coolants.
- Demonstration of a 2.4 kW liquid-cooled PEMFC that uses nanofluids as a coolant
- Quantifying the benefits of using nanofluids as coolants in liquid-cooled PEMFCs
- Selection and design guideline for characterising suitable nanofluids for use as coolants in PEMFC applications. The suitable design in this case is a stable nanofluid with maximum thermal conductivity and minimum electrical conductivity (i.e. minimum effect on the electrical performance of the PEMFC), while being economically viable.
1.7 THESIS STRUCTURE

Following the present introduction chapter, the second chapter is focused on detailed description of the methods and procedures followed to conduct this research study. This chapter focuses on the theoretical and experimental studies planned in this research that also include some introduction to theoretical and experimental approaches including characterisation of nanofluids used in this study. An extensive literature review of previously conducted research studies in this area has been presented in the third chapter. This chapter consists of the subheadings including fuel cell system, fuel cell automotive applications, PEMFCs cooling using nanofluids, electrical and thermo-physical properties of nanofluids, applications of nanofluids in different power supply devices, and the experimental and theoretical studies of PEMFC cooling systems. Chapter 4 presents a one dimensional steady state computer simulation model of PEMFC cooling systems that has been used for analysing the thermal performance of a 2.4 kW liquid-cooled PEMFC as a case study. This computer model is used to determine the size of the heat exchanger and pumping power required for the PEMFC used as case study. The theoretical basis of the model is presented for each component and the system as a whole. Chapter 5 reports the experimental part of the research that has been conducted on a 2.4 kW PEMFC. This chapter also reports on the characterisation of nanofluids prepared and used as coolants in this fuel cell. Chapter 6 elaborately compares and discusses the results obtained from experimental and theoretical study. The experimentally extracted characteristics of nanofluids have been compared with those from theoretical study and used as inputs for the computer simulation model to improve its accuracy. The experimentally obtained results including the most suitable nanofluids, thermal performance of fuel cell, the size of the heat exchanger and pumping power required have been compared with those suggested by the theoretical model. And finally chapter 7 concludes this research by thoroughly reviewing the research objectives and questions, and show how they have been addressed throughout this research. This chapter also provides some recommendations and directions for the future study and expansion of the topic covered by this research.
CHAPTER 2 RESEARCH METHODS

2.1 INTRODUCTION

This chapter describes in details the research methods and procedures followed to conduct this research project. The project started with a comprehensive literature review followed by systematic theoretical and experimental studies.

The detailed activities have been outlines in the flowchart shown in Figure 2.1.

Figure 2.1 The overall approach to the research methods followed in this research
2.2 LITERATURE REVIEW

A comprehensive literature review has been conducted with a view to understanding the state of the art related to potentials and challenges associated with using nanofluids as coolants in the PEMFC cooling systems. This option has been researched in order to explore the opportunities to maximise the thermal performance of the coolant and hence reduce the size of the cooling system without affecting the electrical performance of the fuel cell significantly. The cooling system of PEMFCs has been the focus of a significant number of research studies over the past few decades. This has resulted in an extensive body of literature in this area. In order to properly understand such an extensive body of knowledge, this review was conducted by focusing on the following five major areas:

- Thermal management of PEMFCs
- Fuel cell cooling systems
- Electrical and thermo-physical properties of nanofluids
- Nanofluids in cooling of electronics and power supply devices
- Study of PEMFCs’ liquid cooling systems

2.3 MODELLING OF PEMFC COOLING SYSTEM

The theoretical part of the research was conducted using a computer model of a PEMFC liquid cooling system. The model that has been developed as part of this study was then used to simulate and investigate the effects of different types of coolants (i.e. conventional coolants and nanofluids) on the heat exchanger (i.e. radiator) size and the pumping power required by the system. A 2.4 kW liquid-cooled PEMFC was selected as a case study for this theoretical analysis. The simulation model is capable of simulating the electrical and thermal performances of PEMFC systems and specially investigates the performance of their cooling systems by trying different coolants (i.e. 50/50 water-ethylene glycol mixture and nanofluids).

The main focus of this theoretical study is to investigate the thermal performance of PEMFC cooling systems in particular when different types of coolants are used in the system. In order to achieve the main goal of this study, a steady state one-dimensional analytical computer simulation model is developed using MATLAB to simulate the behaviour of PEMFC cooling systems. All the components of the cooling system including fuel cell stack, heat exchanger (i.e. radiator), coolant pump, and the coolants physical properties were
modelled separately and combined together to investigate the thermal performance of the PEMFC cooling systems with different types of coolants being employed in the system. Different types of coolants including nanofluids were used in the cooling systems and their performances were compared with those the simulation results obtained for conventional coolants (e.g. 50/50 water-ethylene glycol). This computer simulation model simulates the system in steady state condition. The FC stack model was developed to find out the cooling load of the system and generate the polarisation (V-I) curve. This has then been compared with the polarisation curve provided by the manufacturer for validation purpose. The computer simulation model of PEMFC system was also designed for sizing the cooling system of the PEMFC; however, the design of the coolant flow channels has not been considered as part of the scope of this work. The long-term effect of nanofluids on the coolant flow channels as well as the detailed CFD analysis are not included in this project. The pumping power required for circulating the coolants is estimated and differences between the pumping powers required for different coolants are calculated. However, the design of the coolant pump has not been considered to be within the scope of this study. The specifications of a commercially available pump were used for this theoretical study. The computer simulation model was validated and modified (if required) through the experimental performance data of a 2.4 kW PEMFC cooling system that has been obtained as part of this study.

By successfully completing the study of theoretical modelling of PEMFC cooling system, the following objective can be achieved and questions can be addressed:

**Objective 2:** Theoretically study the performance of nanofluids as coolants in PEMFCs cooling system by using a computer simulation model created as part of this research.

**Question 1:** What role the key characteristics of nanoparticles (e.g. volume fraction, and type of the nanoparticles) play in determining the electrical and thermal properties of nanofluids in the context of them being used as PEMFC coolant?

**Question 2:** What potentials and challenges nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performance of PEMFCs?
2.4 EXPERIMENTAL STUDY

2.4.1 An overview

The experimental investigation was designed with a view to studying the electrical and thermo-physical properties of selected nanofluids (prepared by ultra-sonication), moreover, the suitable nanofluids suggested by the theoretical study was used in a 2.4 kW PEMFC as coolants and their actual effects on the thermal and electrical performances of the fuel cell were studied. This was done by comparing the results with the electrical and thermal performances of the PEMFC and its cooling system when a 50/50 mixture of water/EG was used as a coolant.

2.4.2 Characterisation of nanofluids

2.4.2.1 Preparation of nanofluids

A nanofluid is a fluid that contains nano-meter-sized particles (nanoparticles) suspended into a base fluid. The nanoparticles are typically metals, metal oxides, graphite, carbon nanotubes or carbides. Common base fluids include distilled water, ethylene glycol (EG), mixture of water-EG and engine oil are used to prepare nanofluids. Preparing a stable and durable nanofluid is a prerequisite for getting the best expected thermo-physical properties out of it. Among the different types of dispersion methods (i.e. ball milling, homogenisation, sonication methods, and etc.), ultrasonic oscillation has been proved to be the most effective dispersion approach for preparing long lasting stable nanofluids (Fedele et al., 2012). The following equation (Zakaria et al., 2015a) relates the volume percentage of nanoparticles $\phi$, density of base fluid and the nanoparticle used, $\rho_{bf}$ and $\rho_p$ respectively, the mass of base fluid $m_{bf}$ then as well as the mass of the nanoparticles:

$$\phi = \frac{m_p / \rho_p}{m_p / \rho_p + m_{bf} / \rho_{bf}} \times 100 \tag{2.1}$$

Generally, two different methods are applied to prepare nanofluids namely: single-step and two-step methods. The single-step method consists of simultaneously manufacturing, and dispersing the particles into basefluid. On the other hand, in two-step method, that is more common and popular, the nanoparticles are manufactured separately and then dispersed into the base fluids (e.g. using ultrasonic agitation; Figure 2.2). The two-step method is adopted for preparing nanofluids for this study.
Nanofluids have been prepared twice in this study: for characterisation of the nanofluids (~100 ml) and for using in PEMFC cooling. For the preceding one, the VC 750 sonicator with ½” diameter probe was used while for Qsonica Q700 with booster and 1” diameter was used for preparing nanofluids at larger volume. The detailed procedures of preparing nanofluids are described in Appendix A.

2.4.2.2 Assessing the stability of nanofluids

Preparing a homogeneous suspension is still a technical challenge due to strong van der Waals interactions between nanoparticles that always in favour of the formation of aggregates. Achieving long-time stability is not within the scope of this research; however, the simple method of sediment photograph was used to check the condition of the nanofluids before they were used in the fuel cell as coolants or before their thermo-physical properties were measured.

Sediment photograph capturing: A primary method to find out about sedimentation of nanofluids is photo capturing. After preparing nanofluids, some amounts of the nanofluids were put aside to capture photos after certain period of time as illustrated in Figure 2.3. By comparing these photos of nano suspensions, sedimentation of suspension will be apparent.
Figure 2.3 An image of 50/50 water-EG based TiO$_2$ nanofluids at different concentrations (a) 0.05 vol%, (b) 0.1 vol%, (c) 0.3 vol% and (d) 0.5 vol% after one hour of preparation

2.4.2.3 Thermal conductivity measurement of nanofluids

For measuring the thermal conductivity of liquids, different measuring techniques have been adopted over the years by the researchers. A number of such techniques have also been used for measuring the thermal conductivity of nanofluids. A summary of the available measurement techniques is shown in Figure 2.4 (Paul et al., 2010).

![Thermal conductivity measurement techniques diagram](image_url)

Figure 2.4 Thermal conductivity measurement techniques for liquids as well as nanofluids (Paul et al., 2010)
In this study, the thermal conductivity of nanofluids was measured using KD2-Pro thermal property analyser (Figure 2.5) that uses thermal constants analyser technique. The thermal constants analyser utilises the Transient Plane Source (TPS) theory to measure the thermal conductivity of nanofluids. The detailed procedure of measuring thermal conductivity of nanofluids is provided in Appendix A.

There are several advantages of using this method over other methods, including:

- The measurements are fast
- Samples having wide range of thermal conductivities (0.02 to 200 W/mK) can be measured, and
- Sample size can be flexible

Figure 2.5 Thermal conductivity measurement of nanofluids using KD2 Pro thermal analyser in this study

In this study the thermal conductivity of nanofluids was measured using a KD2 Pro (KS-1 sensor) thermal conductivity meter (Figure 2.5). The KS-1 sensor is designed for low viscosity liquids and the needle should be inserted properly into the liquid with vertical orientation.
2.4.2.4 Electrical conductivity measurement technique

For measuring the electrical conductivity of nanofluids, a commercially available electrical conductivity meter (Hach model: CDC401; Figure 2.6) was used. The potentiometric method along with four electrodes is used to measure the electrical conductivity in this meter. The electrodes that are cylindrical and arranged concentrically are usually made of platinum metal to withstand high temperatures and produce accurate readings. It can also measure wider range of thermal conductivities. Hence, this technique allows measuring both high and low electrical conductivities. The probe needs to be rinsed with deionised water and blot dry with a lint-free cloth. Air bubbles under the sensor tip needs to be removed before taking any reading as it may cause slow response or error in measurement. The detailed procedure of measuring electrical conductivity of nanofluid is given in Appendix A.

![Electrical conductivity meter used for measuring the electrical conductivities of nanofluids](image)

2.4.2.5 Viscosity measurement

Rheometer is an instrument that measures both viscosity and viscoelasticity of fluids, semi-fluids and solids. Rheometers operate in both controlled stress as well as controlled rate modes of operation that provide a more general capability for rheological evaluation of flow behaviour. The rotational/shear rheometer (Figure 2.7) has been used in this study. In cone and plate type rotational rheometer, the liquid is placed on a horizontal plate with a cone of
very shallow angle in bare contact placed into it. The angle between the surface of the cone and the plate is around 1 to 2 degrees but can vary depending on the types of tests being run. The detailed procedure of measuring viscosity with DHR-3 is provided in Appendix A.

Figure 2.7 Discovery Hybrid Rheometer-3 (DHR-3) used to measure the viscosity of the coolants (e.g. nanofluids) in this study

2.4.2.6 Specific heat capacity determination

The specific heat capacity of nanofluids is determined by using Differential Scanning Calorimetry (DSC) (Figure 2.8). Generally, DSC measures the specific heat capacity of thermally stable liquids in the temperature range of –100 - 600 °C. In this technique, both the sample and reference are kept in the same temperature while the heat required increasing the temperature of sample and reference are measured. The principle of measuring specific heat by DSC is that, when the sample goes to transform from one phase to another, it absorbs heat from the reference and this heat flow is recorded as a function of temperature. A hermetic aluminium pan is usually used as a reference material.
Along with ASTM E1269-Standard Test Method for Determining Specific Heat Capacity by DSC, the classical three step method has been adopted to determine the viscous characteristics of nanofluids. The classical three step method has been described below:

1st step: Determination of the heat flow rate of the zero line $Q_0$, using empty crucibles of equal weight in the sample and the reference sides. The temperature program should only be started when the isothermal heat flow rate at the starting temperature has been constant for at least one minute. If the DSC is computer controlled, this can easily be automated by checking the differences between the current average heat flow rate and that obtained one minute before with allowance for a predetermined drift level. The scanning region between the starting and ending temperatures must be designed based on the requirement of the specific heat of the sample. At the isothermal end temperature the above computer check must be repeated. The zero line reflects the (inevitable) asymmetry of the DSC.

2nd step: A calibration substance ($Ref$) of known heat capacity $c_{p,ref}$ is placed into the sample crucible ($S$), whereas nothing is changed on the reference side ($R$). The heat flux into the reference, $Q_{ref}$ is recorded throughout the same temperature range of $Q_0$.

3rd step: The calibration substance ($Ref$) in crucible $S$ is replaced by the sample ($S$). The heat flux into the sample $Q_{sample}$ is measured at the same temperature range of step 1 & 2.
The heat flux from the above three steps are used to calculate the specific heat of the sample, \( c_{p,\text{sample}} \) and can be expressed as (O’Hanley et al., 2011):

\[
c_{p,\text{sample}} = \frac{Q_{\text{sample}} - Q_0}{Q_{\text{ref}} - Q_0} \frac{m_{\text{ref}}}{m_{\text{sample}}} c_{p,\text{ref}} \tag{2.2}
\]

2.4.2.7 Density determination

The required pumping power increases with the increase in the coolant’s density, i.e. used in the PEMFC cooling system. The density of nanofluids can be measured by applying any of the following:

- Hydrometer
- Pycnometer
- Density kit
- Digital density meter
- Refractometry
  - Portable optical refractometer
  - ABBE optical refractometer
  - Digital refractometer

For measuring the density of nanofluids, pycnometer (Figure 2.9) has been chosen due to its simplicity. A pycnometer is a simple device with precisely marked volume, used to measure the density of any liquid by weighing the same volume of known and unknown liquids.
The density of unknown liquids (i.e. nanofluids) can be measured by following these steps:

**Step 1:** First fill the pycnometer with known density liquid, $\rho_{H_2O}$ (i.e. distilled water) and measure the weight of liquid, $m_{H_2O}$ (i.e. measured weight minus weight of empty pycnometer):

$$V = \frac{m_{H_2O}}{\rho_{H_2O}}$$  \hspace{1cm} (2.3)

where $m_{H_2O}$ is the measured weight of known density liquid plus pycnometer.

**Step 2:** Following step 1, the pycnometer now should be filled with unknown density, $\rho_{nf}$ liquid (i.e. nanofluids) and measure the weight $m_{nf}$ of unknown liquid (i.e. measured weight minus weight of empty pycnometer). Volume $V$ is the same to that used for water determined from the equation (2.3):

$$V = \frac{m_{nf}}{\rho_{nf}}$$  \hspace{1cm} (2.4)
Step 3: Combining equations (2.3) and (2.4), the density of unknown liquid can be measured (i.e. that their densities are being measured).

\[ \rho_{nf} = \frac{m_{nf}}{m_{H_2O}} \rho_{H_2O} \]  

(2.5)

Upon completion of the characterisation of nanofluids, the following objective and questions can be addressed:

**Objective 1:** study the electrical and thermo-physical characteristics of nanofluids with a view to identifying suitable nanofluids for use as PEMFC coolants;

**Question 1:** What role the key characteristics of nanoparticles (e.g. volume fraction, and type of the nanoparticles) play in determining the electrical and thermal properties of nanofluids in the context of them being used as PEMFC coolant?

**Question 4:** What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?

### 2.4.3 Investigation of PEMFC cooling system

#### 2.4.3.1 Observation plan

The electrical performance of a selected 2.4 kW liquid-cooled PEMFC and the behaviour of its cooling system have been investigated experimentally. Different fluids were used, as coolants, to conduct this experimental study, that included 50/50 water-EG mixture and most importantly different types of nanofluids. This 2.4 kW PEMFC will be run at different operating points in order to study:

- the thermal and electrical performances of the stack when conventional coolants such as a mixture of water and ethylene glycol is used in its cooling system;
- the feasibility, potential benefits, and challenges associated with using nanofluids as coolants in PEMFCs;
- the effects of using different above mentioned coolants on the size of the heat exchanger (of the fuel cell cooling system); and
- the effect of using the above mentioned coolants on the pumping power of the FC cooling system.
2.4.3.2 Data collection and analysis

The details of the start-up procedure to start collecting the data have been provided in appendix A. The main focus of the experimental part of this study is to investigate the electrical and thermal performances of the 2.4 kW PEMFC (used for this experimental study) when different coolants (i.e. conventional 50/50 water-EG mixture and selected nanofluids) are used in its cooling system. It was also planned to investigate the effects of replacing the 50/50 water-EG mixture with nanofluids on the size of the PEMFC cooling system (i.e. potential reduction in the size of the radiator is expected due to better thermal characteristics of nanofluids) and its pumping power (i.e. potential increase in the pumping power is expected due to higher viscosity and density of the nanofluids). In this regard, the following performance indicators of the 2.4 kW PEMFCs stack have been collected at different operating points:

- Output voltage of the stack
- Output power of the stack
- Stack electrical current density
- Hydrogen consumption rate
- Coolant flow rate
- Coolant’s temperature in the inlet and exits of both fuel cell and the heat exchanger
- Coolant’s pressure drop across the heat exchanger
- Coolant’s pressure drop across the PEMFC stack
- The relative humidity of the hydrogen gas entering the stack
- The relative humidity of the air entering the stack

Upon completion of the PEMFCs experimental study, the following objectives can be achieved and the following questions can be addressed:

Objective 2: investigate experimentally the feasibility of using nanofluids as coolants in PEMFCs and identify the potentials and challenges associated with this cooling method;

Objective 3: quantify the effect of using nanofluids as coolants on the thermal and electrical performances of PEMFCs;

Question 3: How much the electrical and thermal performances of PEMFCs are affected by using nanofluids as coolants in PEMFCs?
Question 4: What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?

2.4.3.3 Modification of the computer simulation model

The theoretical coolant properties used the model were checked against the experimental data obtained as part of this study (section 2.4). Following this, the coolants properties were modified where required. Also, the mass flow rates of different coolants used in this study were measured using an inline water flow meter (Model H2F-CU12, TOPARGEE) with the accuracy of +/- 5%. The theoretically estimated mass flow rates of the same coolants were compared with the experimentally measured flow rates and their values (i.e. used in the initial theoretical study) were modified in the model where necessary.
CHAPTER 3: LITERATURE REVIEW

3.1 INTRODUCTION

A comprehensive literature review has been conducted with a view to applying nanofluids as potential coolants in the PEMFC cooling system along with very brief discussion on different fuel cells. As broadly discussed in chapters 1 and 2, the key purpose of using nanofluids as coolants is improving the performance of PEMFC cooling systems that helps reduce their size.

A fuel cell (FC) is an electro-chemical device that converts directly the chemical energy stored in gaseous molecules of a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent (Silva et al., 2012, Song et al., 2011, Hwang, 2013). It consists of an electrolyte layer in contact with a porous anode and cathode on either side. The anode and cathode are the electronic conductors while the electrolyte conducts only the ionic species. The anode and cathode take parts in the anodic and cathodic reactions respectively at the anode/electrolyte and cathode/electrolyte interfaces. At the anode of an acid electrolyte fuel cell, the fuel (hydrogen) oxidises by anodic reaction that involves generation of electrons and H\(^+\) ions (protons). The electrons travel through the outer electrical circuit to the cathode and are responsible for generating power from the fuel cell. The cathodic reaction involves consumption of electrons passing through outer circuit, protons through the electrolytes and oxygen usually from the supplied air, to form water (Giddey et al., 2012).

Different types of fuel cells are currently existed and still under development, each with its own advantages, limitations, and potential applications. By name, the FCs are:

- Polymer Electrolyte (or Proton Exchange) Membrane (PEM) Fuel Cells
- Direct Methanol Fuel Cells
- Alkaline Fuel Cells
- Phosphoric Acid Fuel Cells
- Solid Oxide Fuel Cells
- Molten Carbonate Fuel Cells
- Regenerative Fuel Cells
- Microbial Fuel Cells
- Zinc Air Fuel Cells
Each and every type of fuel cell is characterized by its own particular geometry, dimensions, and material; yet, the core of the device remains the same. Among these different types of fuel cells, PEM fuel cell is the main focus of this study, so the discussion will be limited to PEM fuel cell only. The PEM fuel cell consists of an electrolyte, two electrodes, two gas diffusion layers, two catalyst, and most often bipolar plates separating unit cells (Figure 3.1).

![Schematic representation of PEMFC components](image)

Figure 3.1 Schematic representation of PEMFC components (Shabani and Andrews, 2015a)

The use of nanofluids as coolants in different applications and also their advantages and challenges have been extensively studied by other researchers. The literature is also showing a significant number of studies conducted to date on the cooling system of PEMFCs. In order to systematically review such a broad literature, understand and classify their contributions, and identify the gap of knowledge to be addressed, the present review has been grouped into five major areas:

- Thermal management of PEMFC cooling systems
- Fuel cell cooling systems
- Liquid-based cooling systems for PEMFCs
- Electrical and thermo-physical properties of nanofluids
- Use of nanofluids for cooling of electronics and power supply devices
The first section begins with a brief introduction of the fuel cells and their thermal management systems by focusing on PEMFCs. The second section gives a short overview of the PEMFC cooling system in perspective of the present art of the technology. The third section provides with the electrical and thermo-physical characteristics of nanofluids both theoretically and experimentally focusing on the liquid cooled PEMFC system for automotive applications. The fourth section explores the potential applications of nanofluids in electronics and power supply devices. The fifth section focuses on the theoretical and experimental study of the PEMFC liquid cooling system and the coolants used for cooling the PEMFCs.

3.2 THERMAL MANAGEMENT OF PEMFC COOLING SYSTEMS

In PEMFCs the only by-products are pure water and heat. Heat is generated mainly due to entropic term as well as the irreversibilities associated with the chemical reaction between the oxygen and hydrogen (Zhang and Kandlikar, 2012). The irreversibility of the electrochemical reactions induces a significant heat generation inside the fuel cell. Due to the splitting reaction of the fuel cell into two electrodes, heat is generated on both sides (i.e. anode and cathode). However, heat generation at cathode is higher compared with that of the anode due to asymmetric entropy change (Yan et al., 2004). The ohmic heat is resulted from both the proton current through the membrane and the electron current through the outer circuit (including the bipolar plates). Higher conductivity of materials and less electrical contact resistances are always desired for reducing the ohmic losses (Kandlikar and Lu, 2009).

The heat generation rate in PEMFC increases with the current and exceeds the electric power output at high current densities. The steady-state operation of a PEMFC depends on the heat generation and removal in the system. Hence, the thermal management of a PEMFC is an operational requirement for optimal electrical power generation and determines the FC operating temperature (Atan and Najmi, 2012). Such management mainly includes maintaining the stack’s operating temperature within a desirable range and creating a uniform temperature distribution across the stack and individual membranes (Akbari et al., 2012). In an ideal situation, a fuel cell would operate under identical operating condition; however in reality this is not feasible, as variations inevitably arise due to the design of stack manifold, position of the cell in the stack, and obviously the choice of the thermal management strategy. Various thermal issues can be induced due to improper thermal management. For example, the electrolyte dehydration can be happened due to low relative
humidity, high air stoichiometric ratio, high temperatures, electro-osmotic drag, etc. Similarly, the cathode flooding can be showed due to the accumulation of water in the pores of cathode. Due to the insufficient or non-effective cooling system, excessive local cell temperature can cause membrane dehydration, shrinking or even permanent damage of the cells. The dehydration of the membrane at the anode side is worsened at high current densities that also increase along with high power requirement. The flooding phenomenon which is strongly affected by the temperature distribution is dominated by the condensation/evaporated processes in the cathode. Maintaining uniform temperature distribution is critical for efficient operation of a PEMFC and a number of possibilities of thermal management exist for small stacks, the problem becomes more complicated for larger stacks (Reddy et al., 2014, Pandiyan et al., 2008).

Usually thermal management of PEMFCs can be done through the cathode and/or separate air flow, heat spreaders, antifreeze/coolant and water cooling. However, many researchers have tried differently to find out effective thermal management methods for PEMFCs through trying and investigating various means suitable for different types of PEMFCs.

3.3 FUEL CELL COOLING SYSTEMS

3.3.1 Types of cooling system: An overview

The thermal management of a PEMFC is an operational requirement for optimal power generation (Atan and Najmi, 2012). Such management mainly includes maintaining the stack’s operating temperature within a desirable range and creating a uniform temperature distribution across the stack and its individual components (Akbari et al., 2012). The cooling methods are mainly determined by the size of the fuel cells and use either liquid or air that circulates through cooling flow channels in bipolar plates or through dedicated cooling plates (Li and Sabir, 2005, Inoue et al., 2006, Ju and Wang, 2008). Liquid cooling is usually essential for 10 kW fuel cells and larger, while air cooling alone is suitable for fuel cells up to 2 kW. Between these limits judicious decisions between liquid and air cooling need to be made (Reddy et al., 2013, Zhang and Kandlikar, 2012).

3.3.2 Small and medium size fuel cell (<10 kW) thermal management systems

Both passive and active methods of cooling can be used for thermal management of small and medium size fuel cells (i.e. <10 kW) (Setareh, 2009). Passive cooling refers to the technologies or design features used to cool the systems without using power-consuming
units like pumps and fans that also reduces the mass and complexity of the cooling system (Zhang and Kandlikar, 2012). Cooling with heat spreaders and also using heat pipes are examples of passive cooling techniques (used in conjunction with no active systems such as cooling fans) that can be used for FC thermal management.

A heat spreader is a means to move heat from the heat source to a heat exchanger that prefers heat spreader’s surface area and geometry than those of the heat source. Cooling with heat spreaders (i.e. edge cooling) (Flückiger et al., 2007) relies on heat conduction for removing heat from the central region to the edge (Barbir, 2005), and then convection to remove this heat to the atmosphere surrounding the stack. Graphite based materials (expanded graphite and pyrolytic graphite) with high thermal conductivity and low density are the most widely used materials as heat spreaders in PEMFCs. Wen and Huang (2008) experimentally investigated the thermal performance of a Pyrolytic Graphite Sheet (PGS) in a single PEMFC. They constructed a transparent PEMFC with PGS of thickness 0.1 mm which cut into the shape of a flow channel and bound with the cathode gas channel plate. They obtained the images of the transparent cathode flow channels and measured the temperature at different operating conditions to understand effects of PGS on fuel cell performance. They found that the PGS reduces the maximum cell temperature and improves the cell performance. This cooling method presents challenges to provide the cells with a uniform temperature distribution; especially for low temperature (less than 80 °C) PEMFCs, while this challenge is less in high temperature (HT) PEMFCs (i.e. above 100 °C).

Using heat pipes (Figure 3.2) is another approach that can be deployed through passive or active processes for fuel cell cooling. This technology has proven to be an effective and robust cooling technique particularly for mini/micro PEMFCs (Vasiliev and Vasiliev-Jr, 2008), that can manage the fuel cell heat reliably in long-term operation. Integration of pulsating heat pipes within bipolar plates of the stack would eliminate the need for ancillary cooling equipment, thus also helps reduce the parasitic losses and increase the overall energy efficiency of the system (Song et al., 2011, Zhang and Kandlikar, 2012). Heat pipe effectiveness generally depends on several factors such as heat input, the type of working fluid, its filling ratio (i.e. the percentage of the evaporator section volume filled by the working fluids), the inner diameter and the evaporator length (Clement and Wang, 2013, Qu and Wang, 2013, Faghri and Guo, 2008). Depending on the thermal management requirement of a PEMFC, different types of heat pipes; i.e. micro and miniature heat pipes (1–100 W), loop, pulsating, sorption (100–1000 W) are used for cooling purposes (Vasiliev et al., 2009).
The air stream, on the cathode side of PEMFC stacks (usually used with external fans), provides the required oxygen for the chemical reactions as well as a promising strategy for thermal management of stacks, which reduces the bill of materials and system complexity (Akbari et al., 2012, Shahsavari et al., 2011, Shahsavari et al., 2012). Forced cooling using the cathode air flow is very popular for small size fuel cells (100–1000 W); this method of cooling helps keep dust and dirt away from the PEMFC stack (Chu and Jiang, 1999, Morner and Klein, 2001, Mennola et al., 2002, Sasmito et al., 2010). However, this cooling method has contradictory effects on the heat and water management of PEMFCs. Lower airflow than needed for cooling will increase the stack temperature and provoke a permanent degradation of the electrolyte membrane. On the other hand, an excess air flow can reduce the average temperature causing a decrease in the chemical reaction rate. Moreover, the water produced by the electrochemical reaction at the cathode is advected and evaporated, overall humidity is reduced, and eventually the polymeric membrane dries up causing a reduction in its proton conductivity, and also an increase in ohmic resistance, which in turn manifests itself as a lower performance (Barreras et al., 2011, Sasmito et al., 2011a).

In the case of cooling with cathode air flow, the large temperature variations between the cool incoming air flow and the hot bipolar plates, significant temperature gradients in the flow direction, and pressure drop over the cathode flow fields in the stack affect the overall performance of the PEMFC (Sasmito et al., 2010, Sasmito et al., 2012a, Noponen et al., 2004, Williamson et al., 2011). With high cathode air flow large amounts of heat can be removed from the PEMFC stacks. However, by considering the negative sides of the excess air flow using for cooling purpose, a separate reactant air supply and cooling system make a
much better option for fuel cell cooling from the performance point of view (Larminie et al., 2003, Zhang and Kandlikar, 2012). It is therefore common to add separate air coolant flow channels into the bipolar plates or an additional air cooling plates (Sasmito et al., 2012b), though it adds more weight in the system (Sasmito et al., 2011a).

Ismail et al. (2013) investigated a thermal management system over the cathode surface of the air-breathing PEMFCs. They found that the Joule heating significantly contributes to the total heat generation inside the fuel cell, whereas the entropic heat is less significant with respect to the total heat generated. They observed that by assembling an air-breathing PEMFC in an orientation of vertical (or horizontal facing upwards), the heat dissipation would be far more effective compare to when the fuel cell is faced downwards. Sasmito et al. (2013) investigated a passive thermal management for a PEMFC stack operated in cold climate condition for automotive applications. For this they used Phase Change Materials (PCM) as a passive means to transfer heat. They found that the PCM and insulator maintain the FC temperature above the freezing point (i.e. 0°C) up to two days and the FC thermal management system should be compact compare to the available designed thermal management system.

By using stack integrated cooling plates, the coolant (i.e. air) is uniformly distributed over the active area of the FC stack that reduces the temperature gradient across the cells (Shah et al., 2011). Even though the coiled based channel designs give higher and more uniform heat transfer rate, parallel straight channels are the most common geometry used in open cathode stacks (López-Sabirón et al., 2012, Li and Sabir, 2005, Kurnia et al., 2011, Barreras et al., 2008, Nie and Chen, 2010). A more uniform temperature distribution can be achieved by increasing the size of cooling channels (Matian et al., 2011); however this makes the stack larger. In addition with the size of cooling channels, the length, depth, width and number of channels play influential roles on the fuel cell cooling system performance. Therefore, several studies, both numerical and experimental, have been conducted to optimise the geometric parameters of flow channels (Manso et al., 2012, Ding et al., 2013, Akhtar et al., 2009, Wu and Ku, 2011, Shyam Prasad et al., 2006, Wang et al., 2010, Guo et al., 2013, Nie et al., 2009).
3.3.3 Large size fuel cell (>10 kW) thermal management systems

None of the above-mentioned cooling methods are recommended for large fuel cells of 10 kW or larger, which includes the range usually used in automotive applications. Due to high heat removal capacity offered by liquids, liquid cooling (e.g. by using water, mixture of water-ethylene glycol, or engine oil) (Figure 3.3) is widely used for thermal management of such large fuel cells. This cooling method requires more complex design and additional equipment such as coolant loop, a heat exchanger, a pump, flow regulation valves and a deionising filter that incur additional cost and weight (Sasmito et al., 2011a, Soupremanien et al., 2012). Numerous efforts have been made to improve the performance of liquid-based PEMFC cooling systems through optimising the design of the cooling channel and/or optimising the properties of suitable coolants (Hosseinzadeh et al., 2013, Choi et al., 2008b, Baek et al., 2011, Sasmito et al., 2011b).

PEMFCs that work at low temperatures (e.g. 60-80 °C), have the advantages of quick start-up and rapid response to highly dynamic loads that make them one of the best options for vehicle applications (GAS-2, 2013). In the automotive applications, the heat generated by the FC is rejected through a radiator. Due to the small temperature difference between the

![Figure 3.3 A typical PEMFC liquid cooling system (Soupremanien et al., 2012)](image-url)
stack and the ambient air that can be as low as 15-20 °C of so in a hot summer day, the driving force to reject the fuel cell heat to the ambient is relatively poor. Hence, the size of the radiator needs to be relatively large; this is one of the main limiting factors of PEMFC thermal management system in automotive applications (Rogg et al., 2003, Zhang and Kandlikar, 2012). Freedom car proposed to use the $Q/ITD$ as an indicative factor, in commercially available radiators using conventional coolants (e.g. ethylene glycol and water), to estimate if the size of the radiator falls within an acceptable range or not. In this factor $Q$ is the heat rejected from PEMFCs’ stacks and $ITD$ is the initial temperature difference between PEMFC and the ambient. The $Q/ITD$ target for an 80 kW PEMFC stack, operated at an ambient temperature of 40°C has been suggested to be less than 1.35–1.5 kW/K (Gittleman et al., 2010, Zhang and Kandlikar, 2012).

Although water has a higher thermal conductivity (0.60 W/m."K) than that of ethylene glycol (EG) (0.253 W/m.K) (Han, 2008), the mixture of 50% water and 50% EG is the most popular coolant for automotive applications, mainly due to its capability of lowering the freezing point down to about -35.6°C (Haiping and Walter, 2007). However, in fuel cell applications, due to ion contamination from the bipolar plates or ionic production from oxidation of the glycol, the coolant introduces electrical conductivity, corrosion, degradation of bipolar plates and ultimately decreases the efficiency of PEMFC (Zhang and Kandlikar, 2012). To remove these ions, generally a deionisation filter is employed in the cooling system. An ion exchange bed having positively and negatively charged ion exchange resin beads is provided in the filter housing for removing negative and positive ions, respectively, from the coolant (Mukesh et al., 2005). Other approaches for removing ions from the coolant are to use a ruthenium supporting activated carbon filter and to inject inert-gas into the coolant circulation system (Tsutomu, 2007).

The mixture of water/ethylene glycol produces acidic degradation products upon thermal oxidation and decrease in pH of the aqueous solutions which accelerates the corrosion of metallic components (Rossiter et al., 1985). Anticorrosive and antioxidants can resolve this problem but they are unfavourable in coolant as they obstruct the fuel cell reaction; hence, prevention of coolant degradation without any additives being strongly desired (Tsutomu, 2007). Therefore, the development of new suitable coolants for PEMFCs’ cooling system is carried out in various ways. Coolants, particularly for PEMFCs, must have a flash point greater than 93.33°C (i.e. non-flammable for transportation purposes), freezing point preferably below about -40°C to -50°C and the electrical conductivity should be as less as possible (i.e. <100 µS/cm) (Maes and Lievens, 2003, Mohaparta, 2010). Several proposed coolants for PEMFC are: de-ionised water 10–90% by volume, the organic freezing point
depressant (propylene glycol) 90–10% by volume, the polymeric ion suppressant 0.01–2% by weight and organic corrosion inhibitor 0.01–5% by weight, have been claimed to be suitable for low electrical conductivity through extended periods of use (Mohaparta, 2010); one or more carboxylic acid salts, preferably the amine or ammonium salts selected from C₅–C₉ mono- or di-carboxylic acids is also favourable for low electrical conductivity (Maes and Lievens, 2003); an expensive dielectric coolant consisting of a kerosene hydrocarbon; which can be kerosene or an emulsion of water in kerosene (Grevstad and Gelting, 1976); an environmentally friendly and inexpensive dielectric coolant for fuel cell stacks entailing vegetable oil–based fluid (Elhamid et al., 2002).

Many researchers, e.g. (Abu-Hamdeh and Almitani, 2016, Askari et al., 2016, Devendiran and Amirtham, 2016, Ghazanfari et al., 2016, Haghhighi et al., 2013, Hsieh et al., 2016, Kefayati, 2016, Rafati et al., 2012, Shahrul et al., 2016, Sidik et al., 2015, Soltanimehr and Afrand, 2016b, Tie et al., 2014, Xia et al., 2016, Xu and Kleinstreuer, 2014), found that nanofluids offer better cooling and heating performance for a variety of thermal systems compared to conventional heat transfer fluids. Owing to the fact that there would be less fluid required for removing same amount of heat due to the higher efficiency, it would allow for smaller size and better positioning of the heat exchanger in automotive applications (Singh et al., 2006). Furthermore, the initiative taken by DoE and industrial effort made by Dynalene (without any published results) have proven the potential of nanofluids as PEMFC coolants that suggests the necessity of further research on it (DoE, 2011b, Jeremy et al., 2011, Zhang and Kandlikar, 2012). For automotive applications, the high power output and density are the primary requirements and that can only be encountered by using large FC stack (~100 kW).

3.4 ELECTRICAL AND THERMO-PHYSICAL PROPERTIES OF NANOFLUIDS

3.4.1 Properties of nanofluids: effective parameters

Particles concentration, temperature, particles size, particle shape/aspect ratio, additives, acidity (pH), sonication, and aggregation of nanofluids play vital roles in determining their thermal properties (Leong et al., 2010, Murshed et al., 2009, Philip and Shima, 2012). The following sections review the previous studies conducted on the various important properties of nanofluids such as thermal conductivity, convection heat transfer coefficient, viscosity, specific heat, and density.
3.4.2 Electrical conductivity of nanofluids

In order to use nanofluids as coolants in PEMFC cooling systems, it is necessary to understand their thermo-physical and electrical properties. One of the first models that described the electrical conductivity of suspensions was introduced by Maxwell (1881). This model is applicable only for very low volume concentrations of solid-fluid suspensions with randomly dispersed, uniformly sized and non-interacting spherical particles. The Maxwell model predicts the effective electrical conductivity of suspensions ($\sigma_{nf}$). This parameter is a function of the electrical conductivity of particles ($\sigma_p$), electrical conductivity of base fluids ($\sigma_b$) and the volume fraction ($\phi$) of the particle that can be given as:

$$\sigma_{nf} = \left(1 + \frac{3(\alpha - 1)\phi}{(\alpha + 2) - (\alpha - 1)\phi}\right)\sigma_p$$  \hspace{1cm} (3.1)

where $\alpha = \sigma_p / \sigma_b$ represents the conductivity ratio of the solid and liquid phases.

This Maxwell model is a static model and does not take into account factors such as Brownian motion, aggregation and electrical double layer (EDL). Due to all of these, the Maxwell model is often distinct from the experimental results as reported by researchers (Ganguly et al., 2009, Shoghl et al., 2016b). However, for using Maxwell’s model, Cruz et al. (2005) suggested to consider three special cases in terms of the electrical conductivities of the particles and the base fluid by applying the DLVO theory. This DLVO theory successfully describes the total interaction energy between particle pairs as a function of the distance between them, stating that it is the balance of the repulsive potential due to the electric charges present in the electrical double layer and the attractive potential due to the ever present long distance van der Waals forces.

Case 1: when $\sigma_p << \sigma_b$ (insulating particles), $\alpha \to 0$ then the equation (3.1) can be written as:

$$\sigma_{nf} = \left(1 - \frac{\phi}{1 + \phi/2}\right)\sigma_b$$  \hspace{1cm} (3.2)
By expanding equation (3.2) and omitting the terms of order higher than the first, can be written as:

\[ \sigma_{nf} = \left( 1 - \frac{3}{2} \phi \right) \sigma_b \]  

(3.3)

Case 2: when \( \sigma_p = \sigma_b \), the electrical conductivities of particles and base fluids are equal then \( \alpha = 1 \) and the equation (3.1) becomes:

\[ \sigma_{nf} = \sigma_b \]  

(3.4)

Case 3: when \( \sigma_p \gg \sigma_b \) (electrical conductivity of particles is much higher than that of base fluids), \( \alpha \to \infty \) then by expanding the equation (3.1) as a series and omitting the terms containing higher than first degree, resulting in:

\[ \sigma_{nf} = (1 + 3\phi)\sigma_b \]  

(3.5)

Very recently Zyla and Fal (2016a) experimentally investigated the thermal and electrical conductivity of ethylene glycol based aluminium nitride nanofluids. The electrical conductivity of the aluminium nitride nanoparticles is \( 10^{-8} \) μS/cm. They measured the electrical conductivity over the nanoparticle volume concentration range of 1.8 to 7.9% and found 600 times enhancement of electrical conductivity for the highest measured volume concentration (7.9%) of nanoparticles. They also observed that the electrical conductivity of EG based aluminium nitride nanofluids increase linearly with increasing the volume fraction of nanoparticles in the base fluids. For EG based aluminium nitride nanofluids, they have also developed a correlation based on the experiment results as follows:

\[ \sigma_{nf} = (1 + 6950.56\phi)\sigma_b \]  

(3.6)

Sundar et al. (2014) experimentally investigated the electrical conductivity enhancement of water and EG based nano-diamond-nickel (ND-Ni) nano-composite based magnetic nanofluids. They did their experiments with low particle concentrations of 0.02 vol%, 0.05 vol%, and 0.1 vol% in the temperature range of 24 °C to 65 °C. The enhancement values in
electrical conductivity for 0.1 vol% of water based ND-Ni nanofluid were measured to be
~1340% and ~853% at 24 °C and 65 °C respectively compared to base fluid, whereas for EG
based nanofluid, they found just below and over 200% enhancements at 24 °C and 65 °C
respectively compared to EG. Their findings did not match with the classical electrical
conductivity model of Maxwell, so they developed an empirical correlation base on their
experimental results:

\[
\sigma_{nf} = (2.742 + 4812.5\phi - 0.7527T)\sigma_b
\]  \hspace{1cm} (3.7)

where T is the ratio of temperatures, \( T_{\text{max}}/T_{\text{min}} \) (\( T_{\text{max}} = 65 \degree \text{C}, \ T_{\text{min}} = 24 \degree \text{C} \)). This correlation
is valid for very low concentration nanofluids (up to 0.1 vol%) and up to a maximum
temperature of 65 °C.

Ganguly et al. (2009) investigated the effective electrical conductivity of water based \( \text{Al}_2\text{O}_3 \). The results indicated significant enhancement of electrical conductivity with the increase in both volume fraction and temperature. Since they found a linear relationship between enhancement factor and both the temperature and nanoparticle volume fractions, a two-factor linear regression analysis was employed to develop an empirical correlation as follows:

\[
\left( \sigma_{nf} - \sigma_b \right)/\sigma_b = 3679.049\phi + 1.085799T - 43.6384
\]  \hspace{1cm} (3.8)

where \( T \) is the bulk temperature of the nanofluid in °C.

Khdher et al. (2016b) experimentally determined the thermal and electrical conductivity of bio glycol based \( \text{Al}_2\text{O}_3 \) nanofluids in the temperature range of 30 °C to 80°C with the volume concentration of 0.1%, 0.3%, 0.5%, 0.7% and 1%. They observed that the electrical conductivity of nanofluids increases with the increment of nanoparticle concentration as well as temperature; and also found 154 \( \mu \text{S/cm} \) for 0.5 vol% concentration of particles. Shoghl et al. (2016b) experimentally investigated the electrical conductivity of water based CuO, MgO, CNT, TiO\(_2\), \( \text{Al}_2\text{O}_3 \) and ZnO nanofluids with the concentration of 0.01% to 2% by weight. By increasing the nanoparticle concentration, the interaction between nanoparticles increased that resulted in an enhancement in the electrical conductivity for all types of nanoparticles; however, the rate of increment varies from one nanoparticle to another. Zakaria et al. (2015a) investigated the thermal and electrical conductivity of water-EG based \( \text{Al}_2\text{O}_3 \) nanofluids with the EG concentration ranging from 0% to 100% and nanoparticle

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concentration of 0.1, 0.3 and 0.5 vol%. They found that the electrical conductivity increases as a function of volume concentration.

Minea and Luciu (2012) did an experiment on electrical conductivity of water based Al$_2$O$_3$ nanofluids in the concentration range of 1 vol% to 4 vol%. They observed that the effective electrical conductivity of alumina nanofluids increased linearly with increased volume fractions of the alumina and temperature compared to the base fluid. For 4 vol% of alumina at 70˚C, they noticed the highest electrical conductivity, 4210 μS/cm. Glory et al. (2008) measured the electrical conductivity of water-MWCNT and found that it is almost constant in the nanoparticle range of 0.01-3 wt%; however, undergoes a drop when the weight content decreases to about 0.1 wt%, which suggests that the MWCNT network in the base fluid might be percolating at this very low value. Steven et al (2011b) observed a large increase in electrical conductivity with increasing the volume fraction and decreasing the particle size. Sarojini et al. (2013b) also found the electrical conductivity increment with the decrease in the size of alumina nanoparticles. They also observed that nanofluids with low ionic strength have an enhancement in electrical conductivity while it decreases for high ionic strength. Baby and Ramaprabhu (2010) investigated the graphene based nanofluids with water/EG without any surfactant and found an enormous enhancement of electrical conductivity at 25˚C for a volume fraction of 0.03%.

Some other researchers (Wong and Bhshkar, 2006, Teng et al., 2011, Baby and Sundara, 2011, Shen et al., 2012, Sundar et al., 2016d, Liu et al., Iglesias et al., 2015) also measured the electrical conductivity of different nanofluids and found the electrical conductivity enhancement with the increase of nanoparticle concentration.

Abdolbaqi et al. (2016d) experimentally investigated the thermal and electrical conductivity of BioGlycol-water (BGW) mixture based Al$_2$O$_3$ nanofluids with the particle concentration of 0.5 -2.0 vol%. Contrary to many other studies, they found that the electrical conductivity property of BGW is dramatically decreased by the addition of nanoparticles. They observed the electrical conductivity of BGW in 40:60 decreased from 620 μS/cm to 472 μS/cm for volume concentration of 0 vol% and 2 vol% respectively. This result contradicts with the other experimental findings but most importantly match with the Case 1 $\sigma_p \ll \sigma_b$ (insulating particles) of Maxwell model.

Most of the research conducted so far on the electrical conductivity of nanofluids showed an enhancement of electrical conductivity compared with the base fluids. According to the case
1 (insulating particles) of Cruz et al. (2005) modified Maxwell model, the electrical conductivity of insulating nanoparticles based nanofluids supposed to be decreased with increase of concentrations; however, the above mentioned findings show different results from what was expected. Also considering some contradictory reports on electrical conductivity of nanofluids, this research project has been planned to conduct an experimental study on the electrical conductivity of nanofluids.

### 3.4.3 Thermal conductivity

Thermal conductivity is the most widely studied property of nanofluids in recent literature (Abdolbaqi et al., 2016a, Agarwal et al., 2016, Ahmadloo and Azizi, 2016, Azmi et al., 2016, Colangelo et al., 2016, Farbod et al., 2015, Huminic et al., 2015, Khdher et al., 2016b, Li et al., 2015b, Li et al., 2015c, Shukla et al., 2016, Sundar et al., 2016c, Xie et al., 2016, Xing et al., 2015a, Xing et al., 2016b, Zerradi et al., 2016, Żyla and Fal, 2016a). However, currently there is no absolutely reliable theory to predict the anomalous thermal conductivity of nanofluids as this property depends on various parameters (Wang and Mujumdar, 2007) such as thermal conductivities of base fluids and nanoparticles, the volume fraction, the surface area, the shape of the nanoparticles, and the temperature. Several classical models such as Maxwell, Hemilton and Crosser, Braggeman and Wasp are used to estimate the effective thermal conductivities of two-phase fluids including nanofluids. The static model, developed by Maxwell, is used to determine the effective thermal conductivity of liquid-solid suspensions of mono-disperse, low volume-fraction mixtures of spherical particles that is given by the following equation (Maxwell, 1873, Mehta et al., 2011):

\[
K_{nf} = \frac{K_p + 2K_b + 2(K_p - K_b)\phi}{K_p + 2K_b - (K_p - K_b)\phi}K_b
\]

(3.9)

where

- \(K_{nf}\) is the effective thermal conductivity of the nanofluid in W/m²K,
- \(K_p\) is the thermal conductivity of the nanoparticles in W/m²K,
- \(K_b\) is the thermal conductivity of the base fluid in W/m²K and
- \(\phi\) is the volume fraction of nanoparticle in the nanofluid in vol%.

Hamilton and Crosser (1962) extended Maxwell’s theory to non-spherical particles by the following equation:
\[ K_{nf} = K_b \left[ \frac{K_p + (n-1)K_b - \phi(n-1)(K_b - K_p)}{K_p + (n-1)K_b + \phi(K_b - K_p)} \right] \]  

(3.10)

where \( n = \frac{3}{\psi} \), in which, \( n \) is the empirical shape factor, and \( \psi \) is the sphericity. The sphericity can be defined as the ratio of the surface area of a sphere to that of the particle. The sphericity for the spherical and cylindrical shapes is assumed to be 1 and 0.5 respectively.

Bruggeman (1935) proposed a model to estimate the effective thermal conductivity of randomly distributed particles into liquid. For low solid concentrations, the Bruggeman model (equation (3.11)) provides almost same result as Maxwell model does. However, when the particle concentration increases, the Bruggeman model agrees quite well with the experimental measurements (Wang and Mujumdar, 2007).

\[ K_{nf} = \frac{1}{4} \left[ (3\phi - 1) \frac{K_p}{K_b} + (2 - 3\phi) + \frac{1}{4} \sqrt{\Delta} \right] \]  

(3.11)

where

\[ \Delta = \left[ (3\phi - 1)^2 \left( \frac{K_p}{K_b} \right)^2 + (2 - 3\phi)^2 + 2(2 + 9\phi - 9\phi^2) \left( \frac{K_p}{K_b} \right) \right] \]

It is noteworthy that most of the research studies conducted to date have focused on water–based nanofluids and only limited data exist for ethylene or propylene glycol-based nanofluids. These coolants are more suitable for use in cold (i.e. with sub-zero temperatures) regions. A complete list of the recently developed thermal conductivity models in which the key parameters of nanofluids are considered is provided in Table 3.1.
Table 3.1 Thermal conductivity models for nanofluids

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Expression</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xue (2003)</td>
<td>( g \left( 1 - \frac{\phi}{\lambda} \right) \frac{K_{nf} - K_b}{2K_{nf} + K_b} + \frac{\phi}{\lambda} \left[ \frac{K_{nf} - K_{c,x}}{K_{nf} + \beta_{2,s} (K_{c,x} - K_{nf})} \right] )</td>
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<tr>
<td></td>
<td></td>
<td>Considering the interface effect</td>
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<tr>
<td></td>
<td>( + \frac{\phi}{\lambda} \left[ 4 \frac{K_{nf} - K_{c,y}}{2K_{nf} + (1 - \beta_{2,s}) (K_{c,y} - K_{nf})} \right] = 0 )</td>
<td></td>
</tr>
<tr>
<td>Wang et al. (2003)</td>
<td>( K_{nf} = \frac{(1 - \phi) + 3\phi \int_0^\infty K_{cl}(r)n(r)}{(1 - \phi) + 3\phi \int_0^\infty K_{cl}(r) + 2K_b} )</td>
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<tr>
<td></td>
<td></td>
<td>Considered the effect of particle clustering and cluster distribution.</td>
</tr>
<tr>
<td>Yu and Choi (2003, 2004)</td>
<td>( K_{nf} = \frac{K_p + 2K_b + 2(K_p - K_b)(1 + \beta)^3 \phi}{K_p + 2K_b - (K_p - K_b)(1 + \beta)^3 \phi} )</td>
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<tr>
<td></td>
<td>( 2) \frac{K_{nf}}{K_b} = 1 + n\phi A; A = \frac{1}{3} \sum_{j=a,b,c} \frac{K_{pj} - K_b}{K_{pj} + (n - 1)K_b} )</td>
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<tr>
<td></td>
<td></td>
<td>Considered interfacial layer where (1) modified Maxwell model and (2) modified HC model with ( n=3\psi^a )</td>
</tr>
<tr>
<td>Xue and Xu (2005)</td>
<td>( \left( 1 - \frac{\phi}{\alpha} \right) \frac{K_{nf} - K_b}{2K_{nf} + K_b} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Particle size and interfacial properties are considered</td>
</tr>
<tr>
<td></td>
<td>( + \frac{\phi}{\alpha} \left( K_{nf} - K_b \right) (2K_2 + K_b) - \alpha (K_1 - K_2) (2K_2 + K_{nf}) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( + \alpha (2K_{nf} + K_2)(2K_2 + K_1) + 2\alpha (K_1 - K_2)(K_2 - K_{nf}) )</td>
<td>= 0</td>
</tr>
<tr>
<td>Prasher et al. (2006)</td>
<td>( \frac{K_{nf}}{K_b} = \left( 1 + ARR^m P_r^{0.333} \phi \right) \left[ \frac{K_p + 2K_b + 2(K_p - K_b) \phi}{K_p + 2K_b - 2(K_p - K_b) \phi} \right] )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brownian movement, particle size, thermal interfacial resistance, temperature, etc. are considered.</td>
</tr>
<tr>
<td>Investigator</td>
<td>Expression</td>
<td>Remarks</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Xie et al. (2005)</td>
<td>$\frac{K_{nf}}{K_b} = 1 + 3\Theta \phi_f + \frac{3\Theta^2 \phi_f^2}{1 - \Theta \phi_f}$</td>
<td>Deduced for evaluating the effect of nanolayer.</td>
</tr>
<tr>
<td>Xuan et al. (2003)</td>
<td>$\frac{K_{nf}}{K_b} = \frac{K_p + 2K_b - 2(K_p - K_b)\phi}{K_p + 2K_b + (K_p - K_b)\phi} + \frac{\rho_p \phi C_p}{3K_f} \sqrt{\frac{K_b T}{3\pi \eta}}$</td>
<td>Consider both the random motion and interfacial interactions of nanoparticles.</td>
</tr>
<tr>
<td>Kumar et al. (2004)</td>
<td>$\frac{K_{nf}}{K_b} = 1 + c \frac{2K_b T}{\pi \eta d_p^2} \frac{\sigma_b}{K_b (1 - \varepsilon)\rho_p}$</td>
<td>Include particle size, concentration and temperature.</td>
</tr>
<tr>
<td>Bhattacharya et al. (2004)</td>
<td>$\frac{K_p}{K_b} \phi + (1 - \phi) K_p = \frac{1}{K_b T^2 V} \sum_{j=0}^{\infty} (Q(0)Q(j \Delta t)\Delta t$</td>
<td>Four modes: collisions between fluid molecules, thermal diffusion of nanoparticles, collisions between nanoparticles due to Brownian motion and thermal interaction of dynamic nanoparticles with base fluid molecules.</td>
</tr>
<tr>
<td>Jang and Choi (2004b)</td>
<td>$\frac{K_{nf}}{K_b} = K_p (1 - \phi) + K_p \phi + 3C \frac{d_b}{d_p} K_b \text{Re}_d^2 P_t \phi$</td>
<td>All the nanoparticles are assumed to have the same rotational ellipsoid and volume fraction very low.</td>
</tr>
<tr>
<td>Avsec and Oblak (2007)</td>
<td>$\frac{K_{nf}}{K_b} = \left[ \frac{K_p + (n-1)K_b - \phi (n-1)(K_b - K_p)}{K_p + (n-1)K_b + \phi (K_b - K_p)} \right]$</td>
<td>All suspensions are considered including micro and nanoparticles.</td>
</tr>
<tr>
<td>Emami-Meibodi et al. (2010)</td>
<td>$\frac{K_{nf}}{K_b} = \frac{\alpha \left(1 + \Delta / d_p \right)}{1 + \alpha \Delta / d_p}$ where $\alpha = K_p / K_b$ and $\Delta$ is the distance between two particles</td>
<td>The freezing point of base fluid is considered.</td>
</tr>
<tr>
<td>Corcione (2011)</td>
<td>$\frac{K_{nf}}{K_b} = 1 + 4.4 \text{Re}^{0.4} \text{Pr}^{0.66} \left( \frac{T}{T_b} \right)^{10} \left( \frac{K_p}{K_b} \right)^{0.03} \phi^{0.66}$</td>
<td>Based on experimental data of $\text{Al}_2\text{O}_3$/water nanofluids with a particle size of 36 nm.</td>
</tr>
<tr>
<td>Özerinç et al. (2012)</td>
<td>$\frac{K_{nf}}{K_b} = 1 + 64.7 \phi^{0.746} \left( \frac{d_b}{d_p} \right)^{0.369} \left( \frac{K_p}{K_b} \right)^{0.7476} \text{Pr}^{0.9955} \text{Re}^{1.2321}$</td>
<td></td>
</tr>
<tr>
<td>Investigator</td>
<td>Expression</td>
<td>Remarks</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Xiao et al. (2013)</td>
<td>$K_{ef} = K_{b}^{+} + K_{f}^{+}$: $K_{b}^{+} = \frac{K_{b} + 2\phi (K_{p} - K_{b})}{K_{p} + 2\phi (K_{p} - K_{b})}$, $K_{f}^{+} = \frac{3}{\alpha} \left[ \frac{2K_{b}T}{\pi \rho u} \left( K_{b}^{1/2-d_{f}} - 1 \right) d_{f}^{8} + \frac{2(1-d_{f})^{-1} d_{f}^{8} D_{av}^{3/2}}{(d_{f} - 1)} \right]$</td>
<td>The effect of Brownian motion of nanoparticles is considered. The model is explicitly related to the thermal conductivities of the base fluids and the nanoparticles, the average diameter of nanoparticles, the nanoparticle concentration, the fractal dimension of nanoparticles and physical properties of fluids.</td>
</tr>
</tbody>
</table>
Many researchers over the past decades (Abu-Nada et al., 2008, Farajollahi et al., 2010, Garg et al., 2009, Heyhat et al., 2012, Huminic and Huminic, 2011, Huminic and Huminic, 2013, Jung et al., 2009, Khadangi Mahrood et al., 2011, Kumaresan et al., 2013, Naphon and Nakharintr, 2013, Ruan and Jacobi, 2012, Salman et al., 2012, Turkyilmazoglu and Pop, 2013, Utomo et al., 2012, Yang and Lai, 2011) have also studied the heat transfer characteristics of nanofluids experimentally as well as numerically. Masuda et al. (1993b) dispersed oxide nanoparticles (g-Al2O3 and TiO2 with w = 4.3%) in liquid and found the thermal conductivity increment of 32% and 11% respectively. Lee et al. (1999) showed that for a CuO-ethylene glycol nanofluid the thermal conductivity can be enhanced by more than 20% compared with the base fluid, with a particle volumetric concentration of 4%. Eastman et al. (2001) found that Cu-ethylene glycol with w = 0.3% gave a 40% increase in thermal conductivity (i.e. compared with the base fluid). Keblinski et al. (2002) studied the mechanism of heat transfer in nanofluids by considering Brownian motion, liquid/particle interface and the effect of nanoparticles clustering. They found that the Brownian motion was too slow to transport significant amount of heat, so thermal conductivity enhancements was due to a highly conductive layered structure around the particles and also due to cluster of particles separated by liquid layers. Putra et al. (2003b) demonstrated the temperature dependency of thermal conductivity of nanofluids with water-based CuO and Al2O3 nanoparticles of average particle diameters of 28.6 nm and 30.4 nm respectively. They found the thermal enhancement from 14-36% over the base fluid with the temperature increasing from 21°C to 51°C. Philip et al. (2008) claimed a 300% thermal conductivity increment by using magnetic nanoparticles (Fe3O4 coated with Oleic acid) in a base fluid (hexadecane) in a linear chain using a magnetic field. Evans et al. (2008) analysed the role of aggregation and interfacial thermal resistance on the effective thermal conductivity of nanofluids and nano-composites and found a significant enhancement of thermal conductivity compared with the base fluid.

Kole and Dey (2013) investigated ZnO-ethylene glycol (EG) nanofluids prepared by using prolonged sonication (>60 hours) that resulted in a superior fragmentation and dispersion of ZnO nanoparticles. They measured the effect of the nanoparticles concentration and temperature on the thermal conductivity of nanofluids. They estimated around 40% thermal conductivity enhancement for 3.75 vol% of ZnO at 30°C compared with the base fluid ethylene glycol (i.e. compared to the base fluid itself). They also found that the effective thermal conductivity of ZnO-EG nanofluids increases with increasing the sonication time and attains maximum after 60 hours of sonication. Sundar et al. (2013) also experimentally estimated the thermal conductivity of ethylene glycol and water mixture based Al2O3 and CuO nanofluids at different volume concentration and temperatures. They found the
increment of thermal conductivity of both nanofluids compared to their base fluids. They also found that the thermal conductivities enhancement for 0.8 vol% concentration Al₂O₃ nanofluid and CuO nanofluid vary from 9.8% to 17.89% and 15.6% to 24.56% respectively compared to the base fluid, when the temperature increases from 15 °C to 50 °C. Yu et al. (2010) investigated the thermal conductivity enhancement of kerosene based Fe₃O₄ nanofluids. They found that the nanoparticles (in nanofluids) tend to form larger clusters, and ultrasonication could not decrease the size of the clusters. The enhancement of the thermal conductivity increases linearly with the volume fraction of Fe₃O₄ nanoparticles and the value is up to 34.0 % for a 1.0 vol% nanofluid. Reddy and Rao (2013a) investigated TiO₂ nanofluids based on ethylene glycol-water at different volume concentrations and at different temperature. They found the enhancement of thermal conductivity of TiO₂ nanofluids with the increase of volume concentration of TiO₂ nanoparticles as well as the temperature. The thermal conductivity enhancement for water-based TiO₂ nanofluids increased from 0.659% to just over 5% when the volume concentration of TiO₂ nanoparticles increased from 0.2% to 1.0% (at 30 °C).

### 3.4.4 Convection heat transfer

The convection heat transfer coefficient of fluids is calculated using the Nusselt number. The Nusselt number (Nu) is the ratio of convection to conductive heat transfer across (normal to) the boundary (Vajjha and Das, 2012).

\[
N_u = \frac{hL}{K}
\]  

(3.12)

where \( L \) is the characteristic length, \( K \) is the thermal conductivity, and \( h \) is the convection heat transfer coefficient.

A number of forced convection heat transfer correlations have been developed for laminar, transitional and turbulent flow regime. For laminar flow (\( Re < 2300 \)), the most common and widely used correlation is proposed by Sieder and Tate (1936):

\[
Nu = 1.86 \left( Re \cdot Pr \cdot \frac{D_b}{L} \right)^{1/3} \left( \frac{\mu_b}{\mu_w} \right)
\]  

(3.13)
where $D_h$ is the hydraulic diameter of pipe in meter, $\mu_b$ and $\mu_w$ are the dynamic viscosities in Ns/m$^2$ at bulk and wall respectively, $Re$ and $Pr$ denote the Reynolds and Prandtl number of nanofluids respectively. The Reynolds number is used to predict flow patterns in different fluid flow situations and is defined as the ratio of inertial forces to viscous forces and consequently quantifies the relative importance of these two types of forces for given flow conditions. The Reynolds number can be expressed as follows:

$$Re = \frac{\rho v L}{\mu}$$  

(3.14)

where $\rho$ is the density of the fluid, $v$ is the mean velocity of the object relative to the fluid, $L$ is the characteristic linear dimension and $\mu$ is the dynamic viscosity of the fluid. The Prandtl number ($Pr$) is defined as the ratio of momentum diffusivity (kinematic viscosity) to thermal diffusivity:

$$Pr = \frac{\nu}{\alpha} = \frac{c_p \mu}{k}$$  

(3.15)

where $\nu$ is kinematic viscosity, $\alpha$ is thermal diffusivity, $c_p$ is specific heat of nanoparticles, $\mu$ is the dynamic viscosity and $k$ is thermal conductivity.

For turbulent flow ($Re > 10^4$), Dittus and Boelter (1930) correlation is frequently used:

$$Nu = 0.023 Re_{nf}^{0.8} Pr_{nf}^{0.5}$$  

(3.16)

Webb and Kim (1994) modified the Petukhov (1970) proposed correlation for three-layer turbulence boundary layer which is good for quick approximate calculations:

$$Nu = \frac{(f/2) \cdot Re \cdot Pr}{1.07 + 12.7(f/2)^{2/3} \left( Pr^{2/3} - 1 \right)}$$  

(3.17)

where the Fanning friction factor, $f$ is given:

$$f = \left( 1.58 \ln(Re) - 3.28 \right)^2$$  

(3.18)
Gnielinski (2009) has modified Petukhov (1970) correlation by using experimental data which includes the transitional range (2300<Re<10^4) as well where most automotive radiators operate:

\[
Nu = \frac{(f/2)(Re-1000)Pr}{1+12.7(f/2)^{1/2}(Pr^{2/3}-1)}
\]  (3.19)

All the above mentioned Nusselt number correlations are proposed for single phase liquid. Pak and Cho (1998) proposed a correlation for nanofluids for the Nusselt number very similar to the well-known correlation of Dittus and Boelter (1930).

\[
Nu_{nf} = 0.021Re_{nf}^{0.8}Pr_{nf}^{0.5}
\]  (3.20)

Jung et al. (2009) experimentally measured the data of Nusselt number for water-based nanofluids of laminar flow regime in micro-channels and proposed the following correlation:

\[
Nu = 0.014\phi^{0.095}Re^{0.4}Pr^{0.6}
\]  (3.21)

Maiga et al. (2006) numerically analysed the laminar flow in a tube using Al_2O_3 nanofluids and proposed the following correlations:

\[
Nu_{nf} = 0.086Re_{nf}^{0.55}Pr_{nf}^{0.5} \text{ for constant wall heat flux}
\]  (3.22)

\[
Nu_{nf} = 0.28Re_{nf}^{0.38}Pr_{nf}^{0.36} \text{ for constant wall temperature}
\]  (3.23)

Vajjha et al. (2010a) investigated the heat transfer of three nanofluids under constant boundary conditions and proposed the following heat transfer correlation:

\[
Nu_{nf} = 0.065(Re_{nf}^{0.65}-60.22)(1 + 0.0169\phi^{0.15})Pr_{nf}^{0.542}
\]  (3.24)

None of the above mentioned correlation includes the shape of the particles though the shape is a very important parameter for the convection heat transfer coefficient. Li et al. (2003) and Li and Xuan (2002) presented two equations for the Nusselt number including the Peclet (Pe) number influence of copper-water nanofluids. The Peclet number is defined to be the
ratio of the rate of advection of a physical quantity by the flow to the rate of diffusion of the same quantity driven by an appropriate gradient and can be expressed as:

$$ Pe = \frac{vd_p}{\alpha_{nf}} $$

where $d_p$ is the mean diameter of nanoparticle, $v$ is the local mean velocity and $\alpha_{nf}$ the thermal diffusivity.

$$ \alpha_{nf} = k_{nf} / (\rho_{nf} c_{nf}) $$

$$ Nu_{nf} = 0.4328 \left(1 + 11.285 \phi^{0.754} Pe_d^{0.218}\right) Re_{nf}^{0.333} Pr_{nf}^{0.4} \quad \text{for laminar flow} $$

$$ Nu_{nf} = 0.0059 \left(1 + 7.6286 \phi^{0.6886} Pe_d^{0.001}\right) Re_{nf}^{0.9238} Pr_{nf}^{0.4} \quad \text{for turbulent flow} $$

Ozerinc et al. (2012) tried to fit a curve through the experimental data of Heris et al. (2007) that lead to calculating the empirical constants. In the experiment, particle volume fraction and the Peclet number were varied between 0.2-2.5% and 2500-6500 respectively. The proposed correlation is as follows:

$$ Nu_{nf} = 0.37 \left(1 + 58 \phi^{0.75} Pe_d^{0.72}\right) Re_d^{0.333} Pr_{nf}^{0.4} $$

Compared to the research on thermal conductivity, the research on convection heat transfer of nanofluids is scarce. Based on the literature review, the effect of nanoparticles on the convection heat transfer found to be contradictory. As for example, Pak and Cho (1998) investigated the convection heat transfer of water based Al$_2$O$_3$ and TiO$_2$ nanofluids under turbulent flow conditions and found the convection heat transfer coefficient decreased by 3-12% compared to the base fluid. On the other hand Eastman et al. (1999) investigated the water based CuO nanofluids with 1% volume fraction under dynamic flow conditions and found 15% increment in the convection heat transfer coefficient compared to water. Yu et al. (2011b) numerically studied the natural convection heat transfer of aqueous copper oxide nanofluids with four different volume fractions by considering the effect of Brownian motion. They found that the time averaged Nusselt number is gradually decreased with the increase of the volume fraction of nanoparticles. Similar trends have been found by some other studies (Putra et al., 2003a, Wen and Ding, 2006, Abouali and Falahatpisheh, 2009).
Haddad et al. (2012) studied the natural convection heat transfer of CuO-water nanofluids using Rayleigh-Benard convection problem (a type of natural convection, occurring in a plane horizontal layer of fluid heated from below, in which the fluid develops a regular pattern of convection cells known as Benard cells). They considered the effects of Brownian motion, thermophoresis, thermal conductivity and viscosity. They concluded that by considering the role of thermophoresis and Brownian motion, an enhancement in convection heat transfer occurred at any volume fraction of nanoparticles. However, the enhancement is more dominant at low volume fraction of nanoparticles and the enhancement trend of convection heat transfer decreases by increasing the volume fraction of nanoparticles.

### 3.4.5 Viscosity

Different models of viscosity have been used by researchers to describe the effective viscosity of nanofluids, mainly functions of volume fraction of nanoparticles. Einstein (1906) determined the effective viscosity of a suspension of spherical solids as a function of volume fraction:

$$\mu_{nf} = (1 + 2.5\phi)\mu_b$$

(3.30)

where $\mu_{nf}$ and $\mu_b$ refer to the dynamic viscosity of nanofluid and base-fluid respectively; and $\phi$ denotes the volume fraction of nanoparticles.

Since Einstein’s analysis of the viscosity of a dilute suspension of rigid spheres in a viscous liquid, several equations have been developed in an effort to extend Einstein’s formula to suspensions of higher concentrations, including the effect of non-spherical particle concentrations. Therefore Brinkman (1952) has modified this equation to a more generalised form which is defined as follows:

$$\mu_{nf} = \frac{1}{(1 - \phi)^{3.5}}\mu_b$$

(3.31)

The influence of Brownian motion on the effective viscosity in a suspension of rigid particles was studied by Bacherlor (1977) and for the isotropic structure of suspension the following equation has been proposed:
\[ \mu_{nf} = \left(1 + 2.5\phi + 6.2\phi^2\right)\mu_b \] (3.32)

Furthermore, the different correlations developed by various researchers are summarised in Table 3.2.
Table 3.2 Viscosity models for nanofluids

<table>
<thead>
<tr>
<th>Models</th>
<th>Effective viscosity (μₙ/μₚ)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Einstein (1906)</td>
<td>(1 + 2.5ϕ)</td>
<td>Infinitely dilute suspension of spheres and valid for relatively low</td>
</tr>
<tr>
<td></td>
<td></td>
<td>particle volume fraction (ϕ≤2%)</td>
</tr>
</tbody>
</table>
| Brinkman (1952)         | \[
\frac{1}{(1 - ϕ)^{2.5}}
\]                                                          | Spherical particles with moderate particle concentrations                |
| Bacherlor (1977)        | (1 + 2.5ϕ + 6.2ϕ²)                                                                     | Rigid and spherical particles consider Brownian motion                   |
| Graham (1981)           | \[
1 + 2.5ϕ + 4.5 \left[ \frac{1}{(h/d_p)^2 + \frac{1}{(h/d_p)^2}} \right]
\]               | Spherical particles with \(d_p\) particle radius and \(h\) is inter particle spacing |
| Thomas and Muthukumar   | 1 + 2.5ϕ + 10.05ϕ² + 0.00273e^{1.66ϕ}                                                   | Micro sized particle considered                                         |
| (1991)                  |                                                                                          | For non-spherical particles                                            |
| Choi et al. (2000)      | \[
\ln \left( \frac{\mu_n}{\mu_b} \right) = \frac{\mu_n \phi}{1 - \frac{\phi}{\phi_m}}
\] |                                                                          |
|                         |                                                                                          | The particle volume concentration 2-24% and the constants \(b\) and \(n\) are 1631 and 2.8 respectively |
| Noni et al. (2002)      | \[
1 + b \left( \frac{\phi}{1 - \phi} \right)^n
\]                                      |                                                                          |
|                         |                                                                                          | TiO₂ nanoparticles (7-20 nm) with the particle concentration of 0.05-0.12% |
| Tseng and Chen (2003)   | 0.4513e^{3.598ϕ}                                                                         |                                                                          |
|                         |                                                                                          | Valid for temperature range 5-50°C                                     |
| Kulkarni et al. (2006)  | \[
\log(\mu_n) = A \left( \frac{1}{T} \right) - B
\]                                     |                                                                          |
<table>
<thead>
<tr>
<th>Models</th>
<th>Effective viscosity ($\mu_n/\mu_b$)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen et al. (2007)</td>
<td>$\left(1 - \frac{\phi_d}{\phi_a} \left(\frac{a_a}{a} \right)^{1.2}\right)^{-1.7}\phi_a$</td>
<td>$D$ is the fractal index. $a_a$ and $a$ are the radii of aggregates and primary nanoparticles respectively.</td>
</tr>
<tr>
<td>Rea et al. (2009)</td>
<td>$e^{(4.9\phi/(0.2092-\phi))}$</td>
<td>Performing a least-square fitting based on the experimental data</td>
</tr>
<tr>
<td>Chandrasekar et al. (2010b)</td>
<td>$1 + b \left(\frac{\phi}{1 - \phi}\right)^n$</td>
<td>The constant $b$ and $n$ are 5300 and 2.8 respectively for Al$_2$O$_3$ nanofluid.</td>
</tr>
<tr>
<td>Godson et al. (2010a)</td>
<td>$1.005 + 0.497\phi - 0.1149\phi^2$</td>
<td>Considered volume concentration of 0.3-0.9% and temperature 50-90°C</td>
</tr>
<tr>
<td>Corcione (2011)</td>
<td>$\frac{1}{1 - 34.87(d_p/d_f)^{0.3}(\phi)^{0.03}}$</td>
<td>Considered the various experimental data and $d_p$ is the diameter of particle, $d_f$ is the equivalent diameter of the base fluid molecule</td>
</tr>
<tr>
<td>Boboo et al. (2012)</td>
<td>$1 + a\phi + b\phi^2$</td>
<td>$a=0.50437$ and $b=1.744$ for MWCNT/water; $a=0.36838$ and $b=0.25271$ for TiO$_2$/water.</td>
</tr>
<tr>
<td>Vakili-Nezhaad and Dorany (2012)</td>
<td>$1 + 1.59\phi - 16.36\phi^2 + 50.4\phi^3$</td>
<td>Dispersing single walled carbon nanotubes in lubricating oil</td>
</tr>
</tbody>
</table>
It is seen from the above correlations that the viscosity of a nanofluid is a function of the viscosity of the base fluid and the volume fraction of the nanoparticles dispersed in the mixture. Theoretically speaking, all of the above correlations might be used for the determination of the nanofluid viscosity; however, none of them can fully satisfy all the conditions of nanofluids and hence the experimental study must be conducted to verify these correlations and for getting accurate results. As for example, the Einstein’s (Einstein, 1906) model on viscosity is based on the linearly viscous fluid consisting of dilute, suspended, spherical particles, and volume concentration less than 0.02 vol%. Brinkman has extended Einstein’s formula to a more generalised form for use with moderate particle concentrations (1.0 vol%), hence Brinkman equation (3.31) is used in the modelling PEMFCs cooling system.

The viscosity of nanofluids increases with the increase of particle volume concentration in the base fluid (Bashirnezhad et al., 2016, Sundar et al., 2016a, Żyła and Fal, 2016a). Viscosity measurement with the dispersion of micrometre and nanometre sized nanoparticles has been studied by many researchers (Ahuja, 1975, Masuda et al., 1993a, Pak and Cho, 1998, Kwak and Kim, 2005, Das et al., 2006, Wang et al., 1999). Phuoc and Massoudi (2009) observed the viscosity of Fe₂O₃-deionised water nanofluids and found that the fluid have shown the Newtonian behaviour up to the volume fraction of 0.02%. However beyond this threshold, the fluid acts as a non-Newtonian fluid. Although the viscosity of nanofluids increases with the increase of nanoparticle volume fractions; at higher volume fraction (0.1 vol%) the viscosity increment is smaller. Bobbo et al. (2012) measured the viscosity of water based single wall carbon nano-horn (SWCNH) and titanium dioxide (TiO₂) nanofluids, using a rheometer. Though both fluids showed Newtonian behaviour, negligible variations on the viscosity has been found with the nanoparticle concentration of 0.1%. Similar other studies about the effect of particle concentration, temperature, etc. on the viscosity of nanofluids have been reported in the literature in recent years (Halelfadl et al., 2013, Jeong et al., 2013, Li et al., 2013, Mehrabi et al., 2013).

Nguyen et al. (2007a) investigated the influence of both the temperature and the particle size on the dynamic viscosities of Al₂O₃/water and CuO/water nanofluids. They found that the viscosity of CuO/water was higher than that of Al₂O₃/water nanofluid under the same conditions (e.g. concentration, size of the nanoparticles, base fluid, etc). Kole and Dey (2010c) investigated the viscosity of alumina-water nanofluids to be used as car coolants. They discovered that the viscosity of the nanofluids they studied increases with the increase in nanoparticle concentration and decreases with increase in temperature.
According to Lee et al. (2011) the presence of the surfactant in the base–fluid shows a marginal increase in the viscosity, up to 25 °C of temperature, while the effect is almost nullified at temperatures above 25 °C and the viscosity even decreases gradually at higher temperatures (>80°C). On the other hand, the effective viscosity increases nonlinearly with the increase of nanoparticles concentration. However, it is important to note that the use of nanofluids as coolants in PEMFC cooling can eliminate the requirement for a deionising filter, which on the other hand, reduces the pumping power losses compared to when the conventional coolants (e.g. the mixture of water and EG) are used in the system.

3.4.6 Specific heat

Although the specific heat is an effective and important factor used for determining the thermal performance of nanofluids, it has received very little attention in the literature (Zhou and Ni, 2008a, Ghadimi et al., 2011a). For a given volume concentration of nanoparticles in a base fluid, the specific heat can be calculated using the mixture formula. This formula is valid for homogeneous mixtures and is given by the following equation:

$$C_{\text{pf}} = \frac{(1-\phi)(\rho c_p)_b + \phi(\rho c_p)_p}{(1-\phi)\rho_b + \phi\rho_p}$$

(3.33)

where $C_{\text{pf}}$ is the specific heat of nanofluids, $c_{pp}$ and $c_{pb}$ are the specific heat of nanoparticle and base-fluid respectively, and $\rho_p$ and $\rho_b$ are the density of nanoparticle and base-fluid respectively.

The specific heat of nanofluid can be determined by assuming thermal equilibrium between the nanoparticles and the base fluid. However, most of the researchers used the simple and standard equation based on the volume fraction (Das et al., 2007, Khanafer and Vafai, 2011, Putra et al., 2003b, Jang and Choi, 2004a, Gosselin and da Silva, 2004, Haddad et al., 2012). The expression can be given as:

$$C_{\text{pf}} = \phi c_{pp} + (1-\phi)c_{pb}$$

(3.34)

Other researchers also suggested alternative approaches based on the specific heat of different nanofluids (Duangthongsuk and Wongwises, 2008, Büyük Öğüt, 2009,
\[
\left( \rho c_p \right)_{nf} = \phi \left( \rho c_p \right)_{f} + (1-\phi) \left( \rho c_p \right)_{b} 
\]

\[
C_{pn} = \frac{A(T/T_0) + B(C_{pp}/C_{pb})}{C + \phi} 
\]

Vajjha and Das (2009b) carried out measurements of specific heat of three different nanofluids (Al\(_2\)O\(_3\), SiO\(_2\) and ZnO) and developed a correlation which is given as:

Table 3.3 The value of A, B and C for the selected nanoparticles (Al\(_2\)O\(_3\), SiO\(_2\) and ZnO) (Vajjha and Das, 2009b).

<table>
<thead>
<tr>
<th>Nanofluids</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Max. deviation</th>
<th>Avg. abs. Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.24327</td>
<td>0.5179</td>
<td>0.4250</td>
<td>5</td>
<td>2.28</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.12569</td>
<td>0.9855</td>
<td>0.299</td>
<td>4.4</td>
<td>2.7</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.48294</td>
<td>1.1937</td>
<td>0.8021</td>
<td>3.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Very recently Satti et al. (2016) experimentally investigated the specific heat of 60/40 propylene glycol-water based aluminum (Al\(_2\)O\(_3\)), zinc oxide (ZnO), copper oxide (CuO), titanium oxide (TiO\(_2\)) and silicon dioxide (SiO\(_2\)) at particle volume concentration 0.5-6% and over the temperature range of -30°C to 90°C. They found that the specific heat decreases with increasing nanoparticles concentration and increases with increasing the temperature. However, they noticed that the effect of particle size on the specific heat is insignificant. Tiznobaik and Shin (2013) dispersed four different sized silicon-dioxide nanoparticles (5, 10, 30 and 60 nm) in a molten salt eutectic and observed a specific heat enhancement of 25% above that of the base fluid. They explained this enhancement of the specific heat by the high specific surface energies that are associated with the high surface areas of nanoparticles and the needle-like structures induced by the addition of these particles. Zhou et al. (2009) measured the specific and volumetric heat capacity of CuO nanofluids experimentally and found that the specific heat capacity of CuO nanofluid decreases gradually with increasing the volume concentration of nanoparticle. De-Robertis et al. (2012b) measured the specific heat of copper nanofluids by using the ASTM E2719 standard procedure and applying the
modulated temperature differential scanning calorimetric technique. They noticed that the presence of copper nanoparticles in the base fluid reduces the specific heat values of nanofluids. Kumaresan and Velraj (2012) measured the thermo-physical properties of water-ethylene glycol mixture based CNT nanofluids. A peculiar phenomenon of the higher enhancement in the specific heat value at the lower nanoparticle concentration (0.15%) and the reduction in the enhancement in the specific heat value at the lower nanoparticle concentration have been observed.

3.4.7 Density

Only a few researchers, among them Karimi and Yousefi (2012) have studied the density of nanofluids, even though this parameter plays a significant role in the heat transfer phenomena. The density of nanofluids increases with an increase in the volumetric concentration of the particles as their densities are higher than that of the base fluid; whereas the density of nanofluid decreases very modestly with temperature increase, that is mostly due to the effect of the temperature on the density of the base fluid (Vajjha and Das, 2012).

The density of nanofluid based on the physical principle of the mixture can be represented as (Khanafer and Vafai, 2011, Pak and Cho, 1998):

\[
\rho_{nf} = \frac{m}{V_{nf}} = \frac{m_b + m_p}{V_f + V_p} = \frac{\rho_b V_f + \rho_p V_p}{V_f + V_p} = \left(1 - \phi\right)\rho_b + \phi\rho_p
\]  

(3.37)

where \(m_b\) and \(m_p\) are the masses of base-fluid and nanoparticles respectively; and \(V_f\) and \(V_p\) are the volumes of base-fluid and nanoparticle respectively.

To examine the validity of equation (3.37) Pak and Cho (1998) and Ho et al. (2010) conducted experimental studies and measured the density of \(\text{Al}_2\text{O}_3\)-water nanofluids at room temperature and found an excellent agreement between the experimental results and the predictions made by equation (3.37). Based on the Ho et al. (2010) experimental data, Khanafer and Vafai (2011) developed a new correlation to determine the density of \(\text{Al}_2\text{O}_3\)-water nanofluids at different temperatures:

\[
\rho_{nf} = 1001.064 + 2738.6191\phi - 0.2095T; \ 0 \leq \phi \leq 0.04, \ 5 \leq T (\degree C) \leq 40
\]  

(3.38)
They found the R-squared ($R^2$) of the regression is 99.97% and the maximum relative error is 0.22%. They have also found that the rate of the decrease of the effective density of Al$_2$O$_3$-water nanofluid with increasing temperature is not significant.

### 3.5 Nanofluids in Cooling of Electronics and Other Heat and Power Applications

Last couple of decades, nanofluids have received attention to be used in many heat transfer applications due to their enhanced thermal and rheological prosperities of the fluid by just adding a little amount of nanoparticles. Technological developments such as microelectronic devices with fast operating speeds but smaller features, higher-power engines, and brighter optical devices are driving an increase in flux density thus requiring advances in cooling methods (Lee, 2009). For liquid cooling of electronics using microchannels (1-100 μm) integrated in the chips, nanofluids considered to be attractive alternatives to the existing bulky aluminium heat sinks (Mital, 2012). Several researchers (Vasu et al., 2009, Lai et al., 2012, Escher et al., 2011) have studied thermal performance of nanofluids in cooling of electronics, and found that the use of nanofluids in electronics cooling is promising.

Ijam and Saidur (Ijam and Saidur, 2012) mathematically analysed different types of nanofluids for mini-channel heat sink of copper in the electronics applications. They found that the enhancement in thermal conductivity by dispersing SiC in water at 4 vol% fraction was about 12.5% and TiO$_2$ in water was just below 10% for the same volume fraction. Putra et al. (2011) have investigated the application of nanofluids to a heat pipe liquid-block and the thermoelectric cooling of electronic equipment and observed a significant improvement on the heat transfer from the CPU. Comparing to the other conventional cooling techniques, they found that using nanofluids in the cooling system of these electronics allows for a greater decrease in CPU temperature with higher thermal performance. Nguyen et al. (2006) has investigated the heat transfer enhancement and behaviour of water based Al$_2$O$_3$ nanofluids for use in a closed cooling system for microprocessors or other heated electronic components. For the concentration of 6.8 vol%, they found the heat transfer coefficient increment by as much as 40% compared to that of the base fluid.

Liquids embedded with nanoparticles have reported to enhance performance of the various types of miniature camera lenses, cell phone displays, and other micro-scale fluidic devices (Nagpal, 2008). The application of nanofluids in cooling industry can improve the
performance of refrigeration systems by about 50% and hence reduce their running time (Liu et al., 2011).

Several researchers (Tyagi et al., 2009, Shabani et al., 2010) theoretically investigated the feasibility of using a non-concentrating direct absorption solar collector (DAC) using nanofluids as the absorbing medium and compared its performance with that of a typical flat-plate collector. It was observed that the presence of nanoparticles increases the absorption of incident radiation by more than nine times over that of pure water and the efficiency of a DAC using nanofluid as the working fluid is found to be up to 10% higher than that of a flat-plate collector.

Currently, the great demand in the use of nanofluids as coolants in heat exchangers has garnered a number of research interests. Huminic and Huminic (2016) numerically investigated the heat transfer and entropy generation inside a helically coiled tube-in-tube exchanger in laminar flow regime by using CuO and TiO$_2$ nanofluids. They have achieved 91% and 80% heat transfer enhancement for CuO and TiO$_2$ nanofluids compare to the base fluid respectively. Saeedan et al. (2016) investigated the thermal performance of a helically baffled heat exchanger combined with a 3D fined tube using water based Cu, CuO and CNT nanofluids at different concentrations numerically. They observed a heat transfer increment with the increase of nanoparticles concentration. Aly (2014) observed the heat transfer coefficient effectively enhanced in tube-in-tube heat exchanger when Al$_2$O$_3$/water nanofluid is used. His numerical studies showed that the heat transfer coefficient enhancement is more with increasing nanoparticles concentration. Their study was found to be consistent with conventional correlations for estimating the thermal performance of heat exchanger using nanofluids. Narrein and Mahammed (2013) numerically investigated the effects of the nanoparticles type (i.e. using Al$_2$O$_3$, SiO$_2$, CuO and ZnO), their concentrations (ranges from 1- 4 vol%), size of particles (25-80 nm), and base fluids (i.e. using water, ethylene glycol, and engine oil) on the heat transfer and fluid flow characteristics of a helically coiled tube heat exchanger (HCTHE). They found that the nanofluids can enhance the thermal properties and performance of HCTHE. They also observed that convection heat transfer tends to decrease above 2 vol% concentration of CuO nanofluids. Kumar et al. (2014) obtained 30% increase in the Nusselt number in their numerical investigation by using Al$_2$O$_3$/water nanofluid in a coiled heat exchanger. Elias et al. (2014b) obtained maximum 28% enhancement of overall heat transfer coefficient for cylindrical shape particles with 1 vol% concentration of Boehmite alumina ($\lambda$-AlOOH) used in a shell and tube heat exchanger (compared with when the base fluid was used). Zamzamian et al. (2011) estimated the heat transfer coefficient in turbulent flow regime using different concentrations (0.01 to 1.0%
weight) of nanofluids and a double pipe and plate heat exchangers. They observed convection heat transfer coefficient increment with the increase of concentrations of nanofluids in the range of 2% to 50%. Albadr *et al.* (2013) studied the forced convection heat transfer coefficient of water based Al$_2$O$_3$ nanofluid in a horizontal shell and tube heat exchanger under turbulent flow conditions. The heat transfer coefficient of the nanofluid increases with the increment of the mass flow rate as well as the volume concentration of the water based Al$_2$O$_3$ nanofluid. Abbasian Arani and Amani (2013) experimentally investigated the convection heat transfer coefficient in fully developed turbulent flow of water based TiO$_2$ nanofluid in a horizontal double tube counter-flow heat exchanger. Kumar *et al.* (2014) experimentally investigated the heat transfer and pressure drop of a shell and helically coiled tube heat exchanger using water based Al$_2$O$_3$ nanofluids under turbulent flow condition. They concluded that the water based Al$_2$O$_3$ nanofluids can be applied as a coolant in a heat exchanger with negligible pressure drop. Khedkar *et al.* (2014) observed above 33% enhancement in the overall heat transfer coefficient with 2 vol% water based TiO$_2$ nanofluids compared to the base fluid in a concentric tube heat exchanger. Kumar *et al.* (2014) did the heat transfer and pressure drop analyses on a shell and helically coiled tube heat exchanger by using water-based Al$_2$O$_3$ nanofluids under a turbulent flow regime. They observed an average of around 30% overall heat transfer coefficient enhancement using 0.8 vol% nanofluids.

Peyghambarzadeh *et al.* (2011b) experimentally compared the heat transfer performance of Al$_2$O$_3$ with those of base fluids to be applied as coolants in car radiators. They obtained the heat transfer enhancement of about 40% compared to the based fluids. They concluded that the heat transfer behaviours of the nanofluids highly depend on the particle concentration and the flow conditions. Choi *et al.* (2008a) showed that nanofluids have the potential of being recognised as new generation of coolants for vehicle thermal management due to their higher thermal conductivities compared to their base fluids. Tzeng *et al.* (2005) dispersed CuO and Al$_2$O$_3$ nanoparticles into engine transmission oil and found that CuO nanofluids produced the lowest transmission temperatures at both high and low rotating speeds.

The enhancement of the cooling system in vehicles may increase its efficiency, stability, life span, fuel consumption, while can contribute in maintaining the emission level at a desirable level. It is also expected to help open additional engine compartment space due to smaller size of the radiator to be employed when nanofluids are used as coolants. Some literature has investigated the applicability of nanofluids in vehicle engine cooling systems with a view to increasing the efficiency of heat removal from the engine. The findings of the researchers are given in Table 3.4.
Table 3.4 Summary of studies on using nanofluids in vehicle applications

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Nanofluids</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tzeng <em>et al.</em> (2005)</td>
<td>CuO/Engine oil, Al₂O₃/Engine oil</td>
<td>They obtained the best heat transfer enhancement with CuO nanofluids and the lowest heat transfer distribution for all rotating speeds (400rpm, 800rpm, 1200rpm, and 1600rpm).</td>
</tr>
<tr>
<td>Saripella <em>et al.</em> (2007)</td>
<td>CuO-water/EG (50/50)</td>
<td>Higher heat transfer coefficients of nanofluids resulted in lower engine and coolant temperatures as well as improved the engine power, coolant pump speed, and power.</td>
</tr>
<tr>
<td>Zhang <em>et al.</em> (2008)</td>
<td>Graphite-HDD engine coolant</td>
<td>The cooling capability of HDD coolant is increased by 15% with the 3 wt% nano-graphite.</td>
</tr>
<tr>
<td>Lv <em>et al.</em> (2010)</td>
<td>Cu/Water, Cu/Engine oil</td>
<td>Heat transfer coefficient and heat dissipating capacity enhancement of water based Cu nanofluid with 5 vol% concentration were about 46% and 43.9% respectively compared to the base fluid.</td>
</tr>
<tr>
<td>Vajjha <em>et al.</em> (2010b)</td>
<td>Al₂O₃-Water/EG (40:60)</td>
<td>At a Reynolds number of 1000, 91% and 86% enhancement of heat transfer coefficient has been achieved by using 10 vol% of Al₂O₃ nanofluid and 6 vol% of CuO nanofluid respectively.</td>
</tr>
<tr>
<td>Kole and Dey (Kole and Dey, 2010b)</td>
<td>Al₂O₃-car coolant</td>
<td>The viscosity of nanofluid increases with increasing nanoparticle concentration and decreasing with increase in temperature. They also found that after adding nanoparticle with car coolant, it behaves like non-Newtonian fluid.</td>
</tr>
<tr>
<td>Peyghambarzadeh <em>et al.</em> (2011a)</td>
<td>Al₂O₃-Water</td>
<td>Heat transfer efficiency can be increase up to 45% compared to the base fluid.</td>
</tr>
<tr>
<td>Peyghambarzadeh <em>et al.</em> (2011b)</td>
<td>Al₂O₃-Water/EG</td>
<td>The heat transfer enhancement is obtained around 40% compared to the based fluids.</td>
</tr>
<tr>
<td>Peyghambarzadeh <em>et al.</em> (2013)</td>
<td>CuO-Water</td>
<td>With the concentration of 0.65 vol% of Fe₂O₃, the heat transfer enhancement of about 9% is obtained.</td>
</tr>
<tr>
<td>Raja <em>et al.</em> (2013)</td>
<td>Al₂O₃-Water</td>
<td>The maximum enhancement of overall heat transfer coefficient is obtained around 25% with.</td>
</tr>
<tr>
<td>Researchers</td>
<td>Nanofluids</td>
<td>Findings</td>
</tr>
<tr>
<td>---------------------</td>
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<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Teng and Yu (2013)</td>
<td>MWCNTs-Water/EG</td>
<td>Maximum efficiency factor was 14.1% at low concentration of MWCNT nanoparticle whereas maximum enhancement of thermal conductivity of the MWCNT–EG/W nanofluids was 49.6% with 0.4 vol.% of nanoparticles compared to EG/W.</td>
</tr>
<tr>
<td>(Delavari and Hashemabadi, 2014)</td>
<td>Al₂O₃-Water, Al₂O₃-EG</td>
<td>Nusselt number was 10%-45% higher than that of the base fluids in two-phase approach</td>
</tr>
<tr>
<td>Chougule and Sahu (2014)</td>
<td>Al₂O₃-Water, CNT-Water,</td>
<td>The maximum enhancement of thermal conductivity was obtained around 76% with the 1 vol% CNT-water nanofluids at 80 °C compared to the base fluid</td>
</tr>
<tr>
<td>Heris et al. (2014)</td>
<td>CuO-water/EG (60:40)</td>
<td>55% enhancement of heat transfer achieved with 0.8 vol% nanofluid compared to base fluid</td>
</tr>
<tr>
<td>Ali et al. (2014)</td>
<td>Al₂O₃-Water</td>
<td>The maximum heat transfer enhancement is obtained about 14.45% at 0.01 vol% concentration compare to the base fluid, after that the heat transfer is decreasing with the increase of concentration</td>
</tr>
<tr>
<td>Chavan and Pise (2014)</td>
<td>Al₂O₃-Water</td>
<td>The maximum enhancement of thermal conductivity of the Al₂O₃–water nanofluids was 40–45% with 1 vol.% concentration compared to base fluid</td>
</tr>
<tr>
<td>Nieh et al. (2014)</td>
<td>Al₂O₃-Water/EG, TiO₂-Water/EG</td>
<td>The thermal conductivity of Al₂O₃ and TiO₂ nanofluids are in the range of 24–39% higher than that of EG/water at 0.2-2 wt.% nanoparticle concentrations . Maximum efficiency factor was 27.2% using TiO₂–EG/water with 2 wt.% nanoparticle concentration whereas it is 14.4% using Al₂O₃–EG/water with 2 wt.% nanoparticle concentration compared to EG/W</td>
</tr>
<tr>
<td>Amri et al. (2016a)</td>
<td>Graphene-Water/EG</td>
<td>They achieved the improved thermal conductivity and heat transfer rate due to the highly surface</td>
</tr>
</tbody>
</table>
3.6 STUDY OF PEMFC LIQUID COOLING SYSTEM

In general, the mixtures of water/EG are used as coolant in the radiator of automotive engines due to their low freezing point though these fluids have poor heat transfer performance compared to pure water (Chougule and Sahu, 2014). However, very recently the researchers are trying to apply nanofluids as coolants in the fuel cell applications though only limited studies have been conducted theoretically and no experimental results have been reported in the literature. In this section, we will look at the available literature that discussed the thermal management of liquid-cooled PEMFCs.

Moore et al. (2005) focused on fuel cell stack, the air supply, the water and thermal management, and hydrogen supply of a dynamic fuel cell vehicle simulation tool for the analysis and evaluation of fuel cell vehicle. Each of the four major subsystems is described and the specific simulation methodology is presented. In the water and thermal management system, the heat transfer component and primary water recovery unit are considered for determining their impact as a parasitic power loss for the system. The radiator fan has been sized according to the specific peak load. The stack efficiency is calculated in the simulation as the gross electrical power produced by the stack divided by the lower heating value of the fuel used in the stack.

Bao et al. (2006) analysed the water and thermal management of the PEMFC cooling system analytically consisting of the PEMFC stack, radiator, condenser and membrane humidifier. They sized and rated two compact heat exchangers, radiator and condenser for maintaining the heat and material balance of the PEMFC systems. They considered the influence of air stoichiometric ratio, cathode outlet pressure, recycling humidification, membrane humidification and recycling combining membrane humidification for designing the water and thermal management system in fuel cell systems.
Hosseinzadeh et al. (2013) have developed a general zero-dimensional PEMFC model for forklift truck application comprising of a compressor, an air humidifier, a set of heat exchangers and a recirculation pump. They investigated the water and thermal management of the fuel cell stack as well as the balance of plant (BOP) By substituting liquid water with 50/50 water-EG mixture, the mass flow of coolant increases by about 32-33% in the inner loop and 60-65% in the outer loop for all ranges of current. They observed by using 50/50 water-EG mixture the system can be started up at about -25 °C with negligible change in the efficiency.

Zhang et al. (2004) modelled a PEMFC thermal system to investigate the thermo-physical behaviour and system parameters of the thermal management system. They assessed the effects of operating parameters such as stack power output, cooling water flow rate, air flow rate, and environmental temperature. The model was capable of determining the operating temperatures of the thermal system components, and also fully assesses their performance in dynamic operating conditions applications, i.e. in automobiles. They validated their model experimentally. Zhao et al. (2015) developed and validated semi-mechanical, semi-empirical thermal management model of a water-cooled PEMFC system by increasing the coolant temperature difference between outlet and inlet temperatures, increasing the output current and reducing the coolant inlet temperatures. They found that the modelling results well matched with the experimental results with the same operating conditions.

Zakaria et al. (2015b) numerically analysed the thermal enhancement for a single PEMFC using 0.1 vol.% to 0.5 vol.% concentration of water-EG based Al₂O₃ nanofluids using coolant flows with the Re numbers in the range of 30 to 150. The cooling plates were subjected to a constant heat flux of 100 W. They found 7.3% and 4.6% heat transfer enhancement with 0.5 vol% and 0.1 vol% nanofluids respectively compared to the base fluid. However, they didn’t conduct any experimental study to validate their theoretical findings and even they didn’t consider the electrical conductivity of nanofluids. In this research, we conduct both experimental and theoretical studies on PEMFCs cooling system using three different types of nanofluids (e.g. ZnO, TiO₂ and Al₂O₃). For determining the optimum concentration of nanoparticles, the electrical conductivity has been measured experimentally.

There is almost no any experimental study of PEMFC cooling using nanofluids. Very few researchers tried to investigate the effects of nanofluids on a single-cell PEMFC but not on the stack including the study conducted by Zakaria et al. (2015c). This study investigated the heat transfer and fluid flow performance of 50/50 water/EG based Al₂O₃ nanofluid with the
concentration of 0.1 and 0.5 vol% in a single cooling plate PEMFC where a 100 W heating pad was used as a source of heat mimicking the fuel cell heat generation. They found heat transfer improvement of up to ~13.9% for 0.5 vol% Al$_2$O$_3$ nanofluid compared to the base fluid (i.e. water/EG). They concluded that the water/EG based Al$_2$O$_3$ nanofluid can be potentially suitable to be used as a coolant in PEMFCs. They also repeated their study with 60/40 water/EG used as based fluid and observed a better improvement and as the result recommended that the 60/40 water/EG based Al$_2$O$_3$ is the best coolant for PEMFC between those they had studied.

3.7 SUMMARY

From the comprehensive literature review, the following research gap has been identified

- No experimental study or data has been reported on PEMFCs cooling system using nanofluids such as 50/50 water-EG based Al$_2$O$_3$, TiO$_2$ and ZnO as coolants, and the effects of using nanofluids as coolants on the electrical and thermal performance of PEMFCs have remained untouched.

This research gap will be addressed thoroughly in the following chapters through both theoretical and experimental studies. First of all the theoretical study will be conducted on PEMFCs cooling system using nanofluids as well as conventional coolants (e.g. 50/50 water-EG mixture) as coolants in order to estimate the size of the PEMFCs cooling system. Secondly, the electrical and thermo-physical characteristics of selected nanoparticles will be performed to find out the suitable nanofluids. Thirdly, the experimental study will be conducted on 2.4 kW PEMFC stack using nanofluids to investigate their effects on the electrical and thermal performances of PEMFCs.
CHAPTER 4: USING NANOFLOUIDS AS COOLANTS IN PEMFC COOLING SYSTEMS: A THEORETICAL STUDY

4.1 PEMFC COOLING SYSTEM MODELLING

4.1.1 An overview

Numerous simulation models have been developed on various aspects of PEMFC cooling systems (Ziogou et al., 2011, Saygili et al., 2015, Panos et al., 2012, Panos et al., 2010, Mert et al., 2012, Lisio et al., 2014); however, none of them has involved the use of nanofluids as coolants. During the past several years, many PEMFC models, from zero-dimensional to complex three-dimensional models, have been reported in the literature and some are also available commercially (Haraldsson and Wipke, 2004, Berg and Kulikovsky, 2015, Cao et al., 2015, Haddad et al., 2015, Headley and Chen, 2015, Ismail et al., 2014, Robin et al., 2015).

In this study, by applying a semi-analytical, and steady state model of PEMFC cooling systems, the potential advantages of using nanofluids over conventional coolants (e.g. mixture of water and ethylene glycol) are investigated. The PEMFC cooling system (Figure 4.1) simulation used in this study consists of sub-models of PEMFC stack (both electrical and thermal), heat exchanger, and coolant pump as well as a model describing the thermo-physical behaviour of different coolants used in the system. The effect of nanofluids on heat exchanger size and pumping power has been studied using various concentrations of nanoparticles in different types of nanofluids. This simulation model has been created in MATLAB.

Figure 4.1 The schematic representation of a PEMFC liquid cooling system
4.1.2 PEMFC model

4.1.2.1 Electrochemical model

For modelling the PEMFC stack, the following assumptions were considered in the present study:

- The product water generated at the cathode is assumed to be in the liquid state.
- The water condensation/evaporation rate is not considered; instead, the water vapour and liquid phase are assumed to be in equilibrium.
- Water transport in and out of the electrodes was in the form of vapour.
- The liquid water was assumed to exist at the surface of the channels, and the volume to be negligible.
- Ideal gas law was employed for gaseous species.
- Stack temperature is assumed to be uniform.
- The electrode layers are ultra-thin, so that the gas transport resistance through the electrode porous layer could be neglected.
- For the pressure drop calculation, the liquid water was neglected. The entrance and exit losses were neglected, which were too small compared with the overall pressure drop.

When a fuel cell delivers electrical power to the load, its voltage $V_{cell}$ drops from its level at open circuit condition ($E_{Nernst}$) due to internal current (i.e. fuel crossover) $\Delta V_{cross}$, activation overpotential $\Delta V_{act}$, ohmic overpotential $\Delta V_{ohm}$, and concentration overpotential $\Delta V_{con}$. Hence, the actual voltage of the PEMFC ($V_{cell}$) can be calculated using the following equation (Larminie and Dicks, 2003):

$$V_{cell} = E_{Nernst} - \Delta V_{act} - \Delta V_{cross} - \Delta V_{ohm} - \Delta V_{con}$$

(4.1)

The Nernst equation gives the open circuit cell voltage as follows:

$$E_{Nernst} = E_0 + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \left( P_{O_2} \right)^{1/2}}{P_{H_2O}} \right)$$

(4.2)

where $E_0$ is the electromotive force (EMF) at standard pressure and temperature (i.e. for a 100% efficiency cell); $F$ is the Faraday’s constant that is 96485 coulombs; $R$ is universal gas
constants that is 8.314 kJ/mol; \( T \) is the stack operating temperature in °K, and \( P_{H_2}, P_{O_2} \) and \( P_{H_2O} \) are the partial pressures in kPa of hydrogen, oxygen and water respectively. The partial pressure equations are widely available in literature (Springer et al., 1991, Shabani, 2010).

The partial pressures can be expressed as (Springer et al., 1991):

\[
\log P_{H_2O} = -2.1794 + 0.02953 T_{st} - 9.1837 \times 10^{-5} T_{st}^2 + 1.4454 \times 10^{-7} T_{st}^3
\]

(4.3)

where the stack temperature \( T_{st} \) is in deg C.

\[
P_{H_2} = 0.5 \left[ \frac{P_{H_2}}{e^{\left( \frac{1.658}{T_{st}/1334} \right)}} - P_{H_2O} \right]
\]

(4.4)

where \( P_{H_2} \) is the hydrogen inlet pressure in kPa at the anode side, the ambient temperature \( T \) is in deg K and \( i \) is current supplied by the FC stack.

\[
P_{O_2} = \left[ \frac{P_{air}}{e^{\left( \frac{1.972}{T/1334} \right)}} - P_{H_2O} \right]
\]

(4.5)

where \( P_{air} \) is the air pressure in kPa on the cathode side, the ambient temperature \( T \) is in deg K and \( i \) is current supplied in amp by the FC stack.

**Activation losses:** The slowness of the reaction on the electrode surface causes the activation losses. The activation loss is also known as over-potential and can be calculated by measuring the voltage difference of between the two terminals at open circuit condition. The reaction happens inside the FC is forcing the hydrogen to split into electrons and protons. The protons travel through the electrolyte, while electrons through the outer circuit and combine at the cathode.

The activation losses can be expressed (Larminie and Dicks, 2003, Barbir, 2012):

\[
\Delta V_{act} = A \ln \left( \frac{i}{i_0} \right)
\]

(4.6)
where $i$ is the operating current density, and $i_0$ is the exchange current density of the fuel cell that can be defined as the rate of reaction at the reversible potential (when the overpotential is zero by definition). Usually, the exchange current density at cathode side is very smaller (i.e. $10^5$ times smaller) compared to that of the anode side. Hence the overvoltage at anode side is sometime neglected. The high exchange current density indicates that the electrode surface is more active and the current is likely to flow in one direction. Hence, the high value of $i_0$ is preferable for hydrogen fuel cells (Hirschenhofer et al., 1998, Larminie and Dicks, 2003, Rayment and Sherwin, 2003).

The constant $A$ is a constant that is higher for a slow electrochemical reaction and can be expressed as (Larminie and Dicks, 2003):

$$A = \frac{RT}{2\alpha F}$$

(4.7)

where $\alpha$ is called the charge transfer coefficient which depends on the reaction involved and the material of the electrode, and it is in the range of 0 to 1.0. For hydrogen electrode, its value is about 0.5 for a great variety of electrode materials. The stack temperature $T$ is in deg K.

**Fuel crossover/Internal current losses:** Although the electrolyte, a polymer membrane, is not electrically conductive and is practically impermeable to reactant gases, some small amount of hydrogen will diffuse from anode to cathode that means some electrons may also find a shortcut through the membranes. The electrode is designed to separate the anode from cathode, and provide a means for the proton transfer. The electrode is often made of different materials depending on the type of fuel cell, and is either a solid or a liquid. The electrode is porous, necessary to allow proton transfer, and is also slightly conductive; as a result it is possible for un-reacted fuel and electrons to crossover to the cathode. Since in both of these processes two electrons are wasted, prevented from travelling externally, the losses are similar in source and the same in result. In order to model this phenomenon, the Tafel equation can be modified by adding an internal current density terms to the equation as follows:

$$\Delta V_{\text{cross}} = A \ln \left( \frac{i + i_n}{i_0} \right)$$

(4.8)
**Ohmic losses:** The voltage drop in the PEMFC is linearly proportional to the current density. It is mainly happen due to the resistance to the ions flowing through the electrolyte and the electrons through the electrode. The ohmic losses can be expressed as (Larminie and Dicks, 2003):

\[ \Delta V_{\text{ohm}} = ir \]  

where \( i \) is the current density in amp/cm\(^2\) and \( r \) is the area-specific resistance (ohm/cm\(^2\)) which includes electronic, ionic, and contact resistances.

**Mass transport or concentration losses:** When a reactant is rapidly consumed by the PEMFC electrode through the electro-chemical reaction, concentration gradients are occurred. Slow diffusion rate of the gas phase and reactants passing through the electrolyte are the main causes of mass transportation (Barbir, 2012). However, in reality the fuel cell doesn’t operate in this region and doesn’t face these losses.

### 4.1.2.2 Thermal model

Assuming all the product water leaves the stack as liquid at operating condition, the generated heat \( Q \) in a fuel cell stack can be calculated by the following equation:

\[ Q = (1.48 - V_{\text{cell}})inA \]  

where \( A \) is the active area (cm\(^2\)) of a single cell and \( n \) is the number of cells in a PEMFC stack. \( V_{\text{cell}} \) is the cell voltage calculated in equation (4.1) by deducting all the polarisation losses. However, in a liquid cooled fuel cell, most of the generated heat is removed through the coolant flow and evaporation of water product, with a very small percentage of the total heat removed from the stack by the extra air, hydrogen and water product (Shabani, 2010, Shabani et al., 2010, Shabani and Andrews, 2011), and some from the body of the stack through convection if the stack is not thermally insulated. To estimate the actual cooling load, these components should be taken out from the total heat generated by the fuel cell.

The heat carried out by the unused hydrogen stream can be expressed as:

\[ Q_{H_2,\text{out}} = m_{H_2,\text{out}}(c_{p,H_2}T_s - c_{p,H_2}\text{in}T_{\text{in}}) \]  

(4.11)
where \( m_{H_2,\text{out}} \) is the unused mass of hydrogen, \( c_{p,H_2} \) and \( c_{p,H_2,\text{in}} \) are the specific heats of hydrogen at stack and atmospheric temperature respectively, \( T_s \) and \( T_{\text{in}} \) are the stack and atmospheric temperatures respectively (assuming that hydrogen enters the stack at ambient temperature). The unused mass of hydrogen can be expressed as follows:

\[
m_{H_2,\text{out}} = \left(S_{H_2} - 1\right) \frac{M_{H_2}}{4F} \text{inA} \tag{4.12}
\]

where \( S_{H_2} \) is the stoichiometric ratio of hydrogen and \( M_{H_2} \) is the molecular weight of hydrogen.

Similarly the heat removed by the excess air can be expressed as:

\[
Q_{\text{airout}} = m_{\text{airout}}(c_{p,\text{air},s}T_s - c_{p,\text{air},\text{in}}T_{\text{in}}) \tag{4.13}
\]

where \( m_{\text{airout}} \) is the unused mass of hydrogen, \( c_{p,\text{air},s} \), \( c_{p,\text{air},\text{in}} \) is the specific heat of air at stack and atmospheric temperature respectively, and \( T_s \) and \( T_{\text{in}} \) are the stack and atmospheric temperatures respectively. The unused mass of depleted air flow is simply a sum of the oxygen and nitrogen elements and can be expressed as follows:

\[
m_{\text{air,\text{out}}} = \left[S_{O_2} - 1\right]M_{O_2} + S_{O_2} \frac{1 - r_{O_{2,\text{in}}}}{r_{O_{2,\text{in}}}} M_{N_2} \frac{i\text{n}}{4F} \tag{4.14}
\]

where \( S_{O_2} \) is the oxygen stoichiometric ratio, \( M_{O_2} \) and \( M_{N_2} \) are molecular weight of oxygen and nitrogen respectively and \( r_{O_{2,\text{in}}} \) is mole fraction of oxygen in air.

The water content in the cathode exhaust, that is equal to the amount of water brought into the cell plus the water generated in the cell, also contributes in stack heat removal, due to its thermal capacity and change in its enthalpy when experiencing a phase change.

The amount of water in air can be calculated:

\[
m_{H_2O,\text{in}} = \frac{S_{O_2} M_{H_2O}}{r_{O_2}} \frac{\phi_a P_{H_2O}}{4F} \frac{\phi_a P_{H_2O}}{P_a - \phi_a P_{H_2O}} i\text{nA} \tag{4.15}
\]
where $\phi_a$ is the relative humidity of air, $P_{H,O}$ is the saturation pressure of water and $P_a$ is inlet air pressure. The saturation pressure of water can be expressed as:

$$P_{H,O} = e^\left(\frac{a + b + cT + dT^2 + eT^3 + f \log(T)}{T}\right)$$

(4.16)

where a, b, c, d, e, and f are the coefficients, and their values are assigned as:

- $a = -5800.2206$;
- $b = 1.3914993$;
- $c = -0.048640239$;
- $d = 0.41764768 \times 10^{-4}$;
- $e = -0.14452093 \times 10^{-7}$ and $f = 6.5459673$ with $T$ is in °K.

The mass of the generated water from redox reaction can be expressed as (Spiegel, 2008):

$$m_{H,O_{gen}} = \frac{M_{H,O}}{2F} \text{inA}$$

(4.17)

Therefore, from equations (4.15) and (4.17), we can get the water content in the cathode exhaust:

$$m_{H,O_{out}} = \left(\frac{S_{O_2} M_{H,O}}{r_{O_2}} - \frac{\phi_a P_{H,O}}{P_a} + \frac{M_{H,O}}{2F}\right) \text{inA}$$

(4.18)

The heat removed by the water leaving the stack can be then expressed as (Spiegel, 2008):

$$Q_{H,O_{out}} = m_{H,O_{out}} (c_{p_{H,O}} T_s + h_{fg}) - m_{H,O_{in}} (c_{p_{H,O}} T_{in} + h_{fg})$$

(4.19)

where $m_{H,O_{in}}$ is the amount of water brought into fuel cell by air, $m_{H,O_{out}}$ is the generated water from hydrogen oxygen reaction, plus the amount of water brought into fuel cell, and $h_{fg}$ is the enthalpy of water at gas phase, $T_s$ is the stack temperature in °K, and $T_{in}$ is the air inlet temperature in °K.

By deducting the removal of heat by extra reactants (i.e. hydrogen and air), and also the heat required for vaporising the water product from the generated heat, the cooling load of the fuel cell (to be removed by the stack cooling system) can be calculated using the following equation:

$$Q_{Coolingload} = Q - Q_{H,O_{out}} - Q_{air_{out}} - Q_{H,O_{out}}$$

(4.20)
4.1.3 Cooling system modelling

4.1.3.1 An overview

The fuel cell cooling system is designed and sized to remove the heat generated by the exothermic reaction of hydrogen and oxygen in order to maintain the stack’s temperature at a desirable level (i.e. 60-80 °C in PEMFCs). As discussed earlier (Section 4.1.1), a complete liquid-cooled fuel cell cooling system consists of a number of auxiliary devices a heat exchanger, pump, and coolant. In this study the effectiveness-NTU (ε-NTU) method has been used to determine the effects of nanofluids on the size of the heat exchanger.

For calculating the pumping power for a required flow flux, a typical set-up for a 2.4 kW PEMFC has been considered as a case study. This included of 200 cm long piping of 15 mm diameter with the required fittings. The pressure drop inside the fuel cell should be either measured or obtained from the manufacturer. For example in a 2.4 kW PEMFC used to support this study, the pressure drop is advised to be ~200 Pa for 0.16 kg/s coolant mass flow rate by the manufacturer. The values for the minor losses (e.g. fittings and connectors) have been taken from the available literature. Empirical correlations were used to determine the properties of the base coolant (e.g. ethylene glycol and water) as well as those for nanofluids.

4.1.3.2 Coolant properties

4.1.3.2.1 Thermal conductivity

It has been shown by many researchers (Leong et al., 2010, Murshed et al., 2009, Philip and Shima, 2012, Abdolbaqi et al., 2016c, Abdolbaqi et al., 2016d, Aminian, 2016, Li et al., 2016, Wei et al., 2017) that particle concentration, temperature, particles size, particle shape/aspect ratio, additives, acidity (pH), sonication, aggregation of nanofluids, etc. play roles in determining the thermal conductivity of nanofluids. However, currently there is no absolutely reliable theory to predict the anomalous thermal conductivity of nanofluids as this property depends on various parameters (Wang and Mujumdar, 2007). In this study, the static model developed by Maxwell (equation (3.10)) (Maxwell, 1873) has been used to determine the effective thermal conductivity of nanofluids. The Maxwell’s model is applicable to liquid-solid suspensions of mono-disperse, low volume-fraction mixtures of spherical particles that is well-matched with this project. The Maxwell’s model is also widely used in the literature and claimed to be agreed well with the experimentally observed thermal conductivity of nanofluids (Utomo et al., 2012, Duangthongsuk and Wongwises, 2009, Mintsa et al., 2009, Trisaksri and Wongwises, 2007, Pastoriza-Gallego et al., 2011b).
4.1.3.2.2 Viscosity

Nanoparticles increase the viscosity and density (i.e. to be further discussed in this chapter) of the base fluids thus affecting pumping power of the system. Einstein (1906) determined the effective viscosity of a suspension of spherical solids as a function of volume fraction (i.e. for volume concentrations of 0.02%) (Masoumi et al., 2009) using the phenomenological hydrodynamic equations. Since Einstein’s analysis of the viscosity of a dilute suspension of rigid spheres in a viscous liquid, several equations have been developed in an effort to extend Einstein’s formula to suspensions of higher concentrations, including the effect of non-spherical particle concentrations. Therefore Brinkman (1952) has modified this equation to a more generalized form for spherical particles and moderate concentrations (~4 vol%) (Mahbubul et al., 2013) which is defined in equation (3.26). This equation has been used widely by past researchers as well (Duangthongsuk and Wongwises, 2009, Masoumi et al., 2009, Corcione, 2011, Mahbubul et al., 2013, Godson et al., 2010a, Aladag et al., 2012a).

4.1.3.2.3 Specific heat

Although the specific heat is an important factor in determining the thermal performance of nanofluids, it received very little attention (Zhou and Ni, 2008a, Ghadimi et al., 2011a). For a given volumetric concentration of nanoparticles in the base fluid, the specific heat can be calculated using the mixture formula (equation 3.28). This formula is valid for homogeneous mixtures with spherical particles, and based on the thermal equilibrium between the particles and surrounding fluid. This formula is also related to density and specific heat of base fluid and nanoparticles (O’Hanley et al., 2011).

4.1.3.2.4 Density

There have been only few studies on nanofluid density (Karimi and Yousefi, 2012) even though the density of nanofluids can play a significant role on the heat transfer phenomena. The density of nanofluids increases with an increase in the volumetric concentration of nanoparticles as their densities are usually higher than that of the base fluids. The density of nanofluids decreases very modestly with temperature increase mostly due to the effect of temperature on the density of base fluids (Vajjha and Das, 2012). The density of nanofluids based on the physical principle of the mixture as represented in equation (3.32) was used in the theoretical study of this research (Khanafer and Vafai, 2011, Pak and Cho, 1998).
4.1.3.2.5 Heat exchanger

For removing the generated heat from the PEMFC, a cross flow (fin-tube) heat exchanger is considered where coolant flows through the tube side with air flowing around the outer surface of the finned tube. By knowing the thermal load to be rejected and the inlet temperatures of coolant and air side, a compact heat exchanger can be sized by using the $\varepsilon$-NTU method. The heat exchanger core selected for this study is continuous finned flat aluminium tubes with surface 11.32-737-SR (Kays and London, 1998); however, other types of heat exchangers might be considered in different cases. The required steps for sizing the HE are as follows (Kays and London, 1998, Shah and Sekulic, 2003, Ali et al., 2015):

**Step 1:** Calculate the number of heat transfer unit (NTU)

Considering a cross flow heat exchanger with the temperature distributions for mixed hot and unmixed cold fluids, NTU can be expressed explicitly as a function of $\varepsilon$ and $C^*$:

$$NTU = -\left(\frac{1}{C^*}\right) \ln\left(1 + C^* \ln\left(1 - \varepsilon\right)\right) \quad (4.21)$$

where $C^*$ is the ratio of the minimum heat capacity to the maximum heat capacity ($C_{\text{min}}/C_{\text{max}}$) (between the cold and hot fluids running through the heat exchanger), and $\varepsilon$ is the target effectiveness.

**Step 2:** Initialise the core mass velocities $G_{\text{air}}$ and $G_{\text{c}}$

$$G_i = \sqrt{\frac{2 \Delta P_i^\ast \rho_i}{NTU_i \Pr_i^{2/3} \left(j/f\right)_i}} \quad ; \ i = \text{air or coolant} \quad (4.22)$$

where $\rho_i$ is the density of air or coolant at the average temperature between the inlet and outlet, $\Delta P_i^\ast$ is the target pressure drop at air and coolant sides, the $NTU_i$ for air (a) and coolant (c) can be expressed as (Shah and Sekulic, 2003):

$$NTU_a = 1.11 NTU \quad (4.23)$$

$$NTU_c = 10 C^* NTU \quad (4.24)$$

Since $j/f$ versus Reynolds number ($Re$) characteristics are specified for the surfaces on the liquid and air side, we can find out $j/f$ value from $j/f$ vs ($Re$) surface characteristics curves (Kays and London, 1998). For an unknown ($Re$) value, an approximate average value of $j/f$
(-0.25) can be considered for initial estimation. $Pr$ denotes the Prandtl number and can be expressed as equation (3.15).

**Step 3:** Calculate the heat transfer coefficients and friction factors

The convection heat transfer coefficient and friction factor can be calculated by using the following equations for the coolant side (Kays and London, 1998, Bergman *et al.*, 2011):

$$ Re_c = \frac{4r_{hc}G_c}{\mu_c} \quad (4.25) $$

$$ f_c = \left(1.58 \ln Re_c - 3.28\right)^2 \quad (4.26) $$

As discussed in section 3.4.4 that the automotive radiators usually operate at the transitional range so by using equation (3.19), we can calculate the Nusselt number while by using the following equation the convection heat transfer coefficient for single phase coolant (base fluid) can be calculated:

$$ h_c = \left(Nu_c k_c\right)/4r_{hc} \quad (4.27) $$

where $Nu_c$ is the Nusselt number, $k_c$ is the thermal conductivity of coolant, and $r_{hc}$ is the coolant side flow passage hydraulic radius. It is important to note that if $Re_c$ is less than 2300 then the flow is laminar and the Nusselt number is 6.49 and friction factor can be calculated by equation (4.28) (Kays and London, 1998); and if the $Re_c$ is greater than 2300, the flow is transient or turbulent and the Nusselt number is calculated using equation (3.19).

$$ f = 20.6/Re_c \quad (4.28) $$

However, the equation (3.19) is only applicable for single phase fluids. For using nanofluids, the experimentally developed correlations (equations (3.27) and (3.28)) (concentration up to 2 vol%) by Li and Xuan (2002) can be used for the Nusselt number.

In the case of pressure drop, the friction factor of the nanofluids doesn’t vary significantly with the concentration of nanoparticles under same flow rate (Daungthongsuk and Wongwises, 2007, Pak and Cho, 1998, Li and Xuan, 2002, Xuan and Li, 2003). However, for better accuracy, the developed correlation for nanofluids (concentration up to 2 vol%) flowing in a horizontal double tube counter-flow heat exchanger by Daungthongsuk and Wongwises (2010) has been used in this study.
\[ f_{cnf} = 0.961 \phi^{0.052} \text{Re}^{-0.375} \]  \hspace{1cm} (4.29)

For the air side the equations for calculating the convection heat transfer coefficients and friction factor are as follows (Bergman et al., 2011, Bao et al., 2006, Rathod et al., 2007):

\[
\text{Re}_a = \frac{4 r_{ha} G_a}{\mu_a} \quad \hspace{1cm} (4.30)
\]

\[
\text{St}_a = \frac{0.1448 \text{Re}_a^{-0.3837}}{\text{Pr}_a^{2/3}} \quad \hspace{1cm} (4.31)
\]

\[
h_a = j_a G_a C_{p,a} / \text{Pr}_a^{2/3} \quad \hspace{1cm} (4.32)
\]

\[
f_a = \text{St}_a + 0.0188 \quad \hspace{1cm} (4.33)
\]

\[
j_a = \text{St}_a \text{Pr}_a^{2/3} / f_a \quad \hspace{1cm} (4.34)
\]

where \( \text{St}_a \) is the Stanton number of air, \( h_a \) is air side convection heat transfer coefficient, \( j_a \) is Colburn factor, \( G_a \) is core mass velocity, \( c_{p,a} \) is the specific heat of air, \( f_a \) is airside friction factor and \( r_{ha} \) is the air side flow passage hydraulic radius.

**Step 4:** Calculate the total surface temperature efficiency of the air side

\[
\eta_0 = 1 - \left( 1 - \eta_f \right) \frac{A_f}{A_a} \quad \hspace{1cm} (4.35)
\]

where \( A_f \) is the fin area, \( A_a \) is the total area of air side, and \( \eta_f \) is the fin efficiency.

The efficiency of a single rectangular fin that is normally used in heat exchanger is calculated using the following equation:

\[
\eta_f = \frac{\text{Tanh}(ml)}{ml} \quad \hspace{1cm} (4.36)
\]

where \( l \) is the fin length and \( m \) is obtained from the following equation:
where \( \delta \) is the fin metal thickness and \( k_a \) is the fin material (aluminium) thermal conductivity.

**Step 5:** Calculate the overall heat transfer coefficient based on the air side heat transfer area

\[
U_a = \frac{1}{\eta_0 h_a + \frac{r_a}{\left(\alpha_c/\alpha_a\right) h_c} + \frac{r_c}{\left(\alpha_c/\alpha_a\right)}}
\]  

(4.38)

**Step 6:** Calculate the required heat transfer area on air side and the three dimensional size of the heat exchanger (Kays and London, 1998):

\[
A_a = \frac{NTU.C_a}{U_a}
\]  

(4.39)

\[
A_{ja} = \frac{m_a}{G_a}
\]  

(4.40)

\[
A_c = \alpha_c A_a / \alpha_a
\]  

(4.41)

\[
A_{f,c} = \frac{m_c}{G_c}
\]  

(4.42)

\[
A_{fr,a} = \frac{A_{f,a}}{\sigma_a}
\]  

(4.43)

\[
A_{fr,c} = \frac{A_{f,c}}{\sigma_c}
\]  

(4.44)

\[
V = \frac{A_a}{\alpha_a} \text{ or } \frac{A_c}{\alpha_c}
\]  

(4.45)

\[
L_a = \frac{V}{A_{fr,a}}
\]  

(4.46)

\[
L_c = \frac{V}{A_{fr,c}}
\]  

(4.47)

\[
L = \frac{V}{(L_c \ast L_a)}
\]  

(4.48)
where $\alpha$ is ratio of total heat transfer area to total volume heat exchanger, $\sigma$ is the ratio of free flow area to frontal area of heat exchanger, $V$ is the volume of heat exchanger and $L_c$, $L_a$ and $L$ are coolant, air and non-flow length of heat exchanger.

**Step 7:** Calculate the pressure drops in both sides (Shah and Sekulic, 2003, Kays and London, 1998):

$$
\Delta P_{\text{air}} = \frac{G_a^2}{2 \rho_a^m} \left[ (1 + \sigma_a^2) \left( \frac{\rho_a^m}{\rho_a^m} \right) / \rho_a^m - 1 \right] + 4 f_a L_a \rho_a^m / \left( D_{b.a} \rho_a^m \right)
$$

(4.49)

$$
\Delta P_c = G_c^2 f_c L_c / (2 \rho_c r_{h.c})
$$

(4.50)

Considering an acceptable range of error (<1%), if the calculated $\Delta P$ values are close to a target pressure drop, the solution to the sizing problem is completed and the iteration has to be stopped. If the error is not acceptable then by considering the following equation the process has to be repeated from step 3.

$$
G_{t+1} = G_t \sqrt{\Delta P_{t+1}^*/\Delta P_t}
$$

(4.51)

### 4.1.3.3 Coolant pump

The coolant pump plays an important role in cooling system of a PEMFC. The main role of the pump is to provide a coolant flow at the desired rate, i.e. through the use of a variable speed pump. A steady state semi-analytical model has been used to calculate the required pumping power when different coolants are used (e.g. conventional ethylene glycol and water mixture, or nanofluids). For a pressure head of $H$ (m), and a coolant flow rate of $Q$ ($m^3/s$), the required pumping power, $P$ (W), for a pump with an overall efficiency of $\eta_{\text{pump}}$ can be expressed as (AlfaLaval, 2002):

$$
P = \frac{\rho g Q H}{\eta_{\text{pump}}}
$$

(4.52)

where $\rho$ is the density of the coolant in (kg/m$^3$) and $g$ is the gravitational force (m/s$^2$). The pressure head, $H$ consists of two types of heads, namely total static head ($h_s$) and pressure
head loss due to fluid friction in radiator \((h_r)\), fuel cell \((h_{fc})\), pipe \((h_p)\) and fittings \((h_f)\). The head loss due to the friction in pipeline can be expressed as:

\[
h_p = f \frac{L v^2}{D 2g}
\]  

(4.53)

where \(f\) is the friction factor, \(L\) is the length of pipe, \(D\) is the hydraulic diameter and \(v\) is the mean speed of the coolant flow. For laminar flow we can calculate friction factor by using equation (4.28) but for turbulent flow the friction factor can be then calculated by using Haaland (1983) proposed formula which varies less than two percent from Colebrook equation (White, 1999, Yunus and Cimbala, 2006):

\[
\frac{1}{\sqrt{f}} = -1.8 \log \left[ \frac{6.9}{\text{Re}} + \left( \frac{\varepsilon}{d} \right)^{1.11} \right]
\]  

(4.54)

where \(\varepsilon\) is the surface roughness factor that depends on the metal properties and \(\text{Re}\), as introduced before, is the Reynolds number.

The loss due to the pipe fittings can be calculated as:

\[
h_f = k \frac{v^2}{2g}
\]  

(4.55)

where \(k\) is the pressure loss coefficient which is different for different fittings and connections (White, 1999, Yunus and Cimbala, 2006). Therefore, the pressure head \((H)\) can be written as:

\[
H = h_s + h_r + h_{fc} + h_p + h_f
\]  

(4.56)

4.1.4 System modelling of PEMFC

Finally, all the separate sub-models of PEMFC cooling system components (i.e. PEMFC stack, heat exchanger, coolant pump and coolants) have been connected by using MATLAB in order to get the size of the heat exchanger and pumping power required based on the generated heat by the fuel cell. A 2.4 kW PEMFC stack has been used as a case study and the model has applied to conduct an analysis on a system based on this fuel cell. From PEMFC stack model was used to quantify the cooling load of the 2.4 kW PEMFC stack.
This is the very first input required to size the heat exchanger that has to be used with the fuel cell, particularly with the view to using different types of coolants in the system. Along with piping and fitting pressure losses, the pressure losses in the PEMFC stack and heat exchanger were used to estimate the pumping power required to circulate the required flow of coolants in order to maintain the desired temperature of PEMFC stack (i.e. between 60-80 °C).

4.2 Results and discussions

4.2.1 Thermo-physical characteristics of nanoparticles

4.2.1.1 An overview

The thermo-physical properties of coolants such as thermal conductivity, viscosity, specific heat and density play significant roles in improving the overall heat transfer performance of the cooling systems that used these coolants. In this study, the thermo-physical properties of 50/50 water-EG based nanofluids with different volume concentrations (0.05, 0.1, 0.3, and 0.5) of Alumina (Al₂O₃), Zinc Oxide (ZnO) and Titanium Oxide (TiO₂) nanofluids were theoretically estimated by using equations (3.9), (3.27), (3.28), (3.31), (3.33), and (3.37).

Apart from nanoparticles types and concentration, the temperature of nanofluids also affects their thermo-physical properties significantly; hence the effect of temperature has also been investigated in this study. The results were then compared with the experimental measurements of these properties for different nanofluids, with different concentrations, and at different temperatures. Therefore, handbook values of temperature dependent thermo-physical properties of 50/50 water-EG mixture are used in calculating theoretical nanofluids thermo-physical properties (ASHRAE, 2001). Additionally the thermo-physical properties of nanoparticles were considered to be same as to the thermo-physical properties of particle material in bulk form.

Then the nanoparticles purchased from renowned manufacturer used for the experimental part of this study. According to manufacturer, these particles are spherical in shape and 40 nm in size.
4.2.1.2 Thermal conductivity

The thermal conductivity of different types of nanofluids at various volume concentrations and temperatures is presented in Figure 4.2 and Figure 4.3. It is clearly seen that the thermal conductivity increased with nanoparticles concentrations which has been found by many researchers including (Agarwal et al., 2016, Ahmadloo and Azizi, 2016, Farbod et al., 2015, Karimi et al., 2015, Khdher et al., 2016b, Li et al., 2015b, Li et al., 2015c, Shukla et al., 2016, Xing et al., 2015a, Xing et al., 2016b, Mostafizur et al., 2015, Pang et al., 2012). At 50˚C, the thermal conductivities of all types of nanofluids used in this study with 0.05-0.5 vol% showed ~1.5% increase compared to that of the base fluid (e.g. 50/50 water-EG mixture). This enhancement of thermal conductivity is mainly due to the higher thermal conductivity of nanoparticles, higher particle surface to volume ratio, particle-to-particle interaction, particle cluster, and the Brownian motion of the particles. However, the differences of thermal conductivities among the nanofluids were observed to be insignificant.

![Figure 4.2 The predicted effect of nanoparticle concentration on thermal conductivity of 50/50 water-EG based different nanofluids at 50˚C](image)

The thermal conductivity of nanofluids is also increased with the temperature as shown in Figure 4.3 at 0.3 vol% concentration for all nanofluids. Figure 4.3 shows the thermal conductivity enhancement for the temperature range of 20 °C to 70 °C and it shows the enhancement of thermal conductivity of around ~7.4% at 70˚C compared with that of the 20 °C. The enhancement is due to decrease in viscosity with increasing the temperature that
intensifies the Brownian motion and the effects of convection (Mostafizur et al., 2015). For all the studied nanofluids, the thermal conductivity enhancement showed almost the same trend and growth rates.

4.2.1.3 Viscosity

The viscosity of 50/50 water-EG based nanofluids with different concentrations for different types of nanofluids are shown in Figure 4.4. The results show that the viscosity of nanofluids experience only a marginal increase with increase in volume concentrations, with the nanoparticle concentration of 0.5 vol%, only around ~1.3% viscosity increase is observed compared to the base fluid that is similar to what has been reported by other researchers as well (Lee et al., 2008, Masoumi et al., 2009, Abarashi et al., 2011). The viscosity increment doesn’t vary by changing the types of nanofluids (i.e. using different nanoparticles).
On the other hand, the viscosity of all the nanofluids decreases significantly with increasing temperature of nanofluids as can be seen in Figure 4.5; e.g. ~75% reduction with an increase in temperature from 20 °C to 80 °C. The same trend has been found reported by other researchers (Lee et al., 2008, Sundar et al., 2016b, Bashirnezhad et al., 2016, Abdolbaqi et al., 2016d, Abdolbaqi et al., 2016c).

Figure 4.5 The predicted effect of temperature on the viscosity of 50/50 water-EG based different nanofluids at 0.3 vol% concentrations
4.2.1.4 Specific heat

The predicted values of specific heat of nanofluids decrease slightly with the increase in volume concentration of nanofluids (Figure 4.5). This is an expected trend since a metal or oxidised metal possess less specific heat than that of the base fluid used in this study (i.e. 50/50 water-EG mixture). Among all studied nanofluids, decreasing rate of specific heat is higher for ZnO nanofluid followed by TiO$_2$ nanofluid which is ~2.2% and ~1.4% respectively compared to that of the base fluids for increasing concentration up to 0.5 vol%.

![Figure 4.6 The predicted effect of nanoparticle concentration on the specific heat of 50/50 water-EG based different nanofluids at 50°C](image)

Along with volumetric concentration, the temperature also influences the specific heat of nanofluids and with increasing the temperature, the specific heat increases which has also been confirmed by many other researchers (Satti et al., 2016, Riazi et al., 2016, Cabaleiro et al., 2015b, Vajjha and Das, 2009a, Namburu et al., 2007).
Figure 4.7 The predicted effect of temperature on the specific heat of 50/50 water-EG based different nanofluids at 0.3 vol% concentrations

### 4.2.1.5 Density

Density of nanofluids is an important parameter as it is directly increasing the parasitic loss of the cooling system (Chalgren and Barron, 2003). Figure 4.8 shows that the density of nanofluids is increased with an increase of volume concentration and always higher than that of the base fluid. It is mainly due to the fact that the nanoparticle density is higher than that of the base fluid (i.e. 50/50 water-EG mixture) that causes enhancement of the nanofluid density. The same trend also reported by other researchers; e.g. Vajjha et al. (2009).
On the other hand, the density of nanofluids decreases along with the increase of temperature as shown in Figure 4.9. The same trend of decreasing density with the increase of temperature has been also observed by other researchers (Mahbubul et al., 2013, Mahian et al., 2013).
4.2.2 2.4 kW Liquid cooled PEMFC cooling system: A case study

4.2.2.1 An overview

As it has already been mentioned in section 4.1.1 that the PEMFCs cooling system consists of a PEMFC, a radiator, a pump and coolants, and the theoretical modelling of PEMFCs cooling has been developed based on the 2.4 kW PEMFC as a main component. This is mainly due to the fact that the simulation model has to be validated with the experimental study as part of this project. Though the developed computer simulation model is based on the 2.4 kW PEMFCs, it can easily be scaled up for the automotive applications (i.e. ~100 kW power). The comparison of developed computer model in this study and the automotive requirement can be shown in Table 4.1.

Table 4.1 Comparison of developed computer model and automotive domain (Toyota, 2016)

<table>
<thead>
<tr>
<th>Items</th>
<th>Model</th>
<th>Automotive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rated power</td>
<td>2.4 kW</td>
<td>~100 kW</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>65 °C</td>
<td>~ 65 °C</td>
</tr>
<tr>
<td>Generated heat</td>
<td>~3.0 kW</td>
<td>~130 kW</td>
</tr>
<tr>
<td>Cells in one stack</td>
<td>27</td>
<td>~370 or more</td>
</tr>
<tr>
<td>Fuel</td>
<td>Compressed hydrogen and air</td>
<td>Compressed hydrogen and air</td>
</tr>
<tr>
<td>Coolant freezing point</td>
<td>~35.6 ºC</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

4.2.2.2 Heat exchanger

Compact heat exchangers incorporate a large heat transfer surface area per unit volume that makes them suitable for applications in which the space availability for packaging is an extreme constraint (e.g. automotive). Compared to other types of heat exchangers, cross-flow heat exchangers are much more suitable for these applications as they comprise 10-15% larger frontal area for a given size that gives more flexibility to change the frontal area of the heat exchanger by only changing its width/non-flow length, $L$ (Figure 4.10). Tube fin heat exchangers are employed when one fluid stream is at a higher pressure and has a considerably higher heat transfer coefficient than that of the other fluid stream (Hewitt and Barbosa, 2008). A typical cross-flow heat exchanger, as shown in Figure 4.10 has been considered for this study. In Figure 4.10, $L_w$ is coolant flow length, $L_a$ is air flow length, and $L$ is non-flow length of the heat exchanger. For this study, the air flow length has been kept constant, so that the effect of different coolants on the frontal area ($L_w \times L$) of the heat exchanger could be investigated (i.e. to see their effect on the frontal area of the heat exchanger for a targeted heat removal).
Figure 4.10 A typical cross-flow heat exchanger: schematic diagram (left) and real image (right) (Yamaha, 2015)

4.2.2.3 PEMFC

Figure 4.11 shows the polarisation (V-I) curve of the 2.4 kW PEMFC (used in this study), provided by the manufacturer and that suggested by the theoretical model used by equations (4.1) to (4.9). To fit the theoretical V-I curve with the manufacturer curve, the unknown parameters, i.e. charge transfer coefficient and exchange current density have been calculated by applying Tafel equation (4.6) whereas the internal resistance has been estimated by analysing the slope of the manufacturer provided curve. The input parameters for plotting the fuel cell’s V-I curve have been shown in Table 4.2. It is clearly seen that theoretical V-I curve is in good agreement with the V-I curve, provided by the manufacturer, with the maximum 3% absolute error.
Table 4.2 Essential parameters used for modelling the performance of the PEMFC used in this study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet pressure of hydrogen and air</td>
<td>300 Pa (g)</td>
</tr>
<tr>
<td>Relative humidity of inlet hydrogen and air</td>
<td>95%</td>
</tr>
<tr>
<td>Active area of single cell</td>
<td>202 cm$^2$</td>
</tr>
<tr>
<td>Number of cells</td>
<td>27</td>
</tr>
<tr>
<td>Internal resistance</td>
<td>0.185 ohm/cm$^2$</td>
</tr>
<tr>
<td>Charge transfer coefficient</td>
<td>0.2</td>
</tr>
<tr>
<td>Exchange current density</td>
<td>1.10x10$^{-6}$ A/cm$^2$</td>
</tr>
<tr>
<td>Amplification constant</td>
<td>0.0085</td>
</tr>
<tr>
<td>Limiting current density</td>
<td>0.7 A/cm$^2$</td>
</tr>
<tr>
<td>Mass transport constant</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 4.11 Theoretical and experimental (i.e. provided by the manufacturer) polarisation (V-I) curves of the 2.4 kW PEMFC used in this study

Based on the parameters provided in Table 4.2, the polarisation curve, stack power, generated heat, and cooling load can be calculated by applying equations (4.10) to (4.20). It is important to check the validity of the fuel cell model through the experimental/manufacturer data. Because this model is used to estimate the cooling load of the fuel cell and then the size of the heat exchanger required to reject this cooling load. In the case of the 2.4 kW used for this study, the cooling load to be rejected from the fuel cell has been estimated to be 2.1 kW. According to the model, the maximum cooling load of the 2.4 stack used in this study was calculated to be just over 2.1 kW (i.e. at 2.4 kW operating point).
The calculated stack power, generated heat and cooling load for the 2.4 kW PEMFC used in this study

The design parameters used to design a heat exchanger for handling the 2.4 kW fuel cell’s cooling load (i.e. used as a case study) are summarised in Table 4.3 and Table 4.4.

Table 4.3 Design parameter for the heat exchanger used to extract heat from 2.4 kW PEMFC

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>The maximum cooling load (kW) calculated for a 2.4 kW PEMFC at its rated power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water inlet temperature (°C)</td>
<td>$T_{w in}$</td>
<td>65</td>
</tr>
<tr>
<td>Air inlet temperature (°C)</td>
<td>$T_{a in}$</td>
<td>20</td>
</tr>
<tr>
<td>Target effectiveness</td>
<td>$\varepsilon$</td>
<td>0.60</td>
</tr>
<tr>
<td>Target pressure drop on air side (Pa)</td>
<td>$\Delta P_a^*$</td>
<td></td>
</tr>
<tr>
<td>Target pressure drop on water side (Pa)</td>
<td>$\Delta P_w^*$</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.4 The geometry for the continuous finned flat aluminium tubes with surface 11.32-737-SR (Kays and London, 1998).

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow passage hydraulic radius (m)</td>
<td>$r_{h,a}$</td>
<td>0.878x10^{-3}</td>
</tr>
<tr>
<td>Total air side heat transfer area/total volume (m²/m³)</td>
<td>$a_a$</td>
<td>886</td>
</tr>
<tr>
<td>Fin area/total area (m²/m²)</td>
<td>$A_{f,a}/A_a$</td>
<td>0.845</td>
</tr>
<tr>
<td>Free flow area/frontal area (m²/m²)</td>
<td>$\sigma_a$</td>
<td>0.780</td>
</tr>
<tr>
<td>Fin metal thickness (m)</td>
<td>$\delta_a$</td>
<td>0.102x10^{-3}</td>
</tr>
<tr>
<td>Fin material; aluminium thermal, conductivity (W/m.K)</td>
<td>$k$</td>
<td>173</td>
</tr>
<tr>
<td>Fin length (one half distance between tubes) (m)</td>
<td>$l_a$</td>
<td>5.71x10^{-3}</td>
</tr>
</tbody>
</table>

Water Side: The tubes have straight sides with semicircular ends

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water side flow passage hydraulic radius (m)</td>
<td>$r_{h,w}$</td>
<td>0.933x10^{-3}</td>
</tr>
<tr>
<td>Total water side heat transfer area/total volume (m²/m³)</td>
<td>$a_w$</td>
<td>138</td>
</tr>
<tr>
<td>Free flow area/frontal area (m²/m²)</td>
<td>$\sigma_w$</td>
<td>0.933x10^{-3}</td>
</tr>
</tbody>
</table>

4.2.2.4 Coolants

There are mainly two types of nanoparticles: metallic and non-metallic or metal oxide based nanoparticles. The metallic nanoparticles are of high thermal conductivity which will increase thermal conductivity of the base fluid. On the other hand, they are also highly electrical conductive (>10⁴ Siemens/cm), which has a negative impact on the fuel cell electrical performance. Contrary to the metallic nanoparticles, the non-metallic nanoparticles help increase the thermal conductivity of nanofluids while suggesting higher electrical resistance (>10¹⁴ Ω.cm) than that can be seen with using metallic nano-particles. That is why such nanofluids can be more suitable for fuel cell applications, which need coolants with low electrical conductivity and high thermal conductivity. Non-metallic nanoparticles are expected to behave like electrically insulating materials with high electrical resistivity (Glenn, 2015); however, some experimental studies (Ganguly et al., 2009, Steven et al., 2011a) found that the electrical conductivity of non-metallic nanofluids can be increased by the increment of nanoparticle concentration. Although the detailed theoretical modelling of electrical conductivity of nanofluids is not part of this modelling study, electrical conductivity of nanoparticles has been considered in selecting them for making nanofluids. However, the effect of adding non-metallic nanoparticles on the electrical conductivity of nanofluids will be further investigated experimentally in chapter 5.
Three types of commercially available electrically insulating spherical, 40 nm diameter nanoparticles i.e. Alumina (Al$_2$O$_3$), Zinc Oxide (ZnO) and Titanium Oxide (TiO$_2$) have been investigated for use with 50/50 water-EG mixture as base fluid. Nanoparticle concentrations from 0.05 to 2% have been considered to be used in the model. The predicted thermo-physical properties of nanofluids with different concentrations (i.e. 0.05-2 vol%) and at different temperatures (i.e. 20-80 °C) have been used in this study. The empirical correlations provided in coolant properties section (4.1.3.2) were used to calculate these properties (Figure 4.2 to Figure 4.9).

4.2.2.5 Liquid pump
A commercially available variable speed liquid pump has been chosen to circulate the coolants in the PEMFC cooling system. The pump is brushless 24 V DC pump in which the speed is adjusted by potentiometer. By using equations (4.52) to (4.56), the required pumping power has been calculated. The main features of the water pump are provided in Table 4.5.

Table 4.5 The main features of the variable speed liquid pump

<table>
<thead>
<tr>
<th>Driving method</th>
<th>Brushless, Magnetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition of use</td>
<td>Continuous</td>
</tr>
<tr>
<td>Fluid</td>
<td>Water</td>
</tr>
<tr>
<td>Maximum working</td>
<td>60 °C</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>Power consumption</td>
<td>2.5 W - 86.4 W</td>
</tr>
<tr>
<td>Voltage used</td>
<td>24 V</td>
</tr>
<tr>
<td>Maximum rated current</td>
<td>3.7 A</td>
</tr>
<tr>
<td>Maximum flow rate</td>
<td>26.67 l/min</td>
</tr>
<tr>
<td>Life span</td>
<td>More than 30000 hours</td>
</tr>
</tbody>
</table>

4.2.2.6 Validation of the developed computer simulation model
The main focus of this study is to investigate the effect of using nanofluids on the size of heat exchanger and coolant pumping power. The validation of this theoretical study has been done by comparing Nusselt number over a range of Reynolds number for pure water with several experimental results. In Figure 4.13, the Nusselt number vs Reynolds numbers obtained from theoretical computer simulation model in this study has been compared with the results of experimental investigation of Ali et al. (2015), Sajadi and Kazemi (2011) and
Li and Xuan (2002). The comparison shows a good agreement with the experimental result of Sajadi and Kazemi (2011), with the maximum deviation of around 4%. However, the modelling result shows relatively less agreement with the experimental results of Ali et al. (2015) and Li and Xuan (2002). This could be due to uncertain boundary conditions and/or methods used in those experimental studies.

Figure 4.13 Comparison of Nusselt number for various Reynolds number obtained from developed computer model in present study for water with the experimental results of Ali et al. (2015), Sajadi and Kazemi (2011) and Qiang and Xuan (2002) in fully developed circular pipe flow

Figure 4.14 shows the comparison of Nusselt number vs Reynolds number between the results of this study obtained from theoretical model with the experimental result of Sajadi and Kazemi (2011) for 0.1 vol% concentration of TiO$_2$ nanofluid. It shows around 10% absolute average error. Given that there is no existing correlations for nanofluids that capture all the physics associated with the thermo-physical properties and the boundary layer behaviour of two phase nanofluid mixtures. The overall trend is very similar.
Figure 4.14 Comparison of Nusselt number for various Reynolds number obtained from developed computer model in present study for water based TiO$_2$ nanofluid at 0.1 vol% concentration with the experimental results of Sajadi and Kazemi (2011) in fully developed circular pipe flow

4.2.2.7 The effects of nanofluids on the convection heat transfer coefficient ($h_{nf}$) and frontal area of the heat exchanger

Figure 4.15 depicts the enhancement of convection heat transfer coefficient of the 50/50 water-EG based nanofluids. The study shows that the suspended nanoparticles significantly increase convection heat transfer coefficient of the base fluid. Compared with base fluid, the convection heat transfer coefficient is increased about ~58% with the concentration of 0.05 vol% nanoparticles whereas for 0.5 vol% concentrations the convection heat transfer is increased about ~60%. The findings of different researchers for enhancement of convection heat transfer coefficient using nanofluids vary widely but all are agreed that nanofluids increase the heat transfer compared with base fluids (Minakov et al., 2016, Cadena-de la Peña et al., 2017). Li and Xuan (2002) found 60% increment of convection heat transfer coefficient compared to the base fluid by using water based Cu nanofluids with the concentration of 2.0 vol%. Heris et al. (2013) investigated convection heat transfer enhancement of Al$_2$O$_3$/water nanofluids through square cross-sectional duct in laminar region and found up to 27.6% increment with 2.5 % volume fraction compared with that of the base fluid.
The effect of using 50/50 water-EG based nanofluids (i.e. Al$_2$O$_3$, TiO$_2$ and ZnO) (compared with using only 50/50 water-EG) on convection heat transfer coefficient used to cool a 2.4 kW PEMFCs.

Figure 4.16 presents the effects of different types of nanofluids with various concentrations (0.05-0.5 vol%) as coolants on the frontal area of heat exchanger, while keeping the coolant mass flow rate constant. A significant augmentation of heat transfer can be achieved by suspending a small amount of nanoparticles in a water-EG mixture. However, the effects of different nanofluids on the frontal area of heat exchanger are identical. This might be the result of using same empirical correlations (equations (3.27) and (3.28)) which has been developed for water based Cu nanofluids (Li and Xuan, 2002). By adding only 0.05 vol% nanoparticles with 50/50 water/EG mixture, ~26% reduction of frontal area of HE is obtained compared with the base fluid for same cooling load. With increasing the concentration of nanoparticles up to 0.5 vol%, no significant reduction (less than 1%) of the frontal area has been achieved. The enhanced heat transfer compared with the base fluids is due to the suspended particles increasing the thermal conductivity of the two-phase mixture and the chaotic movement of ultrafine particles accelerates energy exchange process in the fluid (Li and Xuan, 2002). Furthermore, the increased nanoparticle concentrations will increase the electrical conductivity (Bouchard et al., 2013, Ijam et al., 2015b, Jana et al., 2007, Omrani et al., 2012, Sarojini et al., 2013a, Yaduvanshi et al., 2015) which will affect the electrical performance of the PEMFC. Hence, the lowest concentration of nanoparticles possible, with reasonable enhancement of heat transfer rate is better for PEMFC applications.
The effect of using 50/50 water-ethylene glycol based ZnO nanofluids (compared with using only 50/50 water-ethylene glycol) on the heat exchanger size required to cool a 2.4 kW PEMFCs (the effect of ZnO nanofluid is shown as the effects for different nanofluids are identical)

4.2.2.8 The effects of using nanofluids as coolants on the pumping power

As the viscosity of nanofluids increases with concentration more pumping power is required compared to that with the base fluid (i.e. by maintaining the coolant mass flow rate constant). Same trend of pressure drop and pumping power has also been found in many experimental studies by other researchers (Huang et al., 2015, He et al., 2007, Sajadi and Kazemi, 2011). However, for the dilute concentration of nanoparticles (~0.05 vol% or less), the increase in pumping power is almost negligible, that has also been fortified by many experimental findings (Li and Xuan, 2002, He et al., 2007). From Figure 4.17, we can see that for 0.05 vol% concentrations of nanoparticles the required pumping power increases ~5% whereas for 0.5 vol% concentration the increment is around 6%.

It should be also noted here that for using the conventional coolants (i.e. De-ionising (DI) water, mixture of DI water-ethylene glycol, etc.) in the fuel cell cooling systems, it is necessary to use de-ionizing filters to remove the ions. These ions are introduced due to the contacts between the coolant and metallic materials in closed loop cycles. The de-ionising filter will incur a considerable pressure drop in the cooling system, and in fact this part can be eliminated when nanofluids are used as coolants, in fuel cells. Therefore, the increment of
pumping power for using nanofluids can be offset by not using the de-ionising filter in the PEMFC cooling system, when a nanofluid is used as coolant. Furthermore, excessive concentration of nanoparticles doesn’t give the heat transfer enhancement proportionately as seen in Figure 4.15, this is why minimum concentration of nanoparticles is desirable with respect to PEMFC overall electrical performance (i.e. taking into account both the impact of nanofluids electrical conductivity on the fuel cell stack power output and the parasitic energy suggested by the pumping power).

![Figure 4.17 The effect of 50/50 water-EG based Al₂O₃ nanofluids on pumping power under constant mass flow rate suitable for 2.4 kW PEMFCs cooling load](image)

**4.2.3 Summary**

The main purpose of this theoretical study was to find out the effects of using nanofluids as coolants on the size of the heat exchanger size as well as the pumping power used in the cooling system of the PEMFC. 50/50 water-EG based nanofluids were used to investigate the effects of using them as coolants in PEMFC cooling systems. This is in particular with emphasis on vehicle applications where reducing the size of the radiator can be very critical. Different concentrations in the range of 0.05–0.5 vol% of various nanoparticles were considered, in order to investigate the effects of increasing nanoparticle concentration. The main findings of this theoretical modelling study were as follows:
- By adding only 0.05 vol% nanoparticle with 50/50 water/EG mixture, the frontal area of the HE can be reduced by ~26% compared with the base fluid for same coolant mass flow rate.

- With increasing the concentration of nanoparticles (i.e. from 0.05 vol% to 0.5 vol%), the heat transfer rate gradually increasing but compared to the increment of nanoparticle concentration, the enhancement of heat transfer is not so significant. For example, compared with the base fluid used in this study, under laminar flow, the convection heat transfer coefficient can be increased by about 58% with the concentration of 0.05 vol% ZnO nanofluids whereas with 0.5 vol% concentration the convection heat transfer increased by about 60%.

- Hence increasing the nanoparticle concentration from 0.05 vol% to 0.5 vol%, no significant reduction of frontal area has been noticed.

- More pumping power was required when using nanofluids compared with the base fluid and with the increase of concentration of nanoparticles the required pumping power could gradually increase. However, this increase in pumping power is just marginal. As an example, for 0.05 vol% concentrations of nanoparticles the required pumping power increased by around 5% whereas for 0.5 vol% concentration the increment was obtained to be around 6%. It is important to note that with using nanofluids as coolants, there is no need of using de-ionising filters that in turn minimizes the increment of the pumping power.

- Future work for this study will include an experimental investigation of a fuel cell cooling system by using nanofluids as coolants, and observe the effect of using nanofluids (as coolants) on the electrical performance of the fuel cell as well as the thermal performance of its cooling system.
CHAPTER 5: USING NANOFLUIDS AS COOLANTS IN A PEMFC: AN EXPERIMENTAL INVESTIGATION

5.1 INTRODUCTION

Some of the research questions (Questions 1& 2, chapter 4) have already been partially addressed through the theoretical study conducted of this project. The results from the theoretical model provided us some directions for experimental part of the study. For example, with different nanofluids (i.e. 50/50 water-EG based ZnO, TiO$_2$ and Al$_2$O$_3$), the thermal performance of PEMFCs doesn’t vary significantly, therefore the experimental study can be conducted with only one or two nanofluids instead of all. The present experimental study has been designed to validate the theoretical results and help complete our answers to the research questions. This experimental study helped in achieving the following objectives and answer of the questions:

**Objective 3:** investigate experimentally the feasibility of using nanofluids as coolants in PEMFCs and identify the potentials and challenges associated with this cooling method.

**Objective 4:** quantify the effect of using nanofluids as coolants on the thermal and electrical performances of PEMFCs.

**Question 1:** What role the key characteristics of nanoparticles (e.g. volume fraction, and type of the nanoparticles) play in determining the electrical and thermal properties of nanofluids in the context of them being used as PEMFC coolant?

**Question 2:** What potentials and challenges nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performance of PEMFCs?

**Question 3:** How much the electrical and thermal performances of PEMFCs are affected by using nanofluids as coolants in PEMFCs?

**Question 4:** What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?

Accordingly, this experimental investigation has been divided into two main activities:

- Nanofluids preparation and characterisation
• Measurement of PEMFC cooling and electrical performances when nanofluids and base fluid are used as coolants.

Based on the research questions posted in introduction chapter, the aims of the experimental parts of this project are to:

• investigate the electrical and thermo-physical properties of nanofluids experimentally
• set-up an experimental rig suitable for studying the thermo-electrical performance of a liquid-cooled PEMFC (i.e. a 2.4 kW PEMFC in this case).
• identify suitable nanofluids based on their electrical and thermo-physical properties to be used as coolants in PEMFC cooling in automotive applications.
• study the effect of using nanofluids as coolants on the PEMFC electrical and thermal performances.

For handling the nanofluids and running PEMFCs, a very strict safety regimen requires in order to minimise or to nullify the potential hazards associated with working with nanofluids and hydrogen. An appropriate safety set-up system has been implemented to support this experimental work. Details of risk assessment have been provided in Appendix E.

5.2 PREPARATION AND CHARACTERISATION OF NANOFLUIDS

5.2.1 Preparation

The OHAUS PioneerTM Series of analytical and precision balance (Preparing sample nanofluids for electrical and thermo-physical characterisation) and analytical balance BM-252 (preparing nanofluids to be used in PEMFC experimental study) were used to measure the weight of nanoparticles required for prepare the nanofluid samples. The images of both scales have been given in Appendix B. The detailed specifications of OHAUS and BM-252 are given in Table 5.1.

Table 5.1 Specifications of OHAUS Pioneer TM and analytical BM-252 balances

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>OHAUS</th>
<th>A&amp;D Company Ltd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>Pioneer TM</td>
<td>BM-252</td>
</tr>
<tr>
<td>Weighing capacity</td>
<td>110 gm</td>
<td>250 gm</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.1 mg</td>
<td>0.1 mg</td>
</tr>
</tbody>
</table>
The VC 750 sonicator manufactured by Sonics & Materials, Inc. was used to prepare the sample nanofluids for investigating the electrical and thermo-physical properties of nanofluids whereas for applications in PEMFC cooling system, nanofluids are prepared by using Qsonica Q700 sonicator manufactured by Cole-Parmer, USA in this project that has got more capacity. The operating procedures for both sonicators are almost same and detailed procedures have been provided in Appendix A.

5.2.2 Characterisation of nanofluids

Electrical and thermo-physical (i.e. thermal conductivity, viscosity, specific heat and density) properties of nanofluids were investigated with a view to applying them in PEMFCs cooling as coolants. In this section, the specifications and brief description of these equipment are provided.

To apply nanofluids as coolants in PEMFCs, measuring electrical properties of them are very important as they could potentially affect the electrical performance of FC stack. IntelliCAL™ CDC401 (Figure 2.6) is a digital, graphite, hand held, 4-pole conductivity probe which was used for measuring electrical conductivity of nanofluids in this study. The salient features of the CDC401 are:

- Conductivity range: 0.01 µS.cm to 200 mS/cm
- Conductivity accuracy: +/- 0.5% of reading
- Temperature accuracy: 0.03 °C
- Operating temperature range: -10 to 110 °C
- Minimum sample depth: 45 mm

SEM water bath was also used to heat up and stabilize the temperature of nanofluids for measuring electrical conductivity. The temperature was controlled by the thermostat up to 100°C range with push button reset overheat protection. The digital PID controls have 0.1°C resolution and temperature stability of +/-0.2°C.

Thermal conductivity is another key characteristic of nanofluids measured experimentally. KD2 Pro thermal properties analyser (Figure 2.5) manufactured by Decagon Devices, Inc. was used to measure the thermal conductivity of nanofluids. The KD2 Pro is working on the basis of transient hot wire method. There are several sensors available for measuring the thermal conductivities of different types of materials. KS-1 sensor is the one used to measure
the thermal conductivity of nanofluids. The specifications of KD2 Pro thermal conductivity meter are:

- Operating temperature range: -50 to 150 °C
- Thermal conductivity measurement range: 0.02 to 2.00 W/m.K
- Accuracy: +/- 5% from 0.2 - 2 W/m.K
  
  +/- 0.01 W/m.K from 0.02 – 0.2 W/m.K

Viscosity is one of the most important properties of nanofluids, which indicates the resistance of fluid. Considerable engineering problems arise while dealing with high viscous liquids that include higher energy requirement for pumping as well as for mixing. Discovery Hybrid Rheometer (DHR-3 model) (Figure 2.7) was used to measure the viscosity of nanofluids in this study. Plate-Cone geometry with the 60 mm diameter plate and 2.023° cone is used for measuring the viscosity. The temperature of the Peltier plate steel-999459 was controlled by using a temperature controller bath. The samples of nanofluids were prepared and loaded with pipette ensuring that the sample didn’t contain any bubbles. TA instruments Trios version 3.1.4.3642 was used to record the viscosity, temperature, shear stress and shear strain. The Environmental Test Chamber (ETC) used the cryogenic (low-temperature) agent, liquid nitrogen, for cooling. The technical specifications of DHR-3 are given in Table 5.2
Table 5.2 Technical specifications of DHR-3

<table>
<thead>
<tr>
<th>Item description</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>Cones and plates (Dia 20 to 60 mm, angles 1, 2 and 4˚)</td>
</tr>
<tr>
<td>Temperature control</td>
<td>-40°C to 200°C</td>
</tr>
<tr>
<td>Temperature control rate</td>
<td>20 °C/min</td>
</tr>
<tr>
<td>software</td>
<td>TRIOS</td>
</tr>
<tr>
<td>Bearing type, thrust</td>
<td>Magnetic</td>
</tr>
<tr>
<td>Bearing type, radial</td>
<td>Porous carbon</td>
</tr>
<tr>
<td>Motor design</td>
<td>Drag cup</td>
</tr>
<tr>
<td>Minimum torque (nN.m) oscillation</td>
<td>0.5</td>
</tr>
<tr>
<td>Minimum torque (nN.m) steady shear</td>
<td>5</td>
</tr>
<tr>
<td>Maximum torque (mN.m)</td>
<td>200</td>
</tr>
<tr>
<td>Torque resolution (mN.m)</td>
<td>0.05</td>
</tr>
<tr>
<td>Minimum frequency (Hz)</td>
<td>1.0x10^-7</td>
</tr>
<tr>
<td>Maximum frequency (Hz)</td>
<td>100</td>
</tr>
<tr>
<td>Minimum angular velocity (rad/s)</td>
<td>0</td>
</tr>
<tr>
<td>Maximum angular velocity (rad/s)</td>
<td>300</td>
</tr>
<tr>
<td>Displacement transducer</td>
<td>Optical encoder</td>
</tr>
<tr>
<td>Optical encoder dual reader</td>
<td>Standard</td>
</tr>
<tr>
<td>Displacement transducer (nrad)</td>
<td>2</td>
</tr>
<tr>
<td>Step time, strain (ms)</td>
<td>15</td>
</tr>
<tr>
<td>Step time, rate (ms)</td>
<td>5</td>
</tr>
<tr>
<td>Normal/axial force transducer (N)</td>
<td>FRT</td>
</tr>
<tr>
<td>Maximum normal force (N)</td>
<td>50</td>
</tr>
<tr>
<td>Normal force sensitivity (N)</td>
<td>0.005</td>
</tr>
<tr>
<td>Normal force resolution (mN)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The TA instruments Differential Scanning Calorimeter (DSC) 2920 (Figure 2.8) was used to measure the specific heat of nanofluids by following the three-step method and procedure described in section 2.4.2.5. Hermetically sealed aluminium pans (TA Instruments) were used to measure the specific heat of nanofluids.

In these tests, sapphire (60.96 mg) was used as the reference sample, with specific heat values obtained from TA Instrument (Instruments, 2016). The DSC heating procedure consisted of three segments:

- After obtaining equilibrium condition, remain around one minute at isothermal condition at 20°C
- Increase the temperature to 80 °C at the rate of 10 °C/min
- At 80 °C, it should be isothermal for another one minute

A pycnometer (Figure 2.9) is used to measure to density of nanofluids in this study. The specifications of the pycnometer used in this study are given in Table 5.3.
Table 5.3 Specifications of pycnometer used to measure density of nanofluids

<table>
<thead>
<tr>
<th>Brand</th>
<th>DURAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Made</td>
<td>Germany</td>
</tr>
<tr>
<td>Volume</td>
<td>24.836 cm³</td>
</tr>
<tr>
<td>Standard</td>
<td>Water at 20 °C</td>
</tr>
</tbody>
</table>

5.3 Experimental set-up for PEMFC thermal and electrical performances investigation

5.3.1 Overall system design overview

A 2.4 kW liquid cooled PEMFC has been selected first for this study. Based on the selected PEMFC, all the other components of the cooling system have been designed, purchased and installed in the test rig gradually as we can see the overall schematic diagram of the 2.4 kW PEMFC cooling system in Figure 5.1. The hydrogen and air have been supplied to the PEMFC at around 30 kPa from the high-pressure cylinder (13.7 MPa) by reducing the pressure through properly selected and fully certified regulators and gas piping arrangements. Between the hydrogen cylinder and the PEMFC, a number of safety equipment have been implemented to minimise the risk associated with such experiments that involve hydrogen and to conduct the experiment in a highly-safe environment.
Figure 5.1 Experimental investigation into 2.4 kW PEMFC cooling system using conventional coolant (i.e. 50/50 water-EG) and 50/50 water-EG based nanofluids as coolants.
5.3.2 Hydrogen supply line

5.3.2.1 Overall plan

Hydrogen was stored in a high pressure cylinder with the pressure of 13.7 MPa. The high pressure H$_2$ was gradually regulated through two regulators connected in series then supplied to the 2.4 kW PEMFC at about 30 kPa. A solenoid-operated valve was located outside the RMIT Sustainable Hydrogen Energy Laboratory (SHEL) just after a manually-controlled valve, which was closed unless no electrical signal was received by it. This valve was controlled by the safety interlock system and was allowed to be open only when three conditions would be fulfilled simultaneously. A manual valve was located between the solenoid valve and the final regulator to add the possibility of another manual control on the hydrogen supply line in series with the safety interlock system, so that if the safety system fails, the potential danger can be minimised by using this manual valve. The safety interlock system and devices will be discussed in more details in the next section.
5.3.2.2 Hydrogen storage/cylinder, supply line and safety measures

A BOC high-pressure (13.7MPa) hydrogen cylinder (Figure 5.4) manufactured in accordance with relevant Australian, New Zealand or overseas specification approved by SAA Committee ME/2 gas cylinders was used to store and supply H₂ to the PEMFC. The purity of the hydrogen was rated 99.5%.

Figure 5.4 Hydrogen cylinder stored in the cage outside RMIT Sustainable Hydrogen Energy Laboratory (SHEL)
The connectors, pipes, tube, valves, and fittings used for hydrogen line were all Swagelok products (Appendix B) These parts were mainly ¼” size (NPT thread) and depending on the situation, male-female or pressure fittings have been used for hydrogen line. On the high-pressure side of the hydrogen line only stainless steel parts have been used whereas on the low pressure (~30 kPa) side copper and stainless steel have been used to complete the line.

Two regulators have been used in the hydrogen line. The high pressure (13.7 MPa) hydrogen gas in the cylinder was reduced to 2000 kPa by the fixed regulator at the outlet of the cylinder. The reduced pressure hydrogen gas was then passing through manual and solenoid valves and then to another regulator, which reduced the pressure down to 600 kPa. After 600 kPa regulator, the gas pressure was reduced by using a manual regulator valve and at the end hydrogen was supplied to the PEMFC at around 30 kPa.

The solenoid valve was allowed to pass the H₂ gas in the system if and only if the system fulfils the three operating conditions. The three conditions for operating solenoid valve were:

- The extraction fan in the hydrogen experimental cabinet containing the fuel cell rig was correctly functioning and obtaining sufficient air flow
- No hydrogen was detected in the laboratory area by sensors
- The manual switch before the solenoid valve was on

As for safety measures, it is important to highlight some of the properties of hydrogen for safety considerations. Over a wide range of concentration in air (4-75%), hydrogen is usually considered to be highly flammable and explosive over the range of 15-90% of concentrations at standard temperature and pressure. Along with this high flammability, the electrostatic charges carrying by hydrogen can mix with oxygen in the carrying pipe and can be dangerous due to the low energy of ignition of hydrogen. However, the auto-ignition temperature (e.g. 585 °C) is higher than that of the other fuels. Moreover, hydrogen gas possesses very light and small molecules compared with other gasses that can be easily leaked in the pipe. Hydrogen gas leakage must be detected using gas-specific sensors as the gas is odourless and colourless. All the above mentioned facts underline a much secured system for handling the hydrogen in PEMFC system.

The interlock system detects any failure in the ventilation system, as well as the presence of hydrogen above pre-set safe limits (8000 ppm) in the laboratory and the cabinet. The extraction fan system is interlinked with the safety interlock system (Figure 5.5) via an air pressure switch which ensures the extraction fan is properly working and extracting
sufficient amount of air. Two hydrogen detection sensors: one located in the ceiling of the hydrogen lab and the other one inside the hydrogen extraction cabinet are used to ensure no hydrogen above the flammable limit in H₂ lab. The extraction fan must be first on to work the extraction interlock system properly. When the fan is extracting an adequate amount of air, the pressure drop in the exhaust duct reaches a predetermined level in the pressure switch and no hydrogen above safe levels is detected, the pressure switch will be closed allowing the power to be available at the output terminals. A programmable logic controller (PLC) and relays controlled all the functions. Whenever there will be any hydrogen detected inside the hydrogen lab or the cabinet, the hydrogen sensors will send signal to the override safety relay circuit breaker to cut off power supply for all experiments. The extraction fan will be running to ventilate the hydrogen from the hydrogen lab. After extracting the hydrogen, the system has to be run manually from the very beginning.

The system relies on the main rotary isolator to be on at all times for the purpose of detecting a hydrogen presence in the room at all times. If hydrogen is detected, an alarm and visual beacon will activate, the hydrogen supply will be shut off and electrical services to the chamber will shut off and electrical services to the chamber will be disconnected leaving only the extraction fan running.

The whole experimental rig was installed outside and placed inside a fume cupboard made from polyvinyl chloride (PVC) as shown in Figure 5.6. This cabinet is used only for the H₂ related experiments in the Hydrogen Lab at RMIT Bundoora East Campus to ensure that any

Figure 5.5 Safety interlock system used for the experimental study into 2.4 kW PEMFCs
possible hydrogen leakage is confined to this cabinet. The fume cupboard has been designed and installed by Laboratory System Group (Australia) and used for the Capability and Technology Demonstrator (CTD) project. The cabinet is quiet spacious with the size of 1700 mm x 850 mm x 1200 mm to accommodate most of the fuel cell related experimental rig. It is equipped with an externally located centrifugal extraction fan (capacity 660 l/min) powered by a three-phase motor inside the duct connected to the top of the fume cupboard. A hydrogen detecting sensor is placed at the top-right corner at the cabinet. No hydrogen detection by the sensor and properly running of the extraction fan are the preconditions for sending electrical signal to the solenoid valve to allow the hydrogen flowing through the hydrogen line. An additional hydrogen detecting sensor is placed in the hydrogen lab to supplement the sensor inside the hydrogen cabinet and integrated into the safety interlock system and works in parallel with the one inside the fume cupboard.

![Figure 5.6 Fume cupboard used to H₂ related experiments situated at RMIT Sustainable Hydrogen Energy Laboratory (SHEL)](image)

The entire hydrogen gas line is checked by using hand held hydrogen detector and special leak detection soap to ensure that there is no any hydrogen leakage in the joints or connectors of the line.
5.3.2.3 Hydrogen humidifier

In order to operate the PEMFCs at an optimum operating condition, proper water and thermal management arrangement should be in place in accordance to what usually the manufacturer recommends (Dumercy et al., 2006). While the humidity is strongly dependent on the stack temperature (Kim and Hong, 2008), the humidity level should be also adjusted at a desirable level by using a humidifier. In order to maintain the relative humidity level of hydrogen at above 90% (as recommended by PEMFCs manufacturer), a humidifier manufactured by dpoint technologies (i.e. purposely designed for fuel cell systems) was used to humidify the hydrogen gas. The specifications of this humidifier are given in Table 5.4. The humidifier was installed according to the manufacturer’s recommendation as shown in Figure 5.7: i.e. the long side in vertical orientation for optimum performance; the inlet of water will be at the upper side; and the flow arrangement of hydrogen and water must be counter flow.

![Hydrogen humidifier installed in PEMFCs rig with the manufacturer recommended orientation (i.e. in vertical orientation)](image)

Figure 5.7 Hydrogen humidifier installed in PEMFCs rig with the manufacturer recommended orientation (i.e. in vertical orientation)
Table 5.4 Specifications of hydrogen humidifier used in PEMFC experimental investigation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel cell rated power</td>
<td>2.4 kW</td>
</tr>
<tr>
<td>Rated flow</td>
<td>40 SLPM</td>
</tr>
<tr>
<td>RH performance at rated flow and dew-point approach temperature</td>
<td>100% RH</td>
</tr>
<tr>
<td>Dew-point approach temperature at rated flow</td>
<td>&lt;6 °C</td>
</tr>
<tr>
<td>Life time</td>
<td>&gt;5000 hours</td>
</tr>
<tr>
<td>Maximum allowable operating temperature</td>
<td>70 °C</td>
</tr>
<tr>
<td>Minimum allowable operating temperature</td>
<td>-20 °C</td>
</tr>
<tr>
<td>Maximum burst pressure</td>
<td>100 kPa</td>
</tr>
<tr>
<td>Maximum pressure drop across humidifier at rated flow</td>
<td>3 kPa</td>
</tr>
<tr>
<td>Maximum allowable differential pressure between water and hydrogen</td>
<td>21 kPa</td>
</tr>
<tr>
<td>Flow configuration</td>
<td>Counter flow</td>
</tr>
<tr>
<td>Material compatibility</td>
<td>Deionized water and hydrogen</td>
</tr>
<tr>
<td>Minimum freeze thaw cycles</td>
<td>&gt;50 cycles from -20 °C to 65 °C</td>
</tr>
<tr>
<td>Gas cross over (wet &amp; dry)</td>
<td>&lt;0.1 % of rated flow</td>
</tr>
<tr>
<td>Maximum external leakage dimensions</td>
<td>0 cc/min at 35 kPa</td>
</tr>
<tr>
<td>Size</td>
<td>142 mm x 67 mm x 184 mm</td>
</tr>
<tr>
<td>Weight</td>
<td>1.75 L</td>
</tr>
<tr>
<td></td>
<td>0.8 kg</td>
</tr>
</tbody>
</table>

5.3.2.4 Measurement instruments

In this experiment, the following measurement instruments are connected on the hydrogen line:

- **Pressure gauge**: The pressure of the hydrogen at the inlet of PEMFC was monitored continuously using an oil-free (i.e. to avoid membrane contamination) pressure gauge. The fuel cell was operated mainly in dead-ended mode and a normally closed valve is periodically opened to purge the anode side of the fuel cell.

- **Flow meter**: The hydrogen flow meter used in the experiment is a high precision Sierra Smart Track Series C100L model hydrogen mass flow meter manufactured as shown in Appendix B. This flow meter is specially calibrated for measuring hydrogen flow rate in the range of 0-50 SLPM. The specifications of the hydrogen mass flow meter are described in Table 5.5.
Table 5.5 Specification of Sierra C100L hydrogen mass flow meter

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>C100L-DD-13-OV1-SV1-PV2-V1-S0-C0</td>
</tr>
<tr>
<td>Calibrated gas</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Full scale reading</td>
<td>0-50 SLPM</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>60 kPa</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>30 kPa</td>
</tr>
<tr>
<td>Output signal</td>
<td>0-5 VDC/4-20 mA</td>
</tr>
<tr>
<td>Set signal</td>
<td>Polot Module</td>
</tr>
<tr>
<td>Orientation</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Maximum inlet pressure</td>
<td>3.45 MPa</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>10 - 45 °C</td>
</tr>
<tr>
<td>Maximum temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Input power supply</td>
<td>24 VDC</td>
</tr>
<tr>
<td>Connections</td>
<td>¼” NPT</td>
</tr>
<tr>
<td>Set signal</td>
<td>Pilot Module</td>
</tr>
<tr>
<td>Orientation</td>
<td>Horizontal</td>
</tr>
</tbody>
</table>

- **Humidity meter:** According to the recommendation of the PEMFC manufacturer, the inlet hydrogen humidity must be maintained to be at above 90%. Below this humidity range the performance of the fuel cell can be lower than that suggested by the manufacturer. A humidifier is used in the hydrogen line to humidify the hydrogen and Vaisala HUMICAP® Humidity and a temperature transmitter series HMT 330 is used to measure the humidity range. The HMT330 transmitter (Figure 5.8) provides reliable humidity measurements in a wide range of applications.
Figure 5.8 Vaisala HMT330 humidity meter with the RH measurement range: 0-100%; temperature range: 0-180 °C and pressure tolerance: up to 100 bar was used for 2.4 kW PEMFC experiment

- **Thermocouple**: Water proof stainless steel Pt100 temperature probes were used to measure the inlet and outlet temperature of PEMFCs and radiator in this study. The technical specifications of thermocouples are provided in Table 5.6.

Table 5.6 Technical specifications of the Pt100 temperature probes used in 2.4 kW PEMFCs experimental study

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature range</td>
<td>-50 °C to 250 °C</td>
</tr>
<tr>
<td>Probe diameter</td>
<td>4 mm</td>
</tr>
<tr>
<td>Probe length</td>
<td>150 mm</td>
</tr>
<tr>
<td>Material</td>
<td>Platinum (probe), Stainless steel (sheath)</td>
</tr>
<tr>
<td>Connection</td>
<td>1/8” BSP</td>
</tr>
<tr>
<td>Accuracy</td>
<td>+/- (0.1+0.00167xT) °C</td>
</tr>
</tbody>
</table>

5.3.3 **Air supply line**

Similar to the hydrogen line, the air was supplied to the PEMFC from the high-pressure cylinder by gradually reducing the pressure from 20 MPa down to 30 kPa as shown in Figure 5.9. The pressure of air was controlled by regulators and manual valves. In the air supply line, along with valves and regulators, a flow meter, a humidifier, a humidity meter, and a pressure gauge were used.
The high pressure (15 MPa) air, gas code 054 cylinder was supplied by BOC, Australia and stored in a very restricted cage as shown in (Figure 5.10). This type of compressed air was mainly used as a carrier gas, purge gas or detector gas for a range of analytical equipment.
All the connectors, fittings, valves, and pipes (Swagelok products) were mainly ¼” size (NPT thread). On the high-pressure side of the air line, stainless steel parts were used and on the low pressure side (about 50 kPa) both brass and stainless steel were used.

Two regulators were used in the air supply line to reduce pressure from 15 MPa to 2000 kPa and then from 2000 kPa to 600 kPa. Eventually the air was supplied to the PEMFC at around 30 kPa which was measured and monitored by the pressure gauge installed just before the inlet of fuel cell. A flow meter was also installed just before the inlet of the PEMFC which indicated the required air flow. The images of the regulators and measurements instruments are provided in Appendix B.

5.3.4 Cooling system

5.3.4.1 Overall plan

The 2.4 kW PEMFC, used for this study, can be cooled by using de-ionising water, 50/50 water-EG mixture, or any kind of conventional coolants. Whenever the fuel cell stack temperature reached at set temperature of the system (e.g. 40 ºC, 50 ºC and 60 ºC), the cooling pump has to start operation and circulate the coolant throughout the fuel cell stack. The coolant was circulated through the fuel cell as well as heat exchanger in order to extract the heat generated in the fuel cell and rejected it to the atmosphere. This was basically done for maintaining the fuel cell temperature at a desired level. The PEMFC inlet and outlet temperature difference must be in the range between 3 to 10 ºC.

The PEMFC cooling system including the measurement instruments to monitor the performance of this system are shown schematically in Figure 5.11 comprising the following components:

- Water pump
- Heat exchanger
- Water flow meter
- Pressure gauge
- Thermocouples
- Tubing, fittings and connectors
- Insulators
5.3.4.2 Water pump

The water pump injects a coolant into the fuel cell jackets and circulates the coolant throughout the heat exchanger. The pump used in the system was variable speed controlled by PWM and run on 24 VDC at the maximum current of 3.6 A. The maximum head of this pump was 13 m and the maximum flow rate was 26.67 l/min. The pump was 3-phase and could handle water at the maximum temperature of 100 °C for the coolant, that was well above the temperature used in this experimental study (i.e. more or less about 50 °C). According to the 2.4 kW PEMFC manufacturer’s user manual, more than 2.7 l/min of water pumping capacity was required for the fuel cell cooling system. The water flow rate needed to extract the fuel cell heat is less than that of the pumping capacity and the pump can cope with the water path pressure drop while supplying this flow of water. The specifications of the used pump in this experiment are provided in Table 5.7 whereas the pump curve, picture and dimension are given in Appendix B.
Table 5.7 Specification of water pump used in 2.4 kW PEMFC cooling system

<table>
<thead>
<tr>
<th>Model</th>
<th>ZK50B-24130A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving method</td>
<td>Brushless, Magnetic, 3-Phase</td>
</tr>
<tr>
<td>Condition of use</td>
<td>continuously</td>
</tr>
<tr>
<td>Max working temp</td>
<td>100 °C</td>
</tr>
<tr>
<td>Power consumption</td>
<td>2.5W~86.4W</td>
</tr>
<tr>
<td>Rated voltage</td>
<td>24 V</td>
</tr>
<tr>
<td>Max rated current</td>
<td>3.8 A</td>
</tr>
<tr>
<td>Max flow rate</td>
<td>27 l/min</td>
</tr>
<tr>
<td>Max static head</td>
<td>13 m</td>
</tr>
<tr>
<td>Life span</td>
<td>More than 30000 hrs</td>
</tr>
<tr>
<td>Power supply</td>
<td>DC</td>
</tr>
</tbody>
</table>

5.3.4.3 Heat exchanger

A Yamaha YZ85 model motorbike radiator was used for extracting heat from the 2.4 kW PEMFC that can generate up to ~8 kW heat (cooling load ~6 kW). The selected radiator used in this experimental investigation was suitable to extract the generated heat by 2.4 kW PEMFC. The specifications of the radiator are provided in Table 5.8:

Table 5.8 The specifications of the Yamaha YZ85 radiator used in 2.4 kW PEMFC cooling system

<table>
<thead>
<tr>
<th>Model</th>
<th>Yamaha YZ85</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiator size</td>
<td>215 mm x 117 mm x 40 mm</td>
</tr>
<tr>
<td>Rows</td>
<td>2</td>
</tr>
<tr>
<td>Inlet diameter</td>
<td>16 mm</td>
</tr>
<tr>
<td>Outlet diameter</td>
<td>19 mm</td>
</tr>
<tr>
<td>Tank wall thickness</td>
<td>2 mm</td>
</tr>
<tr>
<td>Fill neck thickness</td>
<td>3 mm</td>
</tr>
<tr>
<td>Fill neck ID</td>
<td>31 mm</td>
</tr>
<tr>
<td>Material</td>
<td>Aluminium</td>
</tr>
</tbody>
</table>

5.3.4.4 Piping, fittings, connectors, and insulation

All the piping, fittings, and connectors were arranged according to the necessity of the inlet and outlet of the FC, heat exchanger and pump. The pipes, fittings, and connectors used in the cooling system were 16 mm and 19 mm. The contacts between the coolants and the metal parts were avoided as much as possible so that fewer ions can be attracted into the coolants’ streams; it is important to note that the presence of such ions in the coolant (i.e. that is electrically in touch with the cooling plates) can reduce the performance of the fuel cell. For installing the pressure gauge and thermocouples, an especial rubber union instead of metal
was manufactured and used in the system. Clear vinyl pipe has also been employed in the cooling system. An insulation layer was applied over the pipes, fittings, connectors, and the fuel cell itself to make sure that the experimental environment was controlled and almost the entire cooling load of the fuel cell was captured each time when the stack was operated.

5.3.5  **PEMFC**

5.3.5.1  **Introduction**

A 2.4 kW liquid cooled fuel cell stack has been employed in this experimental study. The fuel cell stack contains 27 cells each has 202 cm² active area. The physical characteristics of the stack are provided in Table 5.9 whereas Figure 5.12 shows the physical appearance along with the various terminals.

Table 5.9  Weight and dimensions of the 2.4 kW fuel cell stack

<table>
<thead>
<tr>
<th>Stack length</th>
<th>Height</th>
<th>Width</th>
<th>Dry mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 cells: 233 mm</td>
<td>180 mm</td>
<td>490 mm</td>
<td>8.3 kg</td>
</tr>
</tbody>
</table>

Figure 5.12 2.4 kW PEMFC and its various terminals

The nominal operating current suggested by the manufacturer is 135 A, the minimum operating current is 34 A, and the maximum operating current is 160 A. However, due to some restriction in the lab such as the hydrogen supply rate, and safety considerations, the stack was operated at considerably lower current (i.e. corresponding to about 1 kW of
The performance of PEMFC can vary (Table 5.10) from stack to stack at Beginning of Life due to manufacturing variability (i.e. based on 100 stacks).

### Table 5.10 Stack performance at Beginning of Life (BOF)

<table>
<thead>
<tr>
<th>Performance parameter</th>
<th>Stack current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Fleet average power (W/cell)</td>
<td>0</td>
</tr>
<tr>
<td>Fleet Average voltage (mV/cell)</td>
<td>971</td>
</tr>
<tr>
<td>Stack to stack performance variability (mV)</td>
<td>+15/-35</td>
</tr>
</tbody>
</table>

### 5.3.3.5.2 Stack nominal operating characteristics

The PEMFC can be operated at different operating conditions but for getting the optimum efficiency, the manufacturer has recommendations for system integrators optimal operation of the stack. Operation at these conditions helps to maximise the stack lifetime while maximising the performance and ensuring a stable operation. These recommended operating conditions are given in Table 5.11. Moreover, the stack safety and performance are also given in Appendix A.2.

### Table 5.11 The nominal operating conditions for 2.4 kW PEMFCs

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Stack current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>34</td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
<td></td>
</tr>
<tr>
<td>Composition (H₂/N₂ Blend) (%H₂)</td>
<td>90</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>4.5</td>
</tr>
<tr>
<td>Inlet pressure (kPa)</td>
<td>13</td>
</tr>
<tr>
<td>Pressure drop (kPa)</td>
<td>5</td>
</tr>
<tr>
<td>Inlet temperature (°C)</td>
<td>60</td>
</tr>
<tr>
<td>Inlet humidity (%RH)</td>
<td>90</td>
</tr>
<tr>
<td><strong>Oxidant</strong></td>
<td></td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>1.8</td>
</tr>
<tr>
<td>Inlet pressure (kPa)</td>
<td>11</td>
</tr>
<tr>
<td>Pressure drop (kPa)</td>
<td>5</td>
</tr>
<tr>
<td>Inlet temperature (°C)</td>
<td>58.9</td>
</tr>
<tr>
<td>Inlet humidity (%RH)</td>
<td>95</td>
</tr>
<tr>
<td><strong>Coolant</strong></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>100% De-ionized water</td>
</tr>
<tr>
<td>Inlet temperature (°C)</td>
<td>60</td>
</tr>
<tr>
<td>Temperature rise (°C)</td>
<td>3</td>
</tr>
<tr>
<td><strong>Environmental conditions</strong></td>
<td></td>
</tr>
<tr>
<td>Ambient temperature, operation (°C)</td>
<td>-5 °C to 70 °C</td>
</tr>
</tbody>
</table>
5.3.6 Electronic load

A programmable DC electronic load (Model M9715) (Appendix B) manufactured by Maynuo Electronics was used for measuring the voltage and power variation of the fuel cell stack against its current by varying the resistance of the electronic load connected to the fuel cell. This DC electronic load was designed with resolution of 0.1 mV and 0.01 mA (the basic accuracy is 0.03%, the basic current rise speed is 2.5 A/μs). As mentioned before due to limitations in hydrogen supply and other safety considerations, the experiment was conducted for up to 1 kW of power production by this stack. The specifications of the electronic load are given in Table 5.12:

Table 5.12 Specification of the programmable electronic load (Model M9715)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input rating</td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>1.8 kW</td>
</tr>
<tr>
<td>Current</td>
<td>0-240 A</td>
</tr>
<tr>
<td>Voltage</td>
<td>0-150 V</td>
</tr>
<tr>
<td>Operation mode</td>
<td>CC, CR, CV, CW, CC+CV, and CR+CW</td>
</tr>
<tr>
<td>CC mode</td>
<td>0.05%+0.1%FS</td>
</tr>
<tr>
<td>CV mode</td>
<td>0.03%+0.2%FS</td>
</tr>
<tr>
<td>CR mode</td>
<td>0.1%+0.1%FS</td>
</tr>
<tr>
<td>Dimension</td>
<td>207mm x 428 mm x 453.5 mm</td>
</tr>
</tbody>
</table>

5.4 Error/uncertainty analysis

No measurement of a physical quantity can be entirely accurate. All measurements, however carefully made, give a range of possible values referred to as an uncertainty or error. Error analysis; the set of techniques of dealing with them, is an essential part of an experimental study. The error is mainly the difference between the measured parameter and its true value, leads to a quantification of the accuracy of the measurement, called here after error/uncertainty.

Generally, the fluctuation about the average measurement can be expressed by the standard deviation of the n measurements.

\[ \sigma(x) = \pm \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \]  

(5.1)
where \( \sigma \) is the standard deviation, \( n \) is the number of measurements, \( x \) is the measured value, and \( \bar{x} \) is the mean of \( x_i \)’s.

Finally, the uncertainty can be calculated by calculating the standard deviation of the mean that denotes the standard measure for describing the precision of a measurement, i.e. how well a number of measurements agree with themselves. Thus, the uncertainty can be expressed as (Shabani, 2010):

\[
u(x) = \pm \frac{\sigma(x)}{\sqrt{n}} = \pm \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n-1)}} \tag{5.2}
\]

\[
Percent \ Error = \pm \frac{\nu(x)}{x} \times 100\% \tag{5.3}
\]

However, sometimes the parameter, studied experimentally \( Y \) depends on a number \( N \) of other experimentally measured parameters \( (x_1, x_2, \ldots, x_n) \). Thus the error of \( Y \) needs to be calculated by calculating the errors involved in measuring each of these variables \( x_i \).

\[
Y = f(x_1, x_2, \ldots, x_N) \tag{5.4}
\]

In this experimental study, the electrical and thermo-physical characteristics of nanofluids as well as the PEMFCs’ voltage, power and hydrogen consumption were measured and calculated through direct measurement of just one parameter for each of them. However, the PEMFCs cooling loads depend on several parameters, i.e. two temperatures and one coolant flow rate. The measurement of each of them comes with an error associated with the measurement instrument. Hence, the standard deviation associated with the indirectly measured parameters (equation (5.4)) is called the combined uncertainty \( \nu(Y) \) which connected with the uncertainties associated with \( x_i \)'s or provided by the manufacturer of the measurement instrument, and can be expressed (Shabani, 2010):

\[
u(Y) = \pm \sqrt{\sum_{i=1}^{N} \left( \frac{\partial f}{\partial x_i} \right)^2 \nu^2(x_i)} \tag{5.5}
\]

Applying equation (5.2) for a measured parameter such as electrical conductivity of nanofluids is possible as all the measured values are supposed to be same. However,
equation (5.2) is not applicable for the measurements of temperature and coolant flow rate as these parameters are changing in nature and their variations are basically coming from the oscillation of the input power to the water pump. Hence, for calculating the combine measurement error in equation (5.5), the uncertainties of the measuring instrument provided by the manufacturers were applied.

Some examples of how the uncertainties associated with the experimental measurements (i.e. electrical and thermo-physical characteristics of nanofluids, PEMFCs voltage, power and cooling load) have been calculated in this present work are provided in Appendix C.

5.5 Results and discussions

5.5.1 Nanofluids characterisation

5.5.1.1 Overview

Three types of nanofluids namely 50/50 Water-EG based Al₂O₃, TiO₂ and ZnO nanofluids at concentration of 0.05, 0.1, 0.3 and 0.5 Vol% have been prepared and their electrical and thermo-physical characteristics (i.e. thermal conductivity, viscosity, specific heat and density) have been investigated experimentally. The two-step method has been adopted as described in section 2.4.2.1 for preparing the nanofluids used in this study. The nanoparticles were purchased from renowned manufacturer and supplier of nanoparticles. Ethylene Glycol (EG) also known as Ethanediol, and Milli-Q were used to prepare the 50/50 Water-EG mixture as base fluids.

5.5.1.2 Electrical conductivity

The electrical conductivity meter was calibrated by introducing a fluid of known electrical conductivity, i.e. pure ethylene glycol (99.90 %) supplied by Chem-Supply, Australia and 50/50 water-EG mixture (Table 5.13). The measured data matched with the available literature (MEGlobal, 2016) with the errors of 4.8% and 3.3% for ethylene glycol and 50/50 water-EG mixture respectively. These errors could be due to measured environmental conditions and/or impurity levels of liquids (i.e. Milli-Q water).
Table 5.13 Comparison of electrical conductivity of ethylene glycol and 50/50 water-ethylene glycol mixture (by volume) with industrial data provided by MEGlobal (2016) at 20 °C

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Measured (μS/cm)</th>
<th>MEGlobal (μS/cm)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>3.14</td>
<td>3.3</td>
<td>4.8</td>
</tr>
<tr>
<td>50/50 water-EG mixture</td>
<td>5.03</td>
<td>5.20</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The electrical conductivities of 50/50 water-EG based ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids with 0.05 vol% to 0.5 vol% concentrations have been illustrated in Figure 5.13 to Figure 5.18. The variations of electrical conductivity have been also shown in Figure 5.13 to Figure 5.15. Based on these experimental measurements, it was observed that the electrical conductivities of the investigated nanofluids increase almost linearly with the temperature. Almost 67%, 91% and 104% enhancement of electrical conductivity for ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids respectively, relative to base fluid, were observed for 0.05 vol% concentration for increasing temperature from 20°C to 70°C while for 0.5 vol% concentration the enhancements were 54%, 52% and 40% for ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids respectively. This is mainly due to the fact that nanoparticles are less sensitive to temperature compared with the liquids, and the increased temperature causes a reduction in the viscosity of the base fluids and an increase in the Brownian motion of nanoparticles leading to a further increase in the electrical conductivity (Liu et al., 2016, Bagheli et al., 2015, Baby and Sundara, 2011).
Figure 5.13 Variation of effective electrical conductivity of base fluid (50/50 water-EG) and various volume concentration of 50/50 WEG based ZnO nanofluids with temperature

Figure 5.14 Variation of effective electrical conductivity of base fluid (50/50 water-EG) and various volume concentration of 50/50 WEG based Al₂O₃ nanofluids with temperature
Figure 5.15 Variation of effective electrical conductivity of base fluid (50/50 water-EG) and various volume concentration of 50/50 WEG based TiO$_2$ nanofluids with temperature

Figure 5.15 to Figure 5.18 show the enhancement of electrical conductivity of 50/50 water-EG based ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids in the concentration range of 0.05 vol% to 0.5vol%. It is clearly seen that the electrical conductivity increases linearly with the increase of nanoparticles volume concentrations. This increment trend has been observed by many researchers (Kole and Dey, 2013, Bagheli et al., 2015, Baby and Sundara, 2011, Shoghl et al., 2016a). At 50 ˚C temperature, the electrical conductivity enhancement observed ~5 times, ~9 times and ~10 times for ZnO, Al$_2$O$_3$ and TiO$_2$ respectively for the concentration increment up to 0.5 vol% compared with those of the base fluid. The enhancement in electrical conductivity is due to the fact that an increase in volume fraction increases the charge transport due to increase in the number of charge carriers. Along with the increase of charge carriers, some factors such as Brownian motion, Electrical Double Layer (EDL) interactions, agglomeration or even electrochemical properties of nanoparticles cause the increase of electrical conductivity of nanofluids (Shen et al., 2012, Dong et al., 2013). As the volume concentration of nanoparticles increase, the thickness of EDL also increases, tends to enhance the bulk carrier phase concentration since greater numbers of counter-ions leave the electronic double layer in the process, which in turn enhances the effective electrical conductivity of the nanofluids (Sundar et al., 2014).
Figure 5.16 Variation of effective electrical conductivity of water-EG based ZnO nanofluids with concentration of nanoparticles

Figure 5.17 Variation of effective electrical conductivity of water-EG based Al₂O₃ nanofluids with concentration of nanoparticles
It is noteworthy to mention that DoE has also emphasized on the low electrical conductive coolants for fuel cells applications as they might be reduced the electrical performance of a fuel cell. In this study, all the measured electrical conductivities are below 100 μS/cm for all nanofluids, and concentrations range of nanoparticles (i.e. 0.05 vol% to 0.5 vol%). All the electrical conductivities were measured from 20 - 70 °C and at the current technology the PEMFCs are operated at the temperature of ~50-65°C (Balasubramanian et al., 1999). The measured electrical conductivities will be compared with the existing models and other researchers’ findings in chapter six.

5.5.1.3 Thermal conductivity

The KD2 Pro sensor used in this study was calibrated by introducing the known thermal conductivity fluid such as glycerine provided by the manufacturer with the thermal conductivity of 0.282 W/m.K at 20°C. The sensor was calibrated each time before measuring the original thermal conductivity with the accuracy of less than +/- 2%. The thermal conductivity meter itself provides an error (percent error) value which should be below 1% for a good data set. All the error values for granted thermal conductivity measurement data in this study are in the range of 0.3% to 0.9%. For error values larger than this range (i.e. 0.3%-0.9%), the data has been discarded and waiting 15 minutes for the next measurement, as recommended by the manufacturer, to ensure the high accuracy of the measurements. The detailed procedure for measuring error value for KD2 Pro thermal conductivity meter has
been provided in Appendix C. For further validation of KD2 Pro thermal analyser, the thermal conductivity of pure ethylene glycol (99.90% minimum) has been measured and compared with available literature data collected from the Design Institute for Physical Properties (DIPPR) of the American Institute of Chemical Engineers (AIChE) by Perry and Green (1999). In the measured temperature range, the obtained thermal conductivity for ethylene glycol was found with maximum ±0.0003 deviation from the mean measured values (Figure 5.19). Along with this, the measured data shows a good agreement with the literature data (Perry and Green, 1999) with maximum 0.13% error.

![Figure 5.19 Comparative thermal conductivities of measured ethylene glycol and available literature data in Perry’s chemical engineer’s hand book (Perry and Green, 1999)](image)

The enhancement of thermal conductivity of nanofluids increased with an increase of nanoparticle volume concentration as well as the temperature compared with that of the base fluids as can be seen in Figure 5.20 to Figure 5.25. The same trend in nanofluids thermal conductivity was observed by many researchers (Abdolbaqi et al., 2016e, Aberoumand et al., 2016b, Amiri et al., 2016b, Azmi et al., 2016, Colangelo et al., 2016, Khdher et al., 2016a, Xing et al., 2016a, Żyła and Fal, 2016b) with different types of nanoparticles and base fluids. By increasing the temperature from 20 °C to 70 °C, the maximum enhancement of thermal conductivity was found to be ~6% for TiO$_2$ nanofluids and ~5% for ZnO and Al$_2$O$_3$ nanofluids with the concentration of 0.05 vol% compared with the thermal conductivity of the base fluid (i.e. 50/50 water-EG mixture). The thermal conductivity of nanofluids increase mainly due to the facts that the nanoparticles alter the fluid composition that affects the energy transport process; moreover the random motion of nanoparticles and interfacial
interactions among the nanoparticles and the liquid molecules enhance energy transport inside the liquid (Xuan et al., 2003).

Figure 5.20 Variation of effective thermal conductivity of base fluid (50/50 water-EG) and various volume concentration of 50/50 water-EG based ZnO nanofluids with temperature

Figure 5.21 Variation of effective thermal conductivity of base fluid (50/50 water-EG) and various volume concentration of 50/50 water-EG based Al₂O₃ nanofluids with temperature
In the various range of the nanoparticles concentration in this experimental study (i.e. 0.05-0.5 vol%), the enhancement of thermal conductivity was found to be in the range of 8-15%, when temperature varied between 20 °C - 70 °C, compared with the thermal conductivity of the base fluid (i.e. 50/50 water-EG). It is noteworthy that the rate of thermal conductivity enhancement is greater for increase of concentration compared with that for the increase of temperature. However, at higher volume fractions, the effect of temperature on the relative thermal conductivity of nanofluid is more tangible, which happens due to more collisions between nanoparticles and the increase in Brownian motion of the particles (Yang et al., 2012). On the other hand, with increase of volume concentrations, the number of dispersed nanoparticles increases which in turn decrease the distance between nanoparticles leading to the enhancement of the fluid’s thermal conductivity.
Figure 5.23 Variation of effective thermal conductivity of 50/50 water-EG based ZnO nanofluids with concentration of nanoparticles

Figure 5.24 Variation of effective thermal conductivity of 50/50 water-EG based Al₂O₃ nanofluids with concentration of nanoparticles
5.5.1.4 Viscosity

To ensure the accuracy of the device before measuring the viscosity of nanofluids, the viscosity instrument (DHR-3) was calibrated by introducing the known viscosity fluid such as ethylene glycol (99.90 % minimum) supplied by Chem-Supply, Australia. The measured values of viscosity show a good precision of the measurement with the maximum deviation of ±1.2 with the mean measure values. The obtained results also show a good agreement with the values provided by the Design Institute for Physical Properties (DIPPR) of the American Institute of Chemical Engineers (AIChE) with the maximum ~3% error (Perry and Green, 1999).
Figure 5.26 Comparison of viscosity of ethylene glycol (99.9%) with Perry and Green (1999) handbook

The viscosity results of all the nanofluids (e.g. ZnO, TiO$_2$ and Al$_2$O$_3$) investigated by this experimental study revealed that the viscosity of nanofluids decreases with increase of temperature (Figure 5.27 to Figure 5.29). The measurements also suggest that this viscosity increases (i.e. compared to base fluid) with the increase of the particle volume concentrations (Figure 5.33 to Figure 5.35). All these findings are in agreement with most of the previous studies (Li et al., 2015a, Li and Zou, 2016, Kwak and Kim, 2005, Kole and Dey, 2010b, Ijam et al., 2015a, Yiamsawasd et al., 2012). The relative viscosity of nanofluids show the same temperature dependency since the viscosity of both the base fluid and the nanofluids nearly decrease by a similar degree by increasing the temperature. The maximum decrease of viscosities for increasing the temperature from 20 °C to 80 °C were ~69%, ~68% and 64% for ZnO, TiO$_2$ and Al$_2$O$_3$ respectively with 0.05 vol% concentration (i.e. compared with the base fluid of 50/50 water-EG). While for 0.5 vol% nanoparticle concentrations, at the same temperature range, the maximum decrease of viscosities were found to be ~64%, ~55% and ~58% for ZnO, TiO$_2$ and Al$_2$O$_3$ respectively. Therefore, it is noticed that with the increase of nanoparticle concentrations, the rate of decrease in viscosity drops; in other words the temperature effect on nanoparticles is less in nanofluids with higher concentrations compared to those with lower nanoparticle concentrations. From the molecular point of view, with the increase of temperature, the intermolecular distance becomes larger that leads to decrease in the viscosity of nanofluids.
Figure 5.27 Variation of viscosity of 50/50 water-EG based ZnO nanofluids with temperature

Figure 5.28 Variation of viscosity of 50/50 water-EG based Al₂O₃ nanofluids with temperature
On the other hand, the viscosity increased with the increase of nanoparticle concentrations shown by Figure 5.33 to Figure 5.35. At 0.05 vol% nanoparticle concentrations, the enhancement of viscosities (i.e. compared to 50/50 water-EG base fluid) were found to be ~30%, ~51%, and ~71% for ZnO, Al₂O₃ and TiO₂ nanofluids respectively at 50 °C. The finding of this study is consistent with the findings of past studies of (Li et al., 2015a, Fedele et al., 2012, Hamid et al., 2016). Interactions between the nanoparticles and the base fluid are the main reason behind the increase in the viscosity. With more nanoparticles, nano-clusters might be formed due to the strong van der Waals interactions between the nanoparticles that hinder the movement of layers of the fluid on each other leading to increase in viscosity.
Figure 5.30 Variation of viscosity of 50/50 water-EG based ZnO nanofluids with concentration of nanoparticles

Figure 5.31 Variation of viscosity of 50/50 water-EG based TiO$_2$ nanofluids with concentration of nanoparticles
Figure 5.32 Variation of viscosity of 50/50 water-EG based Al$_2$O$_3$ nanofluids with concentration of nanoparticles

The shear rate obtained from an applied shear stress depends on the materials resistance to flow (i.e. viscosity). The experimental dynamic viscosity curves are fundamental rheological measurements that can help determine whether the liquid nature is Newtonian or non-Newtonian; and if it is non-Newtonian, how its viscosity changes by changing the shear stress of the fluid flow between its layers.

Figure 5.33 to Figure 5.35 illustrate the viscosity and shear stress variations with the shear rate for nanoparticle concentrations between 0.05 vol% and 0.5 vol% at 25°C. For all the considered nanofluids, the viscosity is decreased along with shear rate which indicates that the nanofluids behave as shear thinning fluids under the experimental conditions as the viscosity decreases along with the decrease of shear rate. The shear thinning behaviour also found by many researchers such as Aladag et al. (2012b) for water based CNT nanofluids, Duan et al. (2011) for water based Al$_2$O$_3$ nanofluids, Kole and Dey (2010a) for water based Al$_2$O$_3$ nanofluids, Kwak and Kim (2005) for CuO based ethylene glycol nanofluid, Yu et al. (2009) for ZnO based ethylene glycol nanofluid, Hojjat et al. (2011) for carboxymethyl cellulose based γ- Al$_2$O$_3$, TiO$_2$ and CuO nanofluids.

There are some debates over the Newtonian or non-Newtonian behaviour of nanofluids as some researchers (Baratpour et al., 2016, Singh et al., 2012, Naik et al., 2010, Cabaleiro et al., 2015a) found them Newtonian fluids, some others (Yu et al., 2011a) found them to be
non-Newtonian and finally some researchers (Li and Zou, 2016, Bahrami et al., Said et al., 2013b) categorised them based on the concentrations of nanoparticles.

From literature it was found that the pure water, ethylene glycol or mixture of water and ethylene glycol behave as Newtonian fluids. In a Newtonian fluid, the relationship between the shear stress ($\tau$) and shear rate ($\gamma$) is linear and passing through the origin, and the constant of proportionality is called coefficient of viscosity ($\mu$):

$$\tau = \mu \gamma$$ (5.6)

It can be seen from Figure 5.33 to Figure 5.35 that for the base fluid (i.e. 50/50 water-EG mixture) the shear stress depends linearly on the shear rate line passing through the origin of the diagram indicating the base fluid behaves like Newtonian fluids while for nanofluids the shear stress depends on the shear rate almost linearly and all the isotherms pass through the origins. The deviation from linearity is almost insignificant and might be happened due to the measurement environmental conditions and error.

Figure 5.33 Viscosity and shear stress of 50/50 water-EG based ZnO nanofluids with respect to shear rate at 25°C
Figure 5.34 Viscosity and shear stress of 50/50 water-EG based Al₂O₃ with respect to shear rate at 25 °C

Figure 5.35 Viscosity and shear stress of 50/50 water-EG based TiO₂ with respect to shear rate at 25 °C
5.5.1.5 Specific heat

The measurement of Heat flux was continuous from 20 °C to 80 °C; however, for analysis, the specific heat capacities were calculated from 25 °C to 70 °C. Prior to the measurement of specific heat of nanofluids, benchmark test was conducted with ethylene glycol (99.90% pure). The results obtained from this measurement were compared against that provided in Ethylene glycol product guide (MEGlobal, 2016). The comparison showed a good agreement with the literature values of specific heat with ±2% error as shown in Figure 5.36.

![Figure 5.36 Validation of DSC methodology using ethylene glycol data from ethylene glycol product guide](image)

After confirming the accuracy of the measurement procedure and apparatus (i.e. DSC) as just discussed, comprehensive measurements of specific heat were conducted for 50/50 water-EG based ZnO, Al₂O₃ and TiO₂ nanofluids in the concentration range of 0.05-0.5 vol%. Figure 5.37 to Figure 5.39 show the variations of nanofluids specific heat with temperature. It is observed that the specific heat of this nanofluids increases with an increase in the temperature. The specific heat increases in the range of ~5-7% for all types of nanofluids when the temperature was varied from 25 °C to 70°C. Same increasing trend of the specific heat of nanofluids has been also found by other researchers (Vajjha and Das, 2009a, Zhou et al., 2010, Zhou and Ni, 2008b, Ijam et al., 2015a).
Figure 5.37 Variation of specific heat of water-EG based ZnO nanofluids with temperature

Figure 5.38 Variation of specific heat of water-EG based Al₂O₃ nanofluids with temperature
On the other hand, the specific heat of the nanofluids decreases by increasing the concentration of nanoparticles that agreed well with the past research findings (Ijam et al., 2015a, Zhou et al., 2010, Zhou and Ni, 2008a). This is mainly due to the suspension of low specific heat nanoparticles into the base fluids and the fact that the specific heats of these nanoparticles (e.g. Al\textsubscript{2}O\textsubscript{3}, ZnO and TiO\textsubscript{2}) are less than that of the base fluids. The reduced specific heat indicates that less heat is required to increase the temperature of nanofluids at higher particle volume concentrations. Therefore, lower specific heat can be a contributing factor for increasing the convection heat transfer of the nanofluids compared to those in the base fluid. The larger specific surface area of nanoparticles also affects the specific heat of the fluids. With the suspension of nanoparticles, the interfacial free energy of solid-liquid is changed that directly affects the specific heat of the nanofluids (He et al., 2012, Mostafizur et al., 2015). The decrease of specific heats were found to be in the range of 2-6% by increasing the nanoparticles concentration from 0.05 vol% to 0.5vol%, while the maximum reduction of specific heat found to be 6% for 0.5 vol% Al\textsubscript{2}O\textsubscript{3} nanofluid with the maximum error of ~0.6%.
Figure 5.40 Variation of specific heat of water-EG based ZnO nanofluids with concentration of nanoparticles

Figure 5.41 Variation of specific heat of water-EG TiO$_2$ nanofluids with concentration of nanoparticles
5.5.1.6 Density

The pycnometer has been calibrated by measuring the density of ethylene glycol (99.90% pure) purchased from Chem-Supply, Australia. The SEM water bath with same specification as described in section (5.5.1.2) was used to increase the temperature of the nanofluids. It is found that the results are agreed well with the density values from Perry and Green’s chemical hand book with the maximum ~0.3% error regardless of nanoparticle concentration.
Nanoparticle concentrations in the range of 0.05 vol% to 0.5 vol% for 50/50 water-EG based ZnO, Al₂O₃ and TiO₂ nanofluids were used to study the density behaviour of the nanofluids in this research. Figure 5.45 to Figure 5.47 show the effect of temperature on the effective density of nanofluids. It was found that the density of nanofluids decreases by increasing their temperature. The decreasing trend closely agrees with the past researchers’ findings (Mostafizur et al., 2015, Li and Zou, 2016, Elias et al., 2014a, Mahian et al., 2013, Saïd et al., 2013a). This happens due to the fact that when the temperature increases the molecules move further apart from each other as their kinetic energy increases, leading to a decrease in the density of nanofluids. For 0.5 vol% of nanoparticle concentrations, the percentage decrease of nanofluids density was measured to be ~3.4%, ~2.6% and ~2.8% for ZnO, TiO₂ and Al₂O₃ respectively. However, the decreasing rate of density of nanofluids is less with the higher concentration of nanoparticles. This is due to the fact that the nanoparticles are less sensitive to the temperature compared to the base fluids (Yang et al., 2005, Mahbubul et al., 2013).
The measurement also illustrated that the density increases with increasing the volume concentrations of nanoparticles. This matched with that found by other researchers (Pastoriza-Gallego et al., 2011a, Mahbubul et al., 2013). For increasing the volume
concentration of nanofluids, the increments of densities were found to be ~1.5%, ~1.5% and ~1.3% for ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids respectively. For all nanofluids, the densities of nanofluids were measured to be higher than that of the base fluid as expected. This is because the density of the nanoparticles mixed in the base fluid is higher than that of the base fluid.

Figure 5.47 Variation of density of 50/50 water-EG based ZnO nanofluids with concentration of nanoparticles
Figure 5.48 Variation of density of 50/50 water-EG based TiO$_2$ nanofluids with concentration of nanoparticles

Figure 5.49 Variation of density of water-EG based Al$_2$O$_3$ nanofluids with concentration of nanoparticles
5.5.1.7 Stability

Many methods have been introduced to evaluate the stability of nanofluids. Sedimentation photograph taken by a camera is always the simplest method to observe the stability of nanofluids. Though sedimentation photograph method cannot quantify the sedimentation exactly, many researchers used this method with a view to getting an idea of the stability of nanofluids. As already mentioned in section 1.2.2, that long-term stability or quantifying the sedimentation rate is out of scope of this research, the photograph method was adopted in this study. Figure 5.50 shows the stability of 50/50 water-EG based ZnO nanofluids. Within up to six hours after preparation, no sedimentation was visible in the image. The detailed photographs for 50/50 water-EG based Al₂O₃ and TiO₂ nanofluids were also provided in Figure 5.51 and Figure 5.52. The Al₂O₃ and TiO₂ nanofluids were found to be stable up to one and half hours after preparation of them. It is noteworthy that all the electrical and thermo-physical characterisation has been done within one hour of nanofluid preparation.

Figure 5.50 An image of 50/50 water-EG based (a) 0.05 vol% ZnO nanofluids, (b) 0.1 vol% ZnO nanofluids, (c) 0.3 vol% ZnO nanofluids, and (d) 0.5 vol% ZnO nanofluids
Figure 5.1 An image of 50/50 water-EG based (a) 0.05 vol% Al₂O₃ nanofluids, (b) 0.1 vol% Al₂O₃ nanofluids, (c) 0.3 vol% Al₂O₃ nanofluids, and (d) 0.5 vol% Al₂O₃ nanofluids
5.5.2 Experimental investigation of a PEMFC performance using nanofluids as coolants

5.5.2.1 An overview

This part of the research was designed to investigate the electrical and thermal performances of PEMFCs using conventional coolant (e.g. 50/50 water-EG) as well as 50/50 water-EG based nanofluids. Then the results were used to validate the theoretical findings obtained through the computer simulation model described in chapter 4. The pressure drops along the coolant flow circuit was also measured by using pressure gauge while using different coolants (i.e. 50/50 water-EG and nanofluids). The electrical performance of the PEMFCs was investigated, and the polarisation (V-I) curves while using nanofluids coolants were compared with that obtained when using conventional coolants (i.e. 50/50 water-EG). Along
with the electrical performance, the thermal performance was also investigated using different coolants (i.e. nanofluids and conventional coolant) with the same radiator. While using different coolants, the mass flow rates of the coolants as well as the inlet temperature of the radiator were almost kept constant for same operating points. This helped minimise the number of variables and made the comparison between the performance of different coolant options or between the theoretical model and the experimental results easier. The outlet temperature of the radiator was allowed to vary in order to see the effects of changing the coolants in the PEMFC cooling system. Using the same approach (i.e. varying radiator outlet temperature but keeping radiator size, coolant mass flow rate and radiator inlet temperature constant), the theoretical computer simulation model was validated. However, the details of this validation task are covered in chapter 6.

It is noteworthy to mention that for such a comparison study (e.g. between the model and the experiments and also between different coolants), it is not necessary to run the stack at its rated power (i.e. 2.4 kW). Hence, to avoid high rate of hydrogen consumption in the laboratory the maximum ~1 kW (mainly for four operating points of 30 A, 40 A, 50 A and 60 A) was selected for this experimental study. To minimise the errors associated with the measurement as well as with human, each operating point was monitored for a while and measured several times to obtain an average value of the measurements (i.e. voltage, power, hydrogen consumption rate, coolant mass flow rate, and radiator inlet and outlet temperatures) at that particular operating point.

5.5.2.2 Electrical performance

To make sure whether there is any electricity leakage within the PEMFC (i.e. while using nanofluids as coolants instead of conventional coolants of 50/50 water-EG), the experimentally measured electrical performance curves (V-I and power curves) were closely monitored. The experimentally obtained polarisation and power curves for 50/50 water-EG based 0.05 vol% ZnO, 0.5 vol% ZnO, 0.5 vol% TiO₂ and 0.5 vol% Al₂O₃ nanofluids were compared with those for 50/50 water-EG as shown in Figure 5.53. It is clearly seen that all the power curves were very much identical with that of the conventional coolant (i.e. 50/50 water-EG) while the polarisation curves for nanofluids were deviated insignificantly (i.e. by the maximum of only below 2%) from that of 50/50 water-EG. This is mainly due to the mismanagement of water in the PEMFC as it was found that the outlet air from fuel cell was saturated (i.e. relative humidity more than 100%) though the relative humidity at outlet of fuel cell should be around 80-90% for optimised operation of PEMFCs. In addition, the fuel
cell was operated in the temperature range of 30 °C to 55 °C (i.e. the cooling system would experience a more critical condition in terms of the temperature gap between the stack and ambient) while the operating temperature recommended by manufacturer is between 60-65°C. Therefore, from this experimental study, it is clear that for up to 0.5 vol% concentrations of ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids, no electric leakage happens through the coolants.

![Polarisation (V-I) and power curves for base fluid (50/50 water-EG), and 50/50 water-EG based 0.05 vol% ZnO, 0.5 vol% ZnO, 0.5 vol% TiO$_2$, and 0.5 vol% Al$_2$O$_3$ nanofluids for 2.4 kW PEMFC stack operating at maximum 60 A](image)

Figure 5.53 Polarisation (V-I) and power curves for base fluid (50/50 water-EG), and 50/50 water-EG based 0.05 vol% ZnO, 0.5 vol% ZnO, 0.5 vol% TiO$_2$, and 0.5 vol% Al$_2$O$_3$ nanofluids for 2.4 kW PEMFC stack operating at maximum 60 A

5.5.2.3 Thermal performance

For studying the performance of the PEMFC cooling system with nanofluids as well as conventional 50/50 water-EG as coolants, the temperatures of the coolants before and after inlet and outlet of the fuel cell as well as the coolant mass flow rates were measured. At the same operating points, the measurements of the cooling load were repeated a few times to enhance the reliability of the measurements.

It is noticeable that the stack generating powers (Figure 5.54) for all the coolants at particular operating point were almost same (error below 2%), whereas the cooling load (Figure 5.55)
varied maximum ~14% at the same operating point. This is due to the fact that though the PEMFCs stack was operated at the same operating point, the different coolants (i.e. different thermo-physical properties) were used in the cooling system to extract the heat. Moreover, the coolant mass flow rates, operating temperatures, relative humidity of air and hydrogen, air stoichiometric ratio and most importantly the environmental conditions were slightly different from each experiment to other that could affect the cooling loads.

The cooling loads at certain operating point were almost double than the generated power at those operating points. As discussed by Shabani (2010), this happens due to the fact that the fuel cell was operated at least at 10-20°C lower temperatures than that of the recommended by the manufacturer (Section 5.4.2.1). At such lower operating temperatures, the generated water inside the fuel cell can stay inside the fuel cells in liquid form instead of leaving the fuel cells as vapour. Therefore, the heat that is supposed to be absorbed by the water during the evaporation process is counted as cooling load in this study. This situation is in a way desirable for the purpose of assessing the performance of the cooling system under an additional load. The unused air and water steam should carry around 30-35% of the cooling load (Shabani and Andrews, 2011); however, in this experiment this portion was found to be around 15-20% (i.e. due to the low operating temperatures). If the fuel cell was operated at the recommended temperatures (i.e. 60-65°C), the generated water inside the fuel cell could absorb some heat during via evaporation that could result in dropping the fuel cell cooling load. The detailed table of the measurements related to thermal performance of PEMFCs are provided in Appendix D.
Figure 5.54 Stack power for base fluid (i.e. 50/50 water-EG), 0.05 vol% ZnO nanofluid and 0.5 vol% ZnO nanofluid at the operating points 30 A, 40 A, 50 A and 60 A while operating conditions remained almost same for all coolants.

Figure 5.55 Stack cooling load for base fluid (i.e. 50/50 water-EG), 0.05 vol% ZnO nanofluid and 0.5 vol% ZnO nanofluid at the operating points 30 A, 40 A, 50 A and 60 A while operating conditions remained almost same for all coolants.
5.5.2.4 **Coolant pressure drop**

The pressure drops along the closed cooling loop were measured for different coolants (i.e. 50/50 water-EG, 50/50 water-EG based 0.05 vol% ZnO nanofluids and 50/50 water-EG based 0.5 vol% ZnO nanofluids) for the required coolants flow to extract heat at different operating points (i.e. 30 A, 40 A, 50 A and 60 A) of the PEMFCs.

From Figure 5.56, it is seen that the pressure drops are almost linearly increased with the increase of coolant flow rate. For 4 l/min coolant flow rate, the pressure drops were found to be ~69 kPa, ~74 kPa and ~76 kPa for 50/50 water-EG, and 50/50 water-EG based 0.05 vol% and 0.5 vol% ZnO nanofluid respectively. Therefore, the increment of pressure drops for 4 l/min coolant flow rate were almost 7% and 10% higher for 50/50 water-EG based 0.05 vol% and 0.5 vol% ZnO nanofluids respectively compared with that of the 50/50 water-EG. While for increasing the concentration of nanoparticles from 0.05 vol% to 0.5 vol%, a slight increment (~3%) of pressure drops were observed. The same pressure drops trend was also found by Duangthongsuk and Wongwises (2010) who investigated the pressure drops for water based TiO$_2$ nanofluids with the concentration of 0.2 to 2 vol% and found ~ 5-15% increment of the pressure drops with the increase of concentration from 0.2-2 vol% compared with that of the base fluid (i.e. water). Fotukian and Esfahany (2010) also did experimental study on the pressure drop for water based CuO nanofluid in circular tube and observed around 20% pressure drop for 0.03 vol% concentration compared with that of the base fluid.

![Figure 5.56 The pressure drops for required coolant flow rate to extract the heat from PEMFC at operating points: 30 A, 40 A, 50 A and 60 A](image-url)
5.6 Summary

The experimental study on the characterisation of nanofluids and on the electrical and thermal performances of 2.4 kW PEMFCs that has been instrumental for this research was presented in this chapter. The key findings of this experimental study are:

- The existing electrical conductivity model is unable to predict the electrical conductivity of nanofluids. The electrical conductivities of the nanofluids were found to be increasing by increasing temperature and concentration of nanofluids. For increasing concentration up to 0.5 vol%, the maximum electrical conductivity increment was found to be ~10 times higher than that of the 50/50 water-EG base fluid used in this study.

- The thermal conductivities of nanofluids were also found to be increasing with the increase of temperature and concentration of nanofluids. The enhancement of thermal conductivities were observed to be in the range of 8-15% for the increase of temperature from 20 °C to 70 °C while for increasing concentration up to 0.5 vol%, the enhancement was found to be maximum ~6%.

- The viscosity of nanofluids was found to be increasing with increasing the concentration of nanofluids while decreasing with increasing temperature. The viscosity increased almost linearly with shear rate and they behave like Newtonian fluids.

- Unlike viscosity, the specific heat of nanofluids was found to be increasing with temperature but decreased with an increase of concentrations.

- The density of nanofluids was found to be increasing with the concentration of nanofluids while decreasing with increasing the temperature.

- ZnO nanofluids were found to be stable more than 6 hours but TiO$_2$ and Al$_2$O$_3$ were stable only around one hour after preparation.

- With up to 0.5 vol% concentration of nanoparticles used to prepared the nanofluid-based coolants, no drops of the V-I curve were observed compared to when 50/50 water-EG used as coolant.

- For 50/50 water-EG based 0.5 vol% ZnO nanofluids, ~10% higher pressure drops were observed for 4 l/min coolant flow rate compared with that of the base fluid (i.e. 50/50 water-EG).
CHAPTER 6: EXPERIMENTAL AND THEORETICAL RESULTS: A COMPARATIVE DISCUSSIONS

6.1 AN OVERVIEW

This chapter focuses on the links between the theoretical and experimental results obtained in this study as well as comparing the results of this study with those (i.e. both experimental and theoretical; if available) provided in the literature.

First of all, the electrical conductivity and thermo-physical properties (i.e. thermal conductivity, viscosity, specific heat and density) of nanofluids are compared with those suggested by the classical models and available literature. The experimental data obtained from this study were used in the modelling of PEMFC cooling system and the outputs (i.e. the reduction of cooling system, enhancement of convection heat transfer coefficient and required pumping power) have been compared with the results obtained by using theoretical data. At last, the PEMFC experimental data were used in the computer simulation model and the size of the cooling system (i.e. size of the radiator) for different coolants (i.e. nanofluids and base fluid) have been compared.

6.2 ELECTRICAL AND THERMO-PHYSICAL CHARACTERISTICS OF NANOFLUIDS

6.2.1 Electrical conductivity of nanofluids

The electrical conductivity of colloidal suspensions containing nano-scale sized conducting or insulating particles is mainly related to the particle volume fraction, temperature, and electrical properties of the base fluid and particles. Classical electro-chemical models, however, tend to grossly under-predict the pertinent effective electrical conductivity values, as compared to those obtained under experimental conditions as also found by other researchers (Liu et al., 2016, Bagheli et al., 2015, Shoghl et al., 2016a, Kole and Dey, 2010b). The Maxwell model (equation (3.9)), that is a pioneer electrical conductivity model, can be applied to all homogeneous, uniformly sized spherical particles, non-interacting and randomly dispersed low volume fraction of solid in liquid suspensions. In this study all the investigated nanoparticles (i.e. ZnO, Al₂O₃ and TiO₂) are of very low electrical conductivity (~10⁻⁸ µS/cm) with respect to the base fluid (~5-8 µS/cm at 20 °C) (50/50 water-EG mixture).
Based on the conducting nature of both particles and base fluid, these nanofluids are
categorised into case I (equation (3.3)) of the Cruz et al. (2005) generalised model of
Maxwell. However, effective electrical conductivity behaviour is under-predicted by the
Maxwell model (Maxwell, 1881) for the case of $\sigma_p \ll \sigma_{bf}$ (insulating particles) as can be
seen from Figure 6.1 to Figure 6.3. It is noteworthy to mention here that the experimental
procedure and measuring equipment for electrical conductivity of nanofluids has been
validated by measuring the electrical conductivity of known electrical conductivity fluid (i.e.
ethylene glycol and 50/50 water-EG) as described in section 5.5.1.2. In the Maxwell’s model
for nanoparticles having very poor electrical conductivity compared with that of the base
fluid (case-I), the slope of the relative electrical conductivity curve for insulating particles
has a negative value (-1.5), therefore, it is expected that the electrical conductivity of the
mixture is reduced. However, from Figure 6.1 to Figure 6.3, it can be seen that the measured
electrical conductivity of the suspension increases almost linearly with volume fraction of
the nanoparticles. This might be happened as the Maxwell’s model has been proved to be
applicable for the dilute suspensions ($\phi << 1$) with the particles size larger than tens of
micrometres (Meredith and Tobias, 1961, Turner, 1976). From Figure 6.1, it can also be seen
that the measured electrical conductivity of nanofluids deviates significantly from Ganguly
et al. (2009) and Minea and Luciu (2012) developed models though both models were
developed based on the experimental study. However, this can be happened due to the facts
that both of them developed their models for water based nanofluids and different
environmental conditions. For enhancement of the electrical conductivity of nanofluids,
along with the electrical double layer in the mixture, the configuration of surface charges
created by nanoparticles’ polarization effect, charged ions in the nanofluids and stability of
nanofluids have significant effects on the electrical conductivity of nanofluids (Ganguly et
Figure 6.1 The electrical conductivity of $\text{Al}_2\text{O}_3$ nanofluids at 50°C: a comparison among the experimentally measured electrical conductivity in this study, and Maxwell’s modified (1881), Ganguly et al. (2009) and Minea and Luciu (2012) electrical conductivity models.

Figure 6.2 The electrical conductivity of $\text{TiO}_2$ nanofluids at 50°C: a comparison between the experimentally measured electrical conductivity in this study and Maxwell’s modified (1881) electrical conductivity model.
6.2.2 Thermal conductivity of nanofluids

The effective thermal conductivities of 50/50 water-EG based ZnO, TiO$_2$ and Al$_2$O$_3$ nanofluids relative to their base fluid as a function of temperature and concentration of nanoparticles are shown in Figure 5.23 to Figure 5.28. It is noteworthy to mention here that the experimental procedure and equipment has been validated as described in section 5.5.1.3 by measuring and comparing with the existing literature (Perry and Green, 1999) thermal conductivity of ethylene glycol. Measured thermal conductivities, compared to those predicted from Maxwell model (1873) (equation (3.9)) and Bruggeman model (1935) (equation (3.11)) are shown in Figure 6.4 to Figure 6.6. From the figures, it can be observed that the thermal conductivities of all nanofluids exhibits higher thermal conductivities compared with the base fluid as well as the predicted thermal conductivities from Maxwell and Bruggeman models. These results contradict with the literature data as it is reported that the relative thermal conductivities of some nanofluids were less than those predicted by Maxwell and Bruggeman models (Timofeeva et al., 2007; Utomo et al., 2012); however, those who observed the less thermal conductivity compared to the prediction values, had used surfactants or other additives to increase the stability of nanofluids (Utomo et al., 2012). Most of the thermal conductivity of nanofluids related studies claimed that the
predicted thermal conductivity values were less than those from measured thermal conductivity values (Beck et al., 2009, Azmi et al., 2016, Deng et al., 2016, Esfahani et al., 2016, Huang et al., 2016, Kumar and Sonawane, 2016, Nurdin et al., 2016, Soltanimehr and Afrand, 2016a, Tian et al., 2016, Usri et al., 2015, Xing et al., 2015b, Yang et al., 2016, Yuan et al., 2016, Żyła et al., 2016, Saleh et al., 2013). While very few studies on thermal conductivity of water-EG based various nanofluids (i.e. TiO$_2$, CNT, Graphite, etc.) including (Reddy and Rao, 2013b, Sundar et al., 2013, Hamid et al., 2016, Li and Zou, 2016) have been conducted and observed the higher thermal conductivities compared with the predicted thermal conductivities. The effective thermal conductivity of TiO$_2$ nanofluids agreed well with the experimental thermal conductivity results of 50/50 water-EG based TiO$_2$ nanofluids with the maximum error less than 1% conducted by Reddy et al. (2013b).

Figure 6.4 Comparisons among the experimental results of this study, Maxwell and Bruggeman predicted values at 50 °C for 50/50 water-EG based ZnO nanofluids
Figure 6.5 Comparisons among the experimental results of this study, Maxwell and Bruggeman predicted values at 50 °C for 50/50 water-EG based Al₂O₃ nanofluids

Figure 6.6 Comparisons between the experimental results of this study, experimental results of Reddy et al. (2013), Maxwell, and Bruggeman predicted values at 50 °C for 50/50 water-EG based TiO₂ nanofluids
6.2.3 Viscosity

The viscosity of 50/50 water-EG based ZnO, TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} nanofluids has been investigated experimentally in this study (Figure 5.27 to Figure 5.32). The experimental procedure and measurement equipment were validated through measuring the known fluid viscosity (i.e. Ethylene glycol) as described in section 5.5.1.4. The viscosity of nanofluids can also be calculated by using viscosity models that are widely used by researchers (Abdolbaqi \textit{et al.}, 2016b, Abdolbaqi \textit{et al.}, 2016d, Aberoumand \textit{et al.}, 2016a, Azmi \textit{et al.}, 2016, Bashirnezhad \textit{et al.}, 2016, Żyła and Fal, 2016b). For comparing the obtained viscosities of nanofluids, Einstein (1906), Brinkman (1952) and Bachelor (1977) models (equations, (3.30), (3.31) and (3.32)), that can be applicable for spherical particles and volume concentrations less than 5 vol\% (Li \textit{et al.}, 2015a), have been used to predict the viscosity of nanofluids. The comparison of the effective viscosity with respect to particle volume fraction for experimental data at 50 °C and theoretical models are shown in Figure 6.7 to Figure 6.9. It is clearly seen that for all the nanofluids, the existing models are unable to predict the viscosity of nanofluids as the predicted viscosity values are much less than those of the measured values of viscosity.

It was also noticed that the actual viscosity of nanofluids is under-predicted by all the models (Li \textit{et al.}, 2015b, Ijam \textit{et al.}, 2015a). This can be because of the fact that these models considered only the particle volume fraction whereas the viscosity of nanofluids depends on many factors such as temperature, size of nanoparticles, nature of particle surface, ionic strength of the base fluid, pH value of base fluid, inter-particle potentials such as repulsive (electric double layer force) and attractive (van der Waals force) forces. Moreover, nanoparticles can easily form clusters and experience surface adsorption. Both clustering and adsorption are responsible for increasing the hydrodynamic diameter of nanoparticles that leads to the increase of relative viscosity of nanofluids (Mursheed \textit{et al.}, 2008a). Therefore, to understand the nature of viscosity of nanofluids, a comprehensive study on viscosity of nanofluids is required, that remains outside the scope of this research.
Figure 6.7 Comparison of the experimental viscosity of 50/50 water-EG based ZnO nanofluids in this study with those predicted by Einstein (1906), Brinkman (1952) and Bachelor (1977) at 50 °C

Figure 6.8 Comparison of the experimental viscosity of 50/50 water-EG based TiO$_2$ nanofluids in this study with those predicted by Einstein (1906), Brinkman (1952) and Bachelor (1977) at 50 °C
6.1.1 Specific heat

The specific heat of nanofluids obtained from the experimental study has been compared with the predicted values of specific heat from specific heat models widely used in the nanofluids literature (Barbés et al., 2013, Vajjha and Das, 2009b). Model-I (equation (3.34)) is similar to mixing theory of ideal gas mixture and it is related to specific heat of base fluid and nanoparticles, and volume fraction of nanoparticles. While this model is simple and widely suggested in the literature, it possess little theoretical justification in context of nanofluids (O’Hanley et al., 2011). On the other hand, model-II (equation (3.33)) is based on the thermal equilibrium between the particles and the surrounding fluid. It shows that the specific heat as well as the density of base fluid and nanoparticles must affect the specific heat of the nanofluids.

Before measuring the nanofluids specific heat as described in section 5.5.1.4, the experimental procedure and equipment were validated through measuring the known specific heat fluid (i.e. ethylene glycol). In this study it was found that with the increase of nanoparticle volume fraction, the specific heat capacity decreases. However, model-I underestimates the decrease of specific heat, while Model-II offers more accurate prediction of nanofluids specification capacity compared to Model-I though both models failed to predict the specific heat of nanofluids accurately. From Figure 6.10 to Figure 6.12, it can be
seen that the experimental results agree better with that of the model-II than what suggested by model-I, though all results indicate a decrease of specific heat with an increase of nanoparticle concentrations as found by other researchers as well (Satti et al., 2016, De Robertis et al., 2012a, Ijam et al., 2015a). The discrepancy between the experimental results and predicted values can arise due to the size and surface effects of the nanoparticles on the specific heat capacity of nanofluids and also the agglomeration of nanoparticles (clustering), which in turn may cause the decrease of specific heat with increasing the nanoparticle volume fraction (Zhou et al., 2009). Usually the large surface area of nanoparticles offers larger contact area with the base fluid, and increasing concentration of nanoparticles causes phase transformation in the fluid that can result in the decrease of specific heat of nanofluid (Ijam et al., 2015a).

Figure 6.10 Comparison of the experimentally obtained specific heat of 50/50 water-EG based ZnO nanofluids in this study with those predicted by the existing specific heat models: model-I (equation (3.34)) and model-II (equation (3.33)) at 50 °C
Figure 6.11 Comparison of the experimentally obtained specific heat of 50/50 water-EG based TiO$_2$ nanofluids in this study with those predicted by the existing specific heat models: model-I (equation (3.34)) and model-II (equation (3.33)) at 50 °C.

Figure 6.12 Comparison of the experimentally obtained specific heat of 50/50 water-EG based Al$_2$O$_3$ nanofluids in this study with those predicted by the existing specific heat models: model-I (equation (3.34)) and model-II (equation (3.33)) at 50 °C.
6.1.2 Density

The experimental densities for 50/50 water-EG based ZnO, Al₂O₃ and TiO₂ obtained in this study were compared with that suggested by the correlations introduced by Pak and Choi (1998) shown in Figure 6.13 to Figure 6.15. The experimental values were matched closely with the above mentioned correlation with maximum error of ~1.5% that can be possibly explained by the fact that the Pak and Cho’s model was developed by using water as the base fluid and not water and ethylene glycol mixture.

![Figure 6.13 Comparison of the experimentally obtained densities of 50/50 water-EG based ZnO in this study with those predicted by applying Pak and Choi (1998) density model at 50°C](image-url)
Figure 6.14 Comparison of the experimentally obtained densities of 50/50 water-EG based TiO$_2$ in this study with those predicted by applying Pak and Choi (1998) density model at 50°C

Figure 6.15 Comparison of the experimentally obtained densities of 50/50 water-EG based Al$_2$O$_3$ in this study with those predicted by applying Pak and Choi (1998) density model at 50°C
6.2 Modified results of the theoretical modelling by using the experimentally measured inputs

6.2.1 An overview

This section presents a comparative discussion on the results obtained from the computer simulation model on sizing and performance study of the 2.4 kW PEMFC presented in chapter 4 by using both experimental and theoretical thermo-physical characteristics data of nanofluids.

Earlier in chapter 4, the thermo-physical characteristics data of nanofluids (i.e. those used in this study), obtained through the models available in the literature and the ASHRAE data (ASHRAE, 2001), has been considered for the base fluid (50/50 water-EG mixture) properties. Now following the experimental investigations conducted as part of this study, the experimentally measured thermo-physical characteristics of these nanofluids are fed into the simulation model (i.e. presented in chapter 4) in order to modify the results. This provides an opportunity to modify the results and see how the real measurements can affect the results of the PEMFC cooling system simulation obtained using the theoretical data (i.e. convection heat transfer coefficient, size of the radiator, pumping power, etc.).

The computer simulation model has also been validated by using experimental results obtained from the 2.4 kW PEMFC when nanofluids as well as 50/50 water-EG were used as coolants. It is noteworthy to mention that the developed computer simulation model was used in chapter 4 to size of the radiator while the inputs such cooling load, coolant mass flow rate, radiator inlet, and outlet temperatures, and etc. were kept constant. However, in this experimental study, the coolants mass flow rate and the radiator inlet temperature were kept constant for all coolants at a certain operating point (i.e. 50 A) while the radiator exit coolant temperature was allowed to vary for different coolants. Applying iteration method the computer simulation model has been validated by using the same experimental approach.

6.2.2 The radiator size and pumping power

As discussed earlier in section 4.2.2.7, by using the theoretically predicted thermo-physical properties of the nanofluids (i.e. used in this study), the enhancement of convection heat transfer coefficient was obtained to be ~60% for 0.05 vol% concentration of nanoparticles compared with that of the base fluid. Almost no further increment with increasing the volume fraction of the nanoparticles from 0.05 vol% to 0.5 vol% was observed (Figure 6.16). On the other hand, by using experimentally measured nanofluids thermo-physical
data, the enhancement in the convection heat transfer coefficient was predicted to be almost same as that predicted by using theoretical thermo-physical data for 0.05 vol% concentrations (i.e. 60% improvement). However, the experimental data suggested slight further enhancements in convection heat transfer coefficient when the concentration of nanoparticles was increased from 0.05 vol% to 0.5 vol% (Figure 6.16). For example, with 0.5 vol% concentration, the convection heat transfer coefficient enhancement was obtained to be 70% for TiO$_2$ and Al$_2$O$_3$ nanofluids, and around ~74% for ZnO nanofluids compared to those calculated for the base fluid (i.e 50/50 water-EG) while the earlier theoretical calculations suggested 60% enhancement for all the nanofluids. However, for convection heat transfer coefficient enhancement all the thermo-physical properties of nanofluids are involved directly or indirectly. The errors were found to be ~0.7%, ~2.75%, ~0.24% and ~0.06% in the experimental measurement of thermal conductivity, viscosity, specific heat and density of 50/50 water-EG based 0.5 vol% ZnO nanofluids.

![Graph showing enhancement of convection heat transfer coefficient](image)

Figure 6.16 Prediction of enhancement of convection heat transfer coefficient by using theoretical and experimental thermo-physical data of nanofluids

The convection heat transfer is one of the key factors affecting the size of the radiator suggested by the simulation model (Chapter 4). Figure 6.17 shows that for 0.05 vol% concentration of nanoparticles (i.e. ZnO, Al$_2$O$_3$ and TiO$_2$) by using the thermo-physical characteristics data obtained through the existing theoretical correlations, ~26% reduction in the HE’s frontal area can be achieved; however, following the trend observed in Figure 6.16,
increasing the concentration of nanoparticles from 0.05 vol% to 0.5 vol% did not lead to further significant reduction in the frontal area of the radiator.

On the other hand, by using the experimentally obtained thermo-physical characteristics of nanofluids, the reduction rate only slightly increased compared to that of the theoretical data. In fact, this small difference can easily fall with the errors involved in the experiment and can be neglected. For 0.05 vol% concentration of nanoparticles, the reduction of the frontal area of the radiator was calculated to be ~27% for all three nanofluids whereas for 0.5 vol% concentration of nanoparticles the reduction rates were only improved by further 1% (i.e. ~28%) for TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, and ~29% for ZnO nanofluids.

This is mainly due to the fact that though most of the theoretical models predictions of thermo-physical properties of nanofluids showed deviation from that of the experimental results (Chapter 5), among the existing models, the most widely used and reliable ones were used in this theoretical study that minimise the deviation from the experimental results. For example, the thermal conductivities of nanofluids measured in this study were found to be ~5% higher than those predicted from Maxwell model (used in theoretical study) at 50˚C. Moreover, the convection heat transfer coefficient affects the heat transfer process significantly but for both cases (i.e. using experimental and theoretical properties of nanofluids) the same empirical correlations (equations (3.27) and (3.28)) were used for convection heat transfer coefficient in computer simulation model.

![Figure 6.17 Prediction of the reduction of frontal area of heat exchanger by using theoretical and experimental thermo-physical characteristics of nanofluids](image-url)
According to the results of theoretical simulation presented in section 4.2.2.8, the required pumping power increased by increasing the nanoparticles concentrations. The same trend was also observed when experimentally measured values were used in the model. By using theoretical nanofluids thermo-physical data, the theoretical model suggested that the required pumping power increased by ~5% for 0.05 vol% concentration and only slightly more (i.e. ~6%) when the concentration was increased to 0.5 vol%. This finding was almost independent of the type of nanoparticles and was valid for all three types of nanofluids used in this study (i.e. 50/50 water-EG based ZnO, TiO₂ and Al₂O₃ nanofluids).

On the other hand, by using experimentally obtained thermo-physical properties of nanofluids almost the same 5% increment in the pumping power was calculated for 0.05 vol% concentration for all three nanofluids used in this study. Ramping up the concentration to 0.5 vol% showed only slightly stronger effects on the pumping power than that suggested with using theoretical value for the thermo-physical properties of nanofluids. For 0.5 vol% concentration, the increment was ~7% for ZnO and Al₂O₃ nanofluids, and ~9% for TiO₂ nanofluid compared to that for the base fluid (i.e. 50/50 water-EG).

It is important to note that the Figure 6.7 to Figure 6.9 suggested earlier that the available theoretical models are not very accurate to predict the viscosity of nanofluids. This matter has also been confirmed earlier by other studies (Żyla and Fal, 2016b, Li et al., 2015a, Shoghl et al., 2016a, Jo and Banerjee, 2014, Murshed et al., 2008a, Chandrasekar et al., 2010a, Turgut et al., 2009). While this can contribute to the slight difference between the pumping powers predicted by the theoretical values and the experimental values (i.e. used in model), the error involved in the experimental measurements can still be partly responsible for such small differences.

For example, with 0.5 vol% concentration of nanoparticles, the pumping power increment for ZnO and Al₂O₃ nanofluids was found to be ~1% while for TiO₂ nanofluid the figure was ~3%. Mainly the density and viscosity of nanofluids are responsible for this increment of pumping power. With the 0.5 vol% concentration of nanoparticles, the errors in measurement of viscosity were found to be 2.75%, 2.94% and 2.58% for ZnO, TiO₂ and Al₂O₃ nanofluids respectively. While for 0.5 vol% concentration of nanoparticles, the errors in measurement of density were found to be 0.06%, 0.07% and 0.07% for ZnO, TiO₂ and Al₂O₃ nanofluids respectively.
On the other hand from the 2.4 kW PEMFC experimental study (Section 5.5.2.4), the maximum pressure drop was found to be ~10% higher for 0.5 vol% ZnO nanofluid than that suggested by using the base fluid (50/50 water-EG) with ~3% error for 4 l/min coolant flow rate. This experimental pressure drop was found to be slightly higher (~3 - ~4%) compared to those found from the computer simulation model using experimentally and theoretically obtained thermo-physical properties of nanofluids. The measurement error and equipment uncertainty (+/- 2 kPa at 50 to 500 kPa) can be involved in this deviation.

6.2.3 Validation of the simulation model

In order to validate the developed computer simulation model (Chapter 4), an experimental study was conducted on a 2.4 kW PEMFC with a view to measuring its thermo-electrical performances (Section 5.5.2). As it is mentioned in chapter 4, one of the outputs of the computer simulation model was the size of the radiator when different coolants are used in the PEMFC cooling system. However, in the experimental study, there was only one radiator (i.e. frontal area 257.24 cm²). Hence for validating the computer model, the radiator size has been kept constant. Along with the radiator, the cooling load, coolant mass flow rate, and the radiator inlet temperature were also kept constant for different coolants at a same operating point (i.e. 50 A). The only variable parameter in the model was the coolant exit temperature of the radiator as can be seen in Table 6.1.
For example from Table 6.1 at 50 A operating point of 2.4 kW PEMFCs stack:

- For 50/50 water-EG as coolant, the cooling load, the radiator inlet and outlet temperature were observed to be 1.94 kW, 49.1 °C and 40.4°C respectfully with coolant mass flow rate of 0.066 kg/s (3.98 l/min) for the radiator frontal area 257.24 cm². While using the same inputs (i.e. cooling load 1.94 kW, radiator inlet temperature 49.1°C, coolant mass flow rate 0.066 kg/s and obviously the same radiator size) into the computer simulation model, the radiator exit temperature was found to be 44.6°C that was about 10% higher than that suggested by the experiments. This deviation was mainly due to the fact that the measurement equipment (i.e. 2 thermocouples and coolant flow meter) consist almost a cumulative error of ~6.7% uncertainty. While for the measured cooling load (i.e. 1.94 kW), the experimental error was found to be ~0.1%

- By using 0.05 vol% ZnO nanofluid as coolant, the cooling load, the radiator inlet and outlet temperature were found to be 1.93 kW, 52.2 °C and 43.4°C respectfully with coolant mass flow rate of 0.064 kg/s (3.85 l/min) for the same radiator. By using these parameters into computer model as inputs, the radiator exit temperature was predicted to be 45.5°C that was ~5% higher than that measured experimentally. In this case the cumulative uncertainty for measurement equipment were ~7.2%, while for the cooling load the experimental measured error was found to be ~1.83%.

- By using 0.5 vol% ZnO nanofluid as coolant, the cooling load, the radiator inlet and exit temperatures were found to be 1.86 kW, 51.3 °C and 42.5 °C respectfully with coolant mass flow rate of 0.064 kg/s (3.85 l/min) for the same radiator. By using these into computer model as inputs, the radiator exit temperature was estimated to be 44.7 °C that was ~5% higher from that measured experimentally. This deviation was found to be within the equipment uncertainty (~7.5%) for the measurement equipment (i.e. 2 thermocouple and coolant flow meter). Also ~0.9% error was observed in measured cooling load.

Therefore, the experimentally obtained results were found to be agreed with those predicted by the computer simulation model while the slight difference between the two is well within the range expected by considering the errors associated with the data obtained experimentally.
Table 6.1 Experimental results obtained from 2.4 kW PEMFCs stack operated at 30 A, 40 A, 50 A and 60 A, and predicted results from computer simulation models providing the results (i.e. cooling load, coolant mass flow rate and radiator inlet temperature) as inputs obtained from experiment by keeping radiator size constant using 50/50 water-EG and nanofluids as coolants

<table>
<thead>
<tr>
<th>Stack operating points (A)</th>
<th>Coolants</th>
<th>FC efficiency (%)</th>
<th>Process</th>
<th>Coolant mass flow rate (kg/s)</th>
<th>Frontal area (cm²)</th>
<th>Cooling load (kW)</th>
<th>Experimental error (%)</th>
<th>Radiator inlet temp. (°C)</th>
<th>Radiator exit temp. (°C)</th>
<th>The difference of predicted values with theoretical and experimental inputs (%)</th>
<th>Estimated uncertainty (%)</th>
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<tr>
<td>30</td>
<td>50/50 water-EG</td>
<td>42.10</td>
<td>Experiment</td>
<td>0.051</td>
<td>257.24</td>
<td>1.06</td>
<td>2.21</td>
<td>38.0</td>
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<td>7.21</td>
<td>7.69</td>
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<td></td>
<td>0.05% ZnO</td>
<td>42.44</td>
<td>Experiment</td>
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<td>1.06</td>
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<td>44.2</td>
<td>36.2</td>
<td>5.06</td>
<td>7.24</td>
</tr>
<tr>
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<td>0.5% ZnO</td>
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<td>Experiment</td>
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<td>257.24</td>
<td>1.47</td>
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<td>37.8</td>
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<td>Experiment</td>
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<td>1.93</td>
<td>1.83</td>
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<td>5.86</td>
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</table>
CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 An overview

This research project was designed mainly to see the effects of using nanofluids as PEMFC coolants on the size of the cooling system (i.e. size of radiator) and also on the electrical performance of PEMFC compared to when 50/50 water-EG is used as coolant. The investigation has been conducted both experimentally and theoretically. In this chapter, the research questions posed in section 1.3 at the beginning of this thesis are addressed followed by conclusions. And finally recommendations will be made on future research and opportunities to expand the current research out of the scope that has already been defined for that.

7.2 Response to the research questions

7.2.1 What role the volume fraction and type of the nanoparticles play in determining the electrical and thermo-physical properties of nanofluids in the context of them being used as PEMFC coolant?

In section 3.4.1, it was mentioned that apart from the particles concentration and type of nanoparticles, temperature, particle size, particle shape/aspect ratio, additives, acidity (pH), sonication, and aggregation of nanofluids play vital roles in determining their electrical and thermo-physical properties of nanofluid. However, in this research, the role of volume fraction and type of nanoparticles have been investigated thoroughly (Chapter 5) with a view to confirming their effects on electrical and thermal properties of nanofluids as well as investigating their effects on the electrical and thermal performances of PEMFCs.

The electrical and thermo-physical characteristics of nanoparticles play roles in determining the electrical and thermo-physical properties of nanofluids. On the other hand, the electrical and thermal performances of PEMFCs vary with the electrical and thermo-physical properties of nanofluids, used as coolants in their cooling system.

The electrical conductivities of nanofluids are different for different nanoparticles as well as for different volume concentrations. In this research, though all the selected nanoparticles were insulating materials, their electrical conductivities were varied from each other. For example, the electrical conductivities of 50/50 water-EG based TiO₂ and Al₂O₃ nanofluids were found to be almost double compared to that of 50/50 water-EG based ZnO nanofluid.
(Chapter 5). Along with the type of nanoparticles, the concentration of nanoparticles could also affect the electrical conductivity of nanofluids significantly. By increasing the concentration of nanoparticles from 0.05 vol% to 0.5 vol%, the electrical conductivities increased by ~70%, ~62% and ~138% at 50 °C for ZnO, Al₂O₃ and TiO₂ nanofluids respectively (Figures 5.18-5.20). However, for applying nanofluids into PEMFCs as coolants, the low electrical conductivity nanoparticles are preferable as they can cause electrical leakage which in turn can affect the electrical performance of the PEMFCs.

Thermal conductivities of nanofluids were found to be slightly different (i.e. less than 3%) from each other (Chapter 5). On the other hand, the concentrations of nanoparticles impose greater effect on the thermal conductivities of nanofluids compared to that suggested by changing the types of the nanoparticles. Increasing the volume fraction from 0.05 to 0.5 led to increase in the thermal conductivities in the range of ~7% - ~10% for 50/50 water-EG based ZnO, Al₂O₃ and TiO₂ nanofluids (Figure 5.26 to Figure 5.28).

The convection heat transfer coefficient is a very important parameter to be known in a nanofluid when it comes to heat transfer applications that involved convection; however unlike many other properties of nanofluids (e.g. thermal conductivity), it cannot be measured directly. In the present study, this parameter was estimated using the existing models recommended in the literature (Chapter 4). The effects of using three nanoparticles (i.e. ZnO, Al₂O₃ and TiO₂) on enhancing the convection heat transfer factor were found to be identical. However, this convection heat transfer coefficient showed more sensitivity to the particles concentrations. For 50/50 water-EG based ZnO nanofluids, the convection heat transfer coefficient increased from ~63% to ~74 when the nanoparticles concentration was increased from 0.05 vol% to 0.5 vol% (i.e. compared to that of the base fluid as shown in Figure 4.15).

The viscosity of nanofluids did not vary much with the type of nanoparticles but the volume fraction of nanoparticles could affect the viscosity significantly (Chapter 5). The viscosity of 50/50 water-EG based ZnO, Al₂O₃ and TiO₂ nanofluids increased by ~22%, ~70% and ~51% respectively for increasing the concentration from 0.05 vol% to 0.5 vol% at 50 °C (Figure 5.30 to Figure 5.32).

Unlike viscosity of nanofluids, the specific heat of nanofluids depends both on the types of nanoparticles and volume fraction (Chapter 5). The specific heat varied around ~3% for different nanoparticles (e.g. ZnO, Al₂O₃ and TiO₂). The specific heat decreased with the increase of nanoparticle concentrations in the range of ~2% to ~6% for increasing concentrations from 0.05 vol% to 0.5 vol% (Figure 5.40 to Figure 5.42).
The density of nanofluids also varies with the type of nanoparticles and the particles concentrations. For example, with the concentration of 0.05 vol%, the density of ZnO nanofluids was found to be only ~1% higher compared to those of the 0.5 vol% of TiO_2 and Al_2O_3 nanofluids. Similarly, the effect of particle concentrations was also recorded to be small within 0.05 vol% to 0.5 vol%, with ~2 % increase (i.e. for 50/50 water-EG based ZnO nanofluids at 50 °C as described in Figure 5.47.

From above individual discussion on the electrical and thermo-physical properties of nanofluids, it is clear that the nanoparticle concentration generally plays stronger role on affecting the thermo-physical properties of nanofluids than the type of nanoparticles. The effects of different types of nanoparticles at the same concentration (i.e. when used in the PEMFC cooling system as coolants), on the electrical performance of fuel cell, the size of the radiator and pumping power were almost identical (Chapter 5). On the other hand, though the concentration of nanoparticles almost did not affect the electrical performance of PEMFC at all (Section 5.5.2.2), the thermal performance were found to be slightly varied while changing the concentration of nanofluids from 0.05 vol% to 0.5 vol%. For example for ZnO nanofluid, the reduction of frontal area of radiator increased from ~27% to ~29% (Figure 6.17), and pumping power required increased from ~5% to ~7% (Figure 6.18) for increasing concentration from 0.05 vol% to 0.5 vol% compared with that of 50/50 water-EG. It is important to note that the errors involved in all measurements and the theoretical equations used in the model deny opportunities to make firm judgements around such small difference.

7.2.2 What potentials and challenges nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performances of PEMFCs?

Depending on the type and concentration of nanoparticles, nanofluids can offer benefits and suggest challenges when used as coolants in the PEMFCs. In this research three types of nanoparticles (i.e. ZnO, Al_2O_3 and TiO_2) with the concentrations of 0.05 vol%, 0.1 vol%, 0.3 vol% and 0.5 vol% have been selected (i.e. to be used as coolants) for investigating their effects on electrical and thermal performances of PEMFCs.

As for the concerns around the electrical performance of PEMFCs, the investigated nanofluids in the above mentioned concentration range did not suggest any negative effect
on the electrical performance of the stack investigated experimentally as part of this study (Chapter 5). However, the finding of this study showed (Section 5.5.2.3) that using such nanofluids as coolants in PEMFCs can offer significant opportunities to improve the performance of the fuel cell cooling system (i.e. compared to when 50/50 water-EG is used as coolant). As discussed before, nanofluids showed a considerably better convection heat transfer coefficient by adding only 0.05 vol% concentration of nanoparticles (i.e. ZnO, Al₂O₃ and TiO₂) with base fluid (i.e. 50/50 water-EG). The convection heat transfer coefficient was found to be increased by 60% compared with that of the base fluid of 50/50 water-EG. By increasing the concentration from 0.05 vol% to 0.5 vol%, the convection heat transfer coefficient could be further enhanced by an extra 14% (i.e. ~74 % compared with that of the base fluid) (Figure 6.16). Along with the enhancement of convection heat transfer coefficient, the nanofluids can also offer benefits in reducing heat exchanger size used in PEMFCs cooling system.

The nanofluids act as anti-freezing agents that help in lowering the freezing point of the coolant. This is an important functionality to consider in automotive application, particularly in cold climate conditions. By adding only 0.2 wt% of D-SWNT in 50/50 water-EG, the freezing point can be lowered from -35.6 down to -42.2 °C (Chapter 1). This effect has not been taken into consideration in this study. However, adding nanoparticles offers an opportunity to reduce the share of EG (for a given targeted freezing point). On the other hand reducing EG would help improving the thermal properties of the coolant (e.g. its thermal conductivity).

The stability of nanofluids due to the strong van der Waals interactions between nanoparticles is considered a challenge for using nanofluids as coolants in PEMFCs cooling system. While detailed study of stability remained to be outside the scope of this work a preliminary observation showed that among the three nanofluids investigated in this research (i.e. 50/50 water-EG based ZnO, Al₂O₃ and TiO₂), only ZnO nanofluid was found to be relatively stable (i.e. more than 6 hours before showing signs of settlement), Al₂O₃ and TiO₂ nanofluids showed settled down just in about an hour. For applying nanofluids in PEMFCs as coolants and especially for PEMFCs in automotive applications, the nanofluids are supposed to remain stable for extended periods. The aggregated nanoparticle can block the PEMFCs cooling channels that can potentially lead to permanent damage to the fuel cell.

All the selected nanoparticles were electrically insulating materials and the electrical conductivity of investigated volume fractions (i.e. 0.05 vol% to 0.5 vol%) were found to be below threshold of 100 μS/cm. Hence, as expected no effect on electrical performance was
observed when these nanofluids were used as coolants. It is noteworthy that both the type of nanoparticles and their volume fraction affected the electrical conductivity of nanofluids significantly; so judicious decision should be taken on selecting type of nanoparticles and volume fraction for PEMFCs applications such that the electrical conductivity of the coolants remains below the above-mentioned threshold.

7.2.3 How much the electrical and thermal performances of PEMFCs are affected by using nanofluids as coolants in PEMFCs?

The generated electricity in PEMFCs creates electrical fields causing polarisation of the nanofluids which affects the electricity leaking through coolants. Hence, the electrical conductive nature of the nanofluids compared to conventional coolants (i.e. 50/50 water-EG) was taken into consideration as a challenge. However, the selected nanoparticles were electrically insulating materials and the volume fractions were chosen to be low (i.e. less than 1 vol%); that is why, the electrical conductivities of all the nanofluids (i.e. 50/50 water-EG based ZnO, Al₂O₃ and TiO₂) were found to be below 100 μS/cm (i.e. maximum ~35 μS/cm, ~68 μS/cm and ~77 μS/cm at 70 °C for ZnO, Al₂O₃ and TiO₂ nanofluids respectively). Following this consideration, no negative impact on the electrical performance of the PEMFCs (i.e. used for in the experimental part of this study) was observed (Figure 5.53).

The fuel cell electrical output can be also discussed at a system. The coolant pump is an integral part of the fuel cell at the system level. The pump is usually powered by the fuel cell stack (e.g. directly or indirectly). Hence considering the parasitic energy of the pump, any increase or decrease in the power consumption of this component can be translated to a change in the overall power output of the fuel cell at a system level. Mainly as the result of increase in the viscosity it was found that the required pumping power while using nanofluids as coolants in PEMFCs increased compared with that of needed with the base fluid (i.e. 50/50 water-EG) (Chapters 4, 5 and 6). With adding 0.05 vol% nanoparticle with 50/50 water-EG, the pumping power increased around 5% compared with that of the 50/50 water-EG. However, the pumping power did not increase much further by increasing the nanoparticle concentrations (Figure 4.17), from 0.05 vol% to 0.5 vol% (i.e. a further 1%). However, it is important to note that using nanofluids would eliminate the use of coolant de-ionising unit in the cooling loop. This old likely offset the effect of nanofluid on the pumping power. Hence, the overall effect of using nanofluids as coolants on the pumping power would likely remain to be insignificant.
On the other hand, the performance of the PEMFCs cooling system improved significantly by using nanofluids as coolants compared to when a conventional coolant (i.e. 50/50 water-EG) was used. By adding only 0.05 vol% nanoparticles with 50/50 water-EG, the convection heat transfer coefficient was enhanced by around 60% compared with that of the base fluid. By increasing the nanoparticles concentrations, the convection heat transfer coefficient increases gradually at a lower rate. For example, by increasing the ZnO nanoparticles concentration from 0.05 vol% to 0.5 vol%, convection heat transfer coefficient increased from 60% to 74% compared with that of the base fluid (i.e. 50/50 water-EG) (Figure 6.16). Consequently, the radiator size was reduced for the same cooling load when nanofluids were used as coolants instead of the 50/50 water-EG coolant. By using 0.05 vol% Al$_2$O$_3$ nanofluids, the required radiator size was reduced by ~26% (i.e. for extracting ~2.1 kW cooling load) compared to that when 50/50 water-EG was used as coolant (Figure 6.17).

7.2.4 What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?

In this research, the electrical and the thermo-physical (i.e. thermal conductivity, viscosity, specific heat and density) characterisations of nanofluids (i.e. 50/50 water-EG based ZnO, Al$_2$O$_3$ and TiO$_2$) have been studied both theoretically and experimentally. Based on these characterisations, a theoretical study on the thermal performance of PEMFCs has been performed for which a 2.4 kW PEMFCs was used as a case study. With a view to validating this theoretical study, an experimental investigation on the same 2.4 kW PEMFC was conducted. This experimental study was focused on measuring the thermo-electrical performance of the stack and the pump (i.e. for power consumption only) when different coolants (i.e. conventional 50/50 water-EG and selected nanofluids) were used as coolants. Based on these theoretical and experimental studies, the following conclusions can be made about the key characteristics of nanofluids that have to be considered for selecting suitable coolants for use in PEMFCs:

**Stability of nanofluids:** Though the detailed study on stability of nanofluids was not in the scope, stability of the nanofluids can be single out as one of the most important characteristics of nanofluids for PEMFCs application as coolants. As can be seen in chapter 3, all the electrical and thermo-physical properties of nanofluids are affected by the stability of nanofluids. Although the stability of nanofluids can be increased in various ways (i.e. adding additives) but additives can contaminate the nanofluids properties as well as
deteriorate their thermal properties. 50/50 water-EG based ZnO nanofluid (in this research) is one of the good examples of stable nanofluids as they found to be stable more than 6 hours before showing signs of settlement.

Electrical conductivity: As discussed in section 1.1.3, the electricity can be leaked through the nanofluids. That is why for applying nanofluids in PEMFCs as coolants, the nanoparticles with low electrical conductivity are more preferable. The experimental measurements showed that the increase of nanoparticle concentrations (Chapter 5), the electrical conductivity gradually increases and at a certain level the electricity can leak through the coolants (i.e. nanofluids).

Thermal conductivity: For heat transfer applications, high thermal conductivity coolants are most preferable as it directly affects the heat transfer performance. However, those nanoparticles possess the high thermal conductivity (i.e. metallic nanoparticles), usually becomes the more electrical conductive as well. Hence, for PEMFCs applications, a well balance between the thermal conductivity and electrical conductivity is very necessary. In this study, 50/50 water-EG based 0.05 vol% to 0.5 vol% ZnO, TiO₂ and Al₂O₃ nanofluids were used to investigate the thermal performance of PEMFC cooling system. The enhancement of thermal conductivities were found to be in the range of 8-15% for 0.5 vol% nanofluids compared with that of the base fluid (i.e. 50/50 water-EG) with the maximum error of 0.96%.

Convection heat transfer coefficient: In heat transfer applications, like high thermal conductivity, high convection heat transfer nanofluids is an important condition as this can greatly affect the performance of the cooling system. The effects of different nanoparticles (i.e. ZnO, Al₂O₃ and TiO₂) on enhancing the convection factor were found to be identical. However, the convection heat transfer coefficient increased from ~63% to ~74 when the nanoparticles concentration was increased from 0.05 vol% to 0.5 vol% (i.e. compared to that of the base fluid as shown in Figure 4.15.

Viscosity: Viscosity of the coolants can affect the pumping power that in turn affects the parasitic loss of the system. For nanofluids, with the increase of concentrations, the viscosity thermal conductivity, convection heat transfer coefficient, and electrical conductivity increase. For increasing concentration of nanoparticles up to 0.5 vol%, the pumping power was found to be increased by ~9% for TiO₂ nanofluid compared to that for the base fluid (i.e. 50/50 water-EG) (Section 6.2.2). However, this pumping power increment can likely be offset by the elimination of the use of de-ionising filter while using nanofluids as coolants.
Hence judicious decision should be taken while selecting the nanoparticles for PEMFCs applications.

**Density:** The density of coolant is directly proportional to the required pumping power in a cooling system. Although the density of nanofluids increases with increasing the concentration of nanoparticles, this effect was measured to be negligible within the concentration range used in this study.

### 7.3 Conclusions

The main focus of this PhD research project was to experimentally and theoretically study the effects of using nanofluids as PEMFCs coolants on the electrical and thermal performances of PEMFCs system with a view to applying PEMFCs in automotive applications. One of the critical challenges of implying the PEMFCs in automotive applications is the excessive size of the radiator. PEMFCs operate at relatively low temperatures (i.e. ~60-65 °C), leading to a small temperature difference between the coolant (i.e. used for fuel cell cooling) and the ambient. Hence heat transfer at such low temperature differences required enlarged radiators. This is usually challenging in terms of packaging as well as air supply on the radiator matrix through the car’s bumper openings and grill.

A comprehensive literature review has been conducted on the thermal management of PEMFCs, their cooling systems and requirements, as well as the properties of nanofluids. The literature review has also addressed their applications, and their potentials and challenges with a view to using them as coolants in PEMFCs. To study the PEMFCs cooling system theoretically, a computer simulation model has been developed consisting of the sub-models of PEMFCs stack, radiator, water pump and coolants in Matlab. The sub-models for the PEMFCs stack, water pump, radiator and coolants incorporated some of the most recently developed correlations for the coolants thermo-physical characteristics. All the sub-models were combined to simulate the overall performance of the PEMFC cooling systems (with different liquids used as coolants). The model can be applied for any capacity PEMFCs cooling system and able to size the radiator, convection heat transfer coefficient of the coolants and pumping power required to circulate the coolants in the cooling loop. In particular the model was customised to investigate the use of nanofluids as coolants in PEMFCs.
The 2.4 kW PEMFCs stack has been used for the experimental and theoretical parts of this study. All the necessary parameters for PEMFCs polarisation curves have been taken from the manufacturer provided V-I curves. The 50/50 water-EG has been taken as the base fluid for making nanofluids and all the temperature dependent thermo-physical properties of base fluid has been taken from 2001 ASHRAE HVAC fundamental handbook. The thermo-physical properties of nanoparticles were considered equal to the thermo-physical properties of the particle material in bulk form. The properties of nanofluids have been predicted by using existing and most reliable correlations in the literature.

The convection heat transfer coefficient enhancement predicted by the theoretical computer simulation model was found to be ~60% for 0.05 vol% concentration of nanofluids, while for 0.5 vol% concentration the enhancement was estimated to be ~74%. As the results of this enhancement, the reduction of the frontal area of the radiator was found to be ~26% by using 0.05 vol% concentration of nanofluids while this could only be increased slightly (i.e. further ~1%) for 0.5 vol% concentration of nanoparticles. With 0.05 vol% concentration, the required pumping power for circulating the required coolants (i.e. nanofluids) for extracting 2.1 kW heat from PEMFC increased by ~5% compared with when 50/50 water-EG was used as coolant in the system. This pumping power showed negligible further increase by increasing the concentration of nanoparticles from 0.05 vol% to 0.5 vol%.

Along with the theoretical prediction of the thermo-physical properties of nanofluids, the sample nanofluids were prepared in the RMIT chemical engineering lab and their electrical and thermo-physical (i.e. thermal conductivity, viscosity, specific heat and density) properties were measured experimentally. The equipment and process were calibrated by measuring the known material properties before measuring the properties of nanofluids. The experimental data were used in the theoretical computer simulation model to compare the outputs of the model with those results obtained by using theoretical predicted properties of nanofluids. The variations in theoretically predicted and experimentally measured thermo-physical data of nanofluids have been reflected into the overall computer simulation model outputs.

A comprehensive error analysis was conducted to assess the uncertainties associated with measured values. The experimental errors for the electrical and thermo-physical properties (i.e. thermal conductivity, viscosity, specific heat and density) of nanofluids, PEMFCs voltage and power, and hydrogen consumption were all confirmed to be within the accuracy range of the measurement instrument. For the combine error analysis PEMFCs cooling load, most of the uncertainties were within the estimated range of uncertainties calculated using
the inherent inaccuracies of the thermocouples and coolant flow meter. Very few of the cooling loads related uncertainties were slightly outside of the estimated range of errors due to the calibration factor of thermocouples used in this experiment.

As mentioned, the experimental rig was developed based on the 2.4 kW PEMFCs with a view to investigating the electrical and thermal performances of the PEMFCs system. All the equipment; i.e. radiator, water pump, flow meters, pressure gauge, etc. were sourced to match with the requirement of this 2.4 kW PEMFC system. 50/50 water-EG based nanofluids were prepared in laboratory and used in the PEMFC cooling system. With a view to investigating the electrical and thermal performances of PEMFC system, the PEMFCs was run first with this 50/50 water-EG. Following the experiment with 50/50 water-EG, more experiments were conducted with 0.05 vol% and 0.5 vol% ZnO nanofluids, 0.5 vol% TiO$_2$ and 0.5 vol% Al$_2$O$_3$ nanofluids. During the experiments with various coolants (i.e. nanofluids and 50/50 water-EG), the coolant mass flow rate and fuel cell inlet temperature were kept constant at the same operating point (i.e. 50 A) of the fuel cells. No variations in the polarisation curves were found while using 50/50 water-EG and different types of nanofluids indicating no electricity leakage due to using nanofluids as coolants. On the other hand, the experimentally obtained thermal performance data were used to validate the computer simulation results. The computer simulation model results were matched with the experimentally obtained PEMFCs results with acceptable errors (i.e. below 10%).
Table 7.1 The summary of the performance obtained in this work based on the research questions

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Research questions</th>
<th>Findings</th>
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| 1.    | What role the volume fraction and type of the nanoparticles play in determining the electrical and thermo-physical properties of nanofluids in the context of them being used as PEMFC coolant? | - The electrical conductivities of nanofluids are varied for different nanoparticles as well as for different volume concentrations.  
- The concentrations of nanoparticles impose greater effect on the thermal conductivities of nanofluids compared to that suggested by changing the types of the nanoparticles.  
- Increasing the volume fraction from 0.05 to 0.5 led to increase in the thermal conductivities in the range of ~7% - ~10% for 50/50 water-EG based ZnO, Al$_2$O$_3$ and TiO$_2$ nanofluids.  
- The effects of using three nanoparticles (i.e. ZnO, Al$_2$O$_3$ and TiO$_2$) on enhancing the convection heat transfer factor were found to be identical.  
- The convection heat transfer coefficient increased from ~63% to ~74 when the nanoparticles concentration was increased from 0.05 vol% to 0.5 vol% (i.e. compared to that of the base fluid.  
- The viscosity of 50/50 water-EG based ZnO, Al$_2$O$_3$ and TiO$_2$ nanofluids increased by ~22%, ~70% and ~51% respectively for increasing the concentration from 0.05 vol% to 0.5 vol% at 50 °C.  
- The specific heat varied around ~3% for different nanoparticles (e.g. ZnO, Al$_2$O$_3$ and TiO$_2$) while the specific heat decreased with the increase of nanoparticle concentrations in the range of ~2% to ~6% for increasing concentrations from 0.05 vol% to 0.5 vol%.  
- The density of nanofluids also varies with the type of nanoparticles and the particles concentrations. |
<p>| 2.    | What potentials and challenges                                                      | - The investigated nanofluids in the concentration range from 0.05 – 0.5 vol% concentration range                                          |</p>
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<th>SL No.</th>
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<th>Findings</th>
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|        | nanofluids can offer as PEMFCs coolants with a view to particularly investigating the thermal and electrical performances of PEMFCs? | did not suggest any negative effect on the electrical performance of the stack investigated experimentally.  
- The convection heat transfer coefficient was found to be increased by 60% compared with that of the base fluid of 50/50 water-EG.  
- By increasing the concentration from 0.05 vol% to 0.5 vol%, the convection heat transfer coefficient could be further enhanced by an extra 14% (i.e. ~74 % compared with that of the base fluid).  
- Both the type of nanoparticles and their volume fraction affected the electrical conductivity of nanofluids significantly.  
  - The generated electricity in PEMFCs creates electrical fields causing polarisation of the nanofluids which affects the electricity leaking through coolants.  
  - the selected nanoparticles were electrically insulating materials and the volume fractions were chosen to be low (i.e. less than 1 vol%); that is why, the electrical conductivities of all the nanofluids (i.e. 50/50 water-EG based ZnO, Al₂O₃ and TiO₂) were found to be below 100 μS/cm.  
  - With adding 0.05 vol% nanoparticle with 50/50 water-EG, the pumping power increased around 5% compared with that of the 50/50 water-EG.  
  - The pumping power did not increase much further by increasing the nanoparticle concentrations (Figure 4.17), from 0.05 vol% to 0.5 vol% (i.e. a further 1%).  
  - By adding only 0.05 vol% nanoparticles with 50/50 water-EG, the convection heat transfer coefficient was enhanced by around 60% compared with that of the base fluid. |
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<th>Sl No.</th>
<th>Research questions</th>
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<tbody>
<tr>
<td>4.</td>
<td>What are the characteristics of suitable nanofluids to be used as coolants in PEMFCs?</td>
<td>• By using 0.05 vol% Al$_2$O$_3$ nanofluids, the required radiator size was reduced by ~26% (i.e. for extracting ~2.1 kW cooling load) compared to that when 50/50 water-EG was used as coolant.</td>
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<tr>
<td></td>
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<td>• The nanoparticles with low electrical conductivity are more preferable for the applications in PEMFCs.</td>
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<td></td>
<td></td>
<td>• For heat transfer applications, high thermal conductivity coolants are most preferable as it directly affects the heat transfer performance.</td>
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<tr>
<td></td>
<td></td>
<td>• In heat transfer applications, like high thermal conductivity, high convection heat transfer nanofluids is an important condition as this can greatly affect the performance of the cooling system.</td>
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<td></td>
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<td>• Viscosity of the coolants can affect the pumping power that in turn affects the parasitic loss of the system.</td>
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<td></td>
<td></td>
<td>• The density of coolant is directly proportional to the required pumping power in a cooling system.</td>
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</table>
7.4 Recommendations for future studies

The present PhD research study has been conducted both experimentally and theoretically. Based on the obtained results and completed the works within the scope of this research, the following recommendations are proposed for further studies:

- The developed computer simulation model in this study is capable of providing outputs for all range of cooling load concerning the PEMFCs application in automotive applications. However, the model did not include the effect of the electrical conductivity of nanofluids on the electrical performance of the fuel cell. This is why the effect of the electrical conductivity of nanofluids on the electrical performance of the fuel cell was investigated experimentally. The model can further improved by including the effects of electrical conductivity of the coolants on the performance of PEMFCs.

- The developed computer simulation model was one dimensional and steady state. The transient behaviour of the fuel cell can be added as the fuel cells are expected to expose to a variable load or restarted after a period of being in operation in automotive applications.

- In this study, all the metal oxide nanoparticles (i.e. ZnO, TiO$_2$ and Al$_2$O$_3$) were intentionally selected with a view to using them in PEMFCs cooling system as coolants. Other types of nanoparticles (i.e. metallic, CNT, graphite, etc.) can be selected to study their effect on thermo-electrical performance of PEMFCs when used as coolants.

- In both the theoretical and experimental studies conducted in this research, the concentrations of nanoparticles were considered to be varied in the range of 0.05 vol% to 0.5 vol%. Future studies can target a wider range of concentrations by (i.e. <0.05 vol% and >0.5 vol%).

- Long term stability of nanofluids was excluded from the experimental investigation of this study. As the stability of nanofluids affects their properties, it is important to investigate the long term stability of nanofluids and to find out the ways to make them stable without affecting their electrical and thermal properties significantly.

- The long term effects of using nanofluids as PEMFCs coolants on the PEMFC’s cooling channel as well as on the electrical performance of PEMFCs is an opportunity for further investigation. While de-ionising unit can be theoretically eliminated with nanofluids as coolants, the long-term effect of removing this part from the cooling loop is recommended to be further studied experimentally.
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APPENDICES

Appendix A: Details experimental procedure

A.1 The 2.4kW PEMFC operating procedure

The details of the start-up procedure for the 2.4 kW PEMFC stack for performing the experiment and collecting data are as follows:

The start-up procedure for the 2.4 kW PEMFC stack in a hydrogen recirculation setup for performing the experiment and collecting data are as follows:

1. Check the hydrogen safety system to make sure that the safety equipment are all in good order
2. The fuel cell utilizes hydrogen and ambient air as the oxygen source
3. The hydrogen and air are stored in compressed cylinders. The hydrogen and air cylinders must be filled prior to running the fuel cell
4. Switch on the fume cupboard
5. Check the hydrogen line for leakage using the handheld hydrogen leak detector (if required)
6. Connect the electronic load to the fuel cell. Programmable direct current (DC) electronic load; models M9715; manufactured by Maynuo Electronics has been used in this project.
   - Power on the electronic load. The electronic load starts power-on-self-test and the vacuum fluorescent display (VFD) shows the software serial No. after few seconds, the display will show the actual input voltage and current value, actual power value and setting value.
   - The electronic load will be operating at constant current operation mode and according to the operating points.
   - Press the key I-SET, then the VFD display will show STANDARD CURR = xxxxxxx A, the current constant current value.
   - Press the numeric keys and decimal point key to enter constant current value required, followed by pressing the key ENTER to confirm.
   - If the input state is in OFF state, the right upper corner of the VFD display will show OFF. Press the key ON/OFF to change the input state into ON state. The right upper corner of the VFD display will show CC or Unreg indicating the load has been successfully set into the expected constant current value or the load could not adjust itself to the expected constant current value respectively.
- Check if the measured power supplier has been correctly connected and turned on; make sure if the expected constant current value is in the range of the measured power supplier.

7. Open the hydrogen and air cylinder valves
8. Open the hydrogen and air valves located on the rig
9. Set the hydrogen and air pressure at around 300 mbar (g) for gas entry into the fuel cell
10. Ensure that all the hydrogen line and airline valves remain closed
11. Switch all the measurement instruments and their respective display panels on
12. Adjust the hydrogen flow rate
13. Adjust the air flow rate based on the air stoichiometry recommended by manufacturer of around 1.8
14. Adjust the hydrogen flow rate based on the recommended stoichiometry by manufacturer and FC operating point
15. Adjust the exit air pressure to about 250 mbar (g) by using the two valves simultaneously in the fuel cell air inlet and exit
16. Adjust the electronic load to operate the fuel cell at 40 A operating current. This load has to be continuously monitored and adjusted since it fluctuates a bit during the experiment
17. Let the water pump run to circulate water into the fuel cell while the cooling fan should be remained off
18. Keep operating the fuel cell until the exit water from the fuel cell goes a few degrees above the desirable operating temperature. For example, if intending to have the fuel cell operated at about 60 °C, let the fuel cell operated until the exit water temperature goes to about 64-65 °C. The fuel cell inlet water temperature is normally at about the same temperature while the cooling fan is closed. This temperature is used as an indicator of the operating temperature of the fuel cell
19. Switch on the cooling fan of the heat exchanger
20. By adjusting the cooling fan speed of the heat exchanger try to maintain the mean water temperature (between the inlet and exit of the fuel cell) at about the fuel cell test temperature (e.g. 60 °C)
21. Wait for a few minutes to make sure that the fuel cell is operating at a steady state condition
22. Start noting the data including fuel cell voltage, coolant flow rate into the fuel cell, hydrogen flow rate (consumption), the water temperatures before and after the fuel cell as well as the radiator
23. Repeat the reading in every 1 minute or so for about 10 times so that the average of all these readings can be used for that particular operating point (e.g. 40 A)

**Shutdown–Normal conditions:**
1. Remove load
2. Turn off the oxidant airflow and stop the fuel flow
3. Allowing pressures to drop equally
4. Stop coolant pump

**Shutdown–Emergency conditions:**
1. Immediate removal of load.
2. Open contactor to fuel cell stack
3. Turn off all oxidant and fuel flows
4. Immediately de-pressurize the system to remove any potential energy in the system
5. Stop coolant pump

### A.2 Stack safety and precaution

During handling 2.4 kW PEMFC, the following safety cautions and considerations should be maintained:

- At idle condition, the residual voltage can be remained in the stack.
- When the system is operating, all guards, screens, and electronic enclosures must be ready in place.
- The objects on clothing that can cause short circuits must be removed when operating the fuel cell.
- The fuel cell stack can reach up to about 75 °C that is why touching any FC components during operation is prohibited.
- The fuel cell voltage is up to 32 VDC (i.e. open circuit) for 27-cells). The external load must be connected before operating FC stack.
- This fuel cell-stack can generate up to 160 amps current. Current leakage from the stack can occur through the stack liquid coolant and/or if there is inadequate isolation elsewhere in the electrical system which may cause fatal accident.
- During installation, the manufacturer recommendation must be followed.
- Stack power connection cables must be checked and approved by the expert before using in PEMFC.
- All electrical connections must be checked by expert.
- Negative cell voltages in one or more cells can be happened for any of the following reasons that can lead to open flame at the stack:
Fuel starvation: operation with insufficient fuel flow, insufficient fuel purge in recirculation mode, or excess liquid water in fuel stream.

Membrane dehydration: this can be caused by:
- Operation above maximum cell temperature rating
- Operation without sufficient coolant flow
- Operation with one or more severely degraded cells in an otherwise healthy stack
- Operating prolonged periods without sufficient reactant humidification

External short circuit of some or all cells due to accidental bridging of cells with conductive materials such as tools.

A.3 Safety inter-lock system

Starting procedure of the safety interlock system

- Ensure main switch is turned on, this is indicated by the “ON” indicating lamp and the “POWER POINT STOP” stop is in the outward position
- Press green “EXTRACTION START” button
- The extraction fan within the chamber will commence and upon sufficient airflow detection, the blue “AIR FLOW ACQUIRED” indicating lamp will illuminate.
- Once air flow has been established press green “POWER POINT START” button. This will turn on the power points located to the right side of the control panel and open the hydrogen solenoid valve allowing hydrogen to be delivered to the chamber.

System shut down

- After all experiments are complete, to turn off the system push “POWER POINT STOP” this will remove supply to the power points and close the solenoid valve supplying hydrogen to the chamber
- Press “EXTRACTION STOP” to turn off the extraction fan within the chamber

A.4 Nanofluids preparation: Two step method

The most common and popular method used for the preparation of nanofluid is two-step method. In the first step, nanoparticles are made into dry powder using physical or chemical means. The second step involves dispersing of nano sized powder into a base fluid using several means; e.g. magnetic force agitation, ultrasonic agitation, high shear mixing, homogenizing, ball milling, etc. This is the most economic method for preparation of nanofluids since industrial productions are already underway. In this project, the two-step method has been adopted and the following procedure is followed to prepare nanofluids:
Step 1: Measuring nanoparticles and base fluids
For measuring nanoparticle and base fluids, weighing scale and measuring cylinder have been used respectively.

- Weighing scale
  - Put the switch ON
  - Place the empty beaker on the scale platform
  - Pre-zero the scale
  - Put the nanoparticle into the beaker and measured the amount required

- Measuring cylinder
  - Measure the required amount of deionized water into the cylinder
  - Measure the required amount of ethylene glycol into the cylinder
  - Make mixture of the de-ionized water and ethylene glycol in another cylinder/beaker

Step 2: Sonicator operation procedure
In this project, Vibra-Cell Auto-tune Series 750 Watt Model sonicator has been used. The operating procedure of this sonicator is as follows:

- Set ON/OFF power switch to ON
- Set amplitude, because the amplitude required to process a sample is application dependent
- Set timer, the processing time function monitors and controls only the ON portion of the duty cycle. To set the processing time, press the TIMER key.
  - Using numeric keys, set the processing time
- Set PULSER. There is ON and OFF cycle, which can be set independently from 01 sec to 59 sec. During the OFF cycle, the red indicator of the PULSER will illuminate. If the OFF portion of the cycle exceeds 3 sec, a cautionary message will display on screen—Sonics is OFF cycle.
- Set TEMP. Temperature function prevents overheating of the sample by continuously monitoring the sample temperature.
- Set ENERGY: The ultrasonic processor generator continuously monitors the amount of energy in joules that is being delivered to the probe
- REVIEW: This function provides a window on the process by displaying various parameters without process interruption. Pressing REVIEW/ENTER will consecutively display information that has already been set.

Step 3: Sonication of nanofluid
- Assess the volume of sample requiring sonication
- Choose the correct sonication probe tip
• Screw on required probe if not already screwed into one of the sonicator units. Probes need to be screwed on tightly to function properly.
• Place beaker holding fluid to be sonicated in ice within another container, e.g. a plastic beaker. Place this sample set-up on the adjustable platform.
• Immerse probe in solution, adjust platform so end of probe is 1/2–way down into the solution. Ensure probe tip does not contact the bottom of the beaker.
• Close noise reduction cupboard doors
• Switch power ON

A.5 Electrical conductivity of nanofluids

The following steps need to flow for measuring electrical conductivity of nanofluids:
• Do not touch the tip of the probe
• Connect the probe to the meter. Make sure that the cable locking nut is securely connected to the meter. Turn on the meter
• Rinse the probe with deionized water. Blot dry with a lint-free cloth
• Put the probe into the sample so that the temperature sensor is completely submerged. Do not put the probe on the bottom or sides of the container.
• Push READ. The display will show “Stabilizing” and a progress bar as the probe stabilizes in the sample. The display will show the lock icon when the reading stabilizes. The measurement is automatically corrected to the selected reference temperature (20 or 25 °C)
• Data is automatically stored in the data log when press to READ or INTERVAL is selected in the measurement mode. When CONTINUOUS is selected, data will only be stored when STORE is selected.
• Air bubbles under the sensor tip when submerged can cause slow response or error in measurement. If bubbles are present, gently shake the probe until bubbles are removed.
• Repeat above steps for additional measurements when measurements are done, store the probe.

A.6 Thermal conductivity of nanofluids

The thermal conductivity measurement of nanofluids was performed through the following steps:
• Attach KS-1 sensor then turn on the KD2 Pro
Properly insert the needle into the material to be measured.

An icon appears on the left and right side of the screen. The icon at left indicates the type of sensor connected. The circular icon indicates that a reading is in process. It changes to a thermometer icon to indicate whether the measurement is currently in heating or cooling mode, when the thermometer is rising, heat is applied to the needle, and when it is falling, heat is off. A progress bar at the bottom of the screen shows the elapsed time.

When dealing with low viscosity liquid samples, the duration of the read time should be as small as possible to minimize the amount of heat added to the sample

The default read time for the KS-1 sensor needle is one minute

In liquid samples, the KS-1 sensor needle should be oriented vertically during the measurement to help prevent free convection

The KS-1 sensor should not use in high power mode in liquids. The sensor must be configured in low power mode to prevent free convection

When the reading is complete, the results will display on the screen

A.7 Viscosity of nanofluids

The following steps/procedure should be followed to measure the viscosity of nanofluids:

Step 1: Trios Software

Before running any experiments, accessories need to be selected according to use. Accessories are sorted into three categories as follows:

- Concentric cylinders: The concentric cylinder fixtures are as follows:
  - Concyl_Rotor_Smooth: Smooth bob
  - Concyl_Rotor_Vaned: Vaned bob
- Custom: The custom fixtures are screw in cones and plates. They are as follows:
  - Custom_25 mm_PP_SB: 25 mm sandblasted parallel plate
  - Custom_25 mm_CP_2˚: 25 mm 2˚ cone and plate
  - Custom_40 mm_CP_2˚: 40 mm 2˚ cone and plate
- Environmental test chamber (ETC)
  - ETC_25 mm_CP_2˚
  - ETC_25 mm_PP

Step 2: Starting sample test

- Click experiment in the bottom right corner to:
  - Name the experiment and add relevant notes if needed
Select the file path and save
No need to change any values under geometry as this has already been set
Under procedure, choose what type of test is going to run and other parameter
There are some parameters that are limited

– Torque should not go beyond 200 mN.m
– Normal force should not go beyond 50 N

Step 3: Preparing the equipment

- Check and make sure the air pressure gage for the bearing is at 30 lbs
- Carefully install the accessories in the top and bottom. The bottom plate is magnetic.
  - To install the top accessory
    - Ensure the heat is fully raised so there is enough space to attach the accessory
    - Hold the lock button on the rheometer until hear a beeping, this will line up the drive shaft
    - Carefully place the accessory on and orient the alignment marks on the accessory with those on the rheometer. Screw the draw rod into the accessory
  - To install the bottom accessory
    - Click the release button
    - A green light should appear signifying that the accessory can be loaded. After clicking the button, the accessory needs to be loaded within 10 seconds
    - Once it is loaded, the tubes and wiring can be attached

- Other equipment
  - For using Peltier geometries, one must turn on the chiller
    - The chiller is located under the desk
    - Flip the switch on the side of the chiller
    - Press start after loading the accessory but before the experiment begun
    - Turn the chiller off before disconnecting the tubing
  - If using the environmental test chamber, the air must be turned on
    - The flow meter is located on the wall next to the rheometer
    - Turn the knob until it is at 10 LPM
  - Zero the rheometer by clicking ‘0’. Ensure the environmental test chamber doors are completely open.
Step 4: Load a sample
- Place the sample on the bottom plate or in the cup
  - For the parallel plate or cone: put enough sample on the plate so when it lowers the sample squishes out from all sides
  - For the cup: fill the cup 1/3 to 1/2 full, enough so that when the rotor is lowered the sample covers the rotor entirely
- Lock the bearing
- Press the trim gap button
- For the parallel plate or cone only
  - Trim the sample
  - Press the trim gap button again to lower the top plate to geometry gap
- If using concentric cylinders no trimming is necessary
- Close the environmental test chamber doors if applicable

Step 5: Start rheometer
- Click either start on the computer (large green arrow on the upper left) or click start on the rheometer (green arrow in the centre of the bar)

Step 6: Obtaining results
- The results screen should come up when the experiment is started. If it doesn’t click results on the bottom left
- There are three options for viewing the results. All three options can be found as tabs on the bottom
  - Experimental parameters
  - Spreadsheet
    - The variables can be edited displayed in spreadsheet by choosing select variables on the top left
    - Equations can be added to spreadsheet by choosing add user column on the top left and entering equation
  - Graph
    - The variables shown on the graph can be adjusted by choosing select on the top left and choose the variables.
    - All of the Y values can have more than one variable associated with it
    - All of Y1 and Y3 are shown on the left and Y2 and Y4 are shown on the right
For more variable options check show extended list or show user variables on the lower left
To overlay two graphs right click on the graph and click new overlay document then drag the graphs to overlay from the file manager on the left to the overlay graph

Step 7: Unload the sample
- Make sure to clean the sample off the accessories
- To uninstall the top accessory
  - Holding the accessory unscrew the draw rod and remove the accessory
- To uninstall the bottom accessory
  - Click the release button
  - When the green light starts flashing, unplug all cables and tubes
  - Push the button again to get a solid green light which allows to remove the bottom accessory
  - Log off the computer when finished

A.8 Specific heat measurement of nanofluids

Procedure
1. Reference material—Synthetic sapphire
   1.1 Purge the DSC apparatus with dry nitrogen at a flow rate of 100+/−5 mL/min throughout the experiment.
   1.2 Weigh a clean, empty specimen holder plus lid to a precision of +/-0.01mg. Record as the tare weight.
   1.3 Position the empty specimen holder plus lid and a reference specimen holder plus lid (weight matched, if possible) in the DSC apparatus.
   1.4 Heat or cool the DSC test chamber to the initial temperature for the experiment at 20 °C.
   1.5 Hold the DSC test chamber isothermally at the initial temperature for at least 4 min to establish equilibrium. Record this thermal curve.
   1.6 Heat the test specimen from the initial to final temperature at a rate of 20 °C/min. Continue to record the thermal curve.
   1.7 Record a steady-state isothermal baseline at the upper temperature limit.
      1.7.1 Terminate the thermal curve after this period.
      1.7.2 Cool the DSC test chamber to ambient temperature
   1.8 Place the sapphire standard and specimen holder plus lid.
1.9 Weigh sapphire standard and specimen holder plus lid to a precision of +/- 0.01 mg and record the weight.

1.10 Follow step 1.4 to 1.7

2. Unknown specimens—follow step 1.1 to 1.7

2.1 Place the test specimen (after conditioning, if necessary) into the empty specimen holder plus lid.

2.2 Weigh the specimen plus specimen holder plus lid to a precision of +/- 0.01 mg and record the weight.

2.3 Repeat steps 1.3 to 1.7

2.4 Reweigh the specimen holder plus specimen. If a mass loss ≥0.3% occurred, the measurement is invalid. Any change in mass should be noted in the report.

For getting fruitful results from classical three step method, the following things should be handled carefully:

**Hazards**

- Safety precautions—If a specimen is heated to decomposition, toxic or corrosive products may be released.
- Technical precautions:
  - The same heating rate should be used for both the calibration and specimen runs.
  - Precision of heating rate, placement of the specimen holder, use of flat specimen holders, and the establishment of equilibrium are essential. Instrument settings should not be adjusted once a specific heat capacity calibration has been performed.

**Sampling**

- Powdered or granular specimens should be mixed prior to sampling and should be sampled by removing portions from various parts of the container. These portions, in turn, should be combined and mixed to ensure a representative specimen for the determinations.
- Liquid specimens may be sampled directly after stirring.
- Solid specimens may be sampled by cutting or slicing with a clean knife or razor blade. Sample uniformity should be ascertained, since segregation within the solid is possible.
Samples are usually analysed as received. If some heat or mechanical treatment is applied to the specimen prior to analysis, this treatment should be noted in the report.

**Calibration**

- Specific heat capacity is a quantitative measurement of energy made as a function of temperature. Thus, the instrument used in its measurement must be calibrated in both the temperature and heat flow modes. Since specific heat capacity is not a rapidly changing function of temperature, the instrument’s temperature mode is ordinarily calibrated and checked only occasionally. The heat flow information, however, is much more critical and becomes an integral part of the specimen heat capacity measurement through the use of a reference material.
- Synthetic sapphire disk (α-aluminium oxide, alumina) is recommended as a heat flow calibration standard for specific heat capacity measurements.
- The heat flow calibration may be performed at some regular interval or prior to every specific heat capacity determination or test specimens.

**Conditioning**

- Specimens and specimen holders for specific heat capacity determinations may be handled in ordinary laboratory environments for screening or qualitative measurements. However, if quantitative data are needed over a wide temperature range, specimen conditioning may be required. Specimens which will be exposed to low temperatures should be protected from moisture. Specimens that will be exposed to very high temperatures should be protected from the effects of oxidation.
- Any volatile specimens suspected of being sensitive to moisture or oxidation should be hermetically sealed in a dry, inert environment. All materials which will come in contact with the specimen should also be purged in a dry, inert environment. Vacuum degassing of specimens to be heated to a very high temperature is recommended.
- Conditioning of non-volatile specimens run in crimped lid or open pans may be accomplished in the DSC apparatus, using the inert purge stream of the instrument. This conditioning procedure will not protect specimens that are hermetically sealed under normal laboratory atmospheric conditions.
- The specimen should be held at the starting temperature for several minutes before initiation of the temperature program. An equilibrium time of four minutes is suggested.
A.9 Density measurement of nanofluids

The following procedure should be followed to measure the density of nanofluids

1. Obtain a dry pycnometer, DO NOT WASH THE PYCNOMETER. It must be dry for the accurate determination of its mass. It is important that the stoppers are not exchanged from bottle to bottle, since each stopper is ground to fit one bottle and no other.
2. Weigh the clean dry bottle to the nearest 0.1 mg.
3. Obtain approximately 50 mL of the unknown liquid.
4. Pour the deionized water into bottle until the bottle is completely full.
5. Insert the stopper so the ground glass (frosted) end is in the bottle.
6. Carefully dry the outside of the bottle with a tissue and weigh.
7. For unknown liquid, follow 4-6
8. Calculate the density by using equation (2.5)
Appendix B: Components used in the 2.4 kW PEMFC experimental study

Figure B.1 The dimension and image of water pump used in 2.4 kW PEMFC experimental study

Figure B.2 Power curve of water pump used in 2.4 kW PEMFC experimental study
Table B.1 Specifications of water pump used in 2.4 kW PEMFC experimental study

<table>
<thead>
<tr>
<th>Items</th>
<th>Specs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sizes and weight</td>
<td>100.5x84.5x64;480g</td>
</tr>
<tr>
<td>Dimension of inlet</td>
<td>22.5mm</td>
</tr>
<tr>
<td>Dimension of outlet</td>
<td>22.5mm</td>
</tr>
<tr>
<td>Driving method</td>
<td>Brushless, Magnetic, 3 phase</td>
</tr>
<tr>
<td>Pump material</td>
<td>PA66+GF30% (optional)</td>
</tr>
<tr>
<td>Condition of use</td>
<td>Continuously</td>
</tr>
<tr>
<td>Fluids</td>
<td>Water, oil, acid and alkali solution</td>
</tr>
<tr>
<td>Max working temp</td>
<td>100°C</td>
</tr>
<tr>
<td>Power consumption</td>
<td>2.5W~86.4W</td>
</tr>
<tr>
<td>Rated voltage</td>
<td>24V DC</td>
</tr>
<tr>
<td>Max rated current</td>
<td>3.8A</td>
</tr>
<tr>
<td>Max flow rate</td>
<td>27 l/min</td>
</tr>
<tr>
<td>Max Static Head</td>
<td>13m</td>
</tr>
<tr>
<td>Life span</td>
<td>More than 30000 hrs</td>
</tr>
</tbody>
</table>

Figure B.3 Q-Sonica sonicator used in preparing nanofluids
Figure B.4 Sierra 100 hydrogen flow meter used in 2.4 kW PEMFC experiment

Figure B.5 Image of air flow meter used in 2.4 kW PEMFC experiment
Figure B.6 Coolant flow meter used in 2.4 kW PEMFC experiment

Figure B.7 A programmable DC electronic load used in this experiment
Figure B.8 OHAUS PioneerTM Series of analytical and precision balance used to measure nanoparticles

Figure B.9 BM 252 with the accuracy of 0.01 mg used to measure the nanoparticles for preparing nanofluids used in 2.4 kW PEMFC cooling system
Figure B. 10 Pt 100 thermocouple probes and display used in 2.4 kW PEMFC experiment

Figure B.11 Pressure gauge used to measure the pressure drops across the coolant flow loop in 2.4 kW PEMFC experiment

Figure B.12 Swagelok fittings, tube and valves used in 2.4 kW PEMFC experiment
Figure B.13 Regulators used in 2.4 kW PEMFC experiment
Appendix C: Error analysis

C.1 Experimental error analysis

C.1.1 Cooling load error calculation

The cooling load error analysis has been calculated based on the data provided in Table following the procedure described in section 5.4.

Table C.1 Cooling load at the 50 A operating point of 2.4 kW PEMFC

<table>
<thead>
<tr>
<th>Measured cooling load</th>
<th>1st observation ($x_1$)</th>
<th>2nd observation ($x_2$)</th>
<th>3rd observation ($x_3$)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1840.58</td>
<td>1837.25</td>
<td>1887.49</td>
<td>0.87</td>
</tr>
</tbody>
</table>

According to equations (5.2) and (5.3),

$$u(x) = \pm \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 / n(n-1)} = \pm \sqrt{\left(\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2}{n(n-1)}\right)}$$

where $\bar{x} = (x_1 + x_2 + x_3 / 3) = (1840.58+1837.25+1887.49)/3 = 1855.11$ and $n = 3$

Therefore,

$$u(x) = \pm \sqrt{\left(\frac{(1840.58 - 1855.11)^2 + (1837.25 - 1855.11)^2 + (1887.49 - 1855.11)^2}{3(3-1)}\right)}$$

$$= \pm \sqrt{\frac{211.12 + 318.98 + 1048.46}{3(3-1)}}$$

$$= \pm 16.22$$

$$Error\% = \pm \frac{u(x)}{x} 100\% = \pm \frac{16.22}{1855.11} 100\% = 0.87\%$$

Therefore, the percentage of error: 0.87%
C.1.2 The cooling load uncertainty related to the measurement equipment

The uncertainty related to the measurement equipment has been estimated based on the data provided in Table C.2 for cooling load. The equipment involved in this measurement are two thermocouples and one coolant flow meter.

Table C.2 Estimation of the measurement equipment related uncertainty for 50/50 water-EG based 0.5 vol% ZnO nanofluid

<table>
<thead>
<tr>
<th>Fuel cell inlet temp. ($x_1$)</th>
<th>Fuel cell exit temp. ($x_2$)</th>
<th>Coolant flow rate ($x_3$) (l/min)</th>
<th>Experimental cooling load (W)</th>
<th>Experimental error (%)</th>
<th>Estimated uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.8</td>
<td>45.2</td>
<td>2.99</td>
<td>1220.39</td>
<td>0.69</td>
<td>7.52</td>
</tr>
<tr>
<td>37.8</td>
<td>46.2</td>
<td>3.21</td>
<td>1471.05</td>
<td>0.5</td>
<td>7.36</td>
</tr>
<tr>
<td>42.5</td>
<td>51.3</td>
<td>3.83</td>
<td>1855.31</td>
<td>0.87</td>
<td>7.30</td>
</tr>
<tr>
<td>45.3</td>
<td>54.7</td>
<td>4.28</td>
<td>2218.27</td>
<td>0.41</td>
<td>7.22</td>
</tr>
</tbody>
</table>

The parameters can be expressed as:

$x_1$ = Fuel cell inlet temperature (°C)

$x_2$ = Fuel cell exit temperature (°C)

$x_3$ = Coolant flow rate (l/min)

The extracting cooling load ($Q$) is the function of fuel cell inlet and exit temperatures, and coolant flow rate. Therefore, the cooling load can be expressed as (1 litre of water = 1 kg water):

$$Q = f(x_1, x_2, x_3) = \frac{x_3}{60} \times 4180 \times (x_2 - x_1)$$

By using the measurement data (row 1) from Table C.2 and uncertainties associated with each of the contributing parameters (Table 5.6), the uncertainty can be estimated by using equation (5.5) as:

$$u(x_1) = \pm (0.1 + 0.00167 \times 37.8) = \pm 0.163 \degree C$$

$$u(x_2) = \pm (0.1 + 0.00167 \times 45.2) = \pm 0.175 \degree C$$

$$u(x_3) = \pm \frac{5}{100} \times 2.99 = \pm 0.1495 \text{ l/min}$$
\[ u(Q) = \pm \sqrt{\sum_{i=1}^{N} \left( \frac{\partial f}{\partial x_i} \right)^2 u^2(x_i)} \]

\[ u(Q) = \pm \sqrt{\left( \frac{4180}{60} \right)^2 \left[ (2.99)^2 \times (0.163)^2 + (2.99)^2 \times (0.175)^2 + (45.2 - 37.8)^2 \times (0.1495)^2 \right] } \]

\[ u(Q) = \pm 91.77 \]

Therefore, the percentage of uncertainty:

\[ Error\% = \pm \frac{u(Q)}{Q} \times 100\% = \pm \frac{91.77}{1220.39} \times 100\% = 7.52\% \]

C.2 The method that used by KD-2 Pro thermal analyser for estimating error

The temperature response over time for the applied heat \( q \) can be expressed as:

\[ \Delta T = -\frac{q}{4\pi k} E_i \left( \frac{-r^2}{4Dt} \right) \]

where \( k \) is the thermal conductivity, \( D \) is thermal diffusivity, \( r \) is distance between heater and sensor and \( E_i \) is exponential integral.

Sum of Square of Error (SSE) for temperature rise \( T^* \) can be expressed:

\[ SSE = \sum (T_i^* - M_i^*)^2 \]
where $T_i^*$ are the measured values and $M_i^*$ are values modelled with $\Delta T$ equation.

Therefore, the standard error of estimate for the measurements:

$$S_{yx} = \sqrt{\frac{SSE}{n}}$$

where $n$ is the number of measurements. The units of $S_{yx}$ are mC/W. By multiplying it by $k$, the obtained dimensionless value will provide the KD2 Pro error value.

$$Error = kS_{yx}$$
Appendix D: Experimental measurements of 2.4 kW PEMFCs

Table D.1 2.4 kW PEMFC experimental data using 50/50 water-EG as coolant at the operating points 30 A, 40 A, 50 A and 60 A at room temperature 14.2 °C

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Error (%)</th>
<th>Power (W)</th>
<th>Error (%)</th>
<th>Hydrogen flow rate (l/m)</th>
<th>Error (%)</th>
<th>Coolant flow rate (l/m)</th>
<th>Error (%)</th>
<th>Estimated Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>20.38</td>
<td>0.09</td>
<td>611.35</td>
<td>0.09</td>
<td>6.76</td>
<td>0.07</td>
<td>3.04</td>
<td>0.22</td>
<td>7.69</td>
</tr>
<tr>
<td>40</td>
<td>19.27</td>
<td>0.07</td>
<td>770.97</td>
<td>0.07</td>
<td>8.7</td>
<td>0.05</td>
<td>3.56</td>
<td>1.06</td>
<td>7.47</td>
</tr>
<tr>
<td>50</td>
<td>17.37</td>
<td>0.04</td>
<td>868.37</td>
<td>0.04</td>
<td>10.63</td>
<td>0.03</td>
<td>3.98</td>
<td>0.33</td>
<td>7.14</td>
</tr>
<tr>
<td>60</td>
<td>15.82</td>
<td>0.12</td>
<td>949.48</td>
<td>0.12</td>
<td>12.59</td>
<td>0</td>
<td>4.44</td>
<td>0.26</td>
<td>7.13</td>
</tr>
</tbody>
</table>

Table D.2 2.4 kW PEMFC experimental data using 50/50 water-EG based 0.05 vol% ZnO nanofluid as coolant at the operating points 30 A, 40 A, 50 A and 60 A at room temperature 14.2 °C

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Error (%)</th>
<th>Power (W)</th>
<th>Error (%)</th>
<th>Hydrogen flow rate (l/m)</th>
<th>Error (%)</th>
<th>Coolant flow rate (l/m)</th>
<th>Error (%)</th>
<th>Estimated Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>20.48</td>
<td>0.24</td>
<td>616.06</td>
<td>0.24</td>
<td>6.76</td>
<td>0.07</td>
<td>3.01</td>
<td>1.02</td>
<td>7.55</td>
</tr>
<tr>
<td>40</td>
<td>19.26</td>
<td>0.1</td>
<td>770.68</td>
<td>0.1</td>
<td>8.71</td>
<td>0.05</td>
<td>3.20</td>
<td>0.25</td>
<td>7.24</td>
</tr>
<tr>
<td>50</td>
<td>17.47</td>
<td>0.04</td>
<td>873.65</td>
<td>0.04</td>
<td>10.63</td>
<td>0.03</td>
<td>3.85</td>
<td>0.80</td>
<td>7.08</td>
</tr>
<tr>
<td>60</td>
<td>15.83</td>
<td>0.15</td>
<td>949.86</td>
<td>0.15</td>
<td>12.59</td>
<td>0</td>
<td>4.31</td>
<td>0.41</td>
<td>7.13</td>
</tr>
</tbody>
</table>

Table D.3 2.4 kW PEMFC experimental data using 50/50 water-EG based 0.5 vol% ZnO nanofluid as coolant at the operating points 30 A, 40 A, 50 A and 60 A at room temperature 13.7 °C

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
<th>Error (%)</th>
<th>Power (W)</th>
<th>Error (%)</th>
<th>Hydrogen flow rate (l/m)</th>
<th>Error (%)</th>
<th>Coolant flow rate (l/m)</th>
<th>Error (%)</th>
<th>Estimated Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>20.44</td>
<td>0.08</td>
<td>613.25</td>
<td>0.08</td>
<td>6.87</td>
<td>0.19</td>
<td>2.93</td>
<td>0.65</td>
<td>7.52</td>
</tr>
<tr>
<td>40</td>
<td>19.2</td>
<td>0.82</td>
<td>768.18</td>
<td>0.82</td>
<td>8.56</td>
<td>0.91</td>
<td>3.2</td>
<td>0.53</td>
<td>7.36</td>
</tr>
<tr>
<td>50</td>
<td>17.39</td>
<td>0.25</td>
<td>874.94</td>
<td>0.25</td>
<td>10.49</td>
<td>0.03</td>
<td>3.85</td>
<td>1.08</td>
<td>7.3</td>
</tr>
<tr>
<td>60</td>
<td>15.89</td>
<td>0.26</td>
<td>950.96</td>
<td>0.26</td>
<td>12.43</td>
<td>0</td>
<td>4.31</td>
<td>0.6</td>
<td>7.22</td>
</tr>
</tbody>
</table>
Table D.4 50/50 water-EG temperature dependent properties used to estimate the nanofluids properties in theoretical study

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Density (kg/m³)</th>
<th>Viscosity (m.Pa.s)</th>
<th>Specific heat (kJ/kg.K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Prandtl number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1081.08</td>
<td>8.09</td>
<td>3.203</td>
<td>0.364</td>
<td>71.188</td>
</tr>
<tr>
<td>10</td>
<td>1077.46</td>
<td>5.50</td>
<td>3.242</td>
<td>0.373</td>
<td>47.804</td>
</tr>
<tr>
<td>20</td>
<td>1073.35</td>
<td>3.94</td>
<td>3.2810</td>
<td>0.380</td>
<td>34.019</td>
</tr>
<tr>
<td>30</td>
<td>1068.75</td>
<td>2.94</td>
<td>3.3190</td>
<td>0.387</td>
<td>25.214</td>
</tr>
<tr>
<td>40</td>
<td>1063.66</td>
<td>2.26</td>
<td>3.3580</td>
<td>0.394</td>
<td>19.262</td>
</tr>
<tr>
<td>50</td>
<td>1058.09</td>
<td>1.78</td>
<td>3.3960</td>
<td>0.399</td>
<td>15.150</td>
</tr>
<tr>
<td>60</td>
<td>1052.04</td>
<td>1.43</td>
<td>3.4350</td>
<td>0.404</td>
<td>12.159</td>
</tr>
<tr>
<td>70</td>
<td>1045.49</td>
<td>1.17</td>
<td>3.4740</td>
<td>0.408</td>
<td>9.962</td>
</tr>
<tr>
<td>80</td>
<td>1038.46</td>
<td>0.98</td>
<td>3.5120</td>
<td>0.411</td>
<td>8.374</td>
</tr>
</tbody>
</table>

Table D.5 Properties of nanoparticles provided by manufacturer

<table>
<thead>
<tr>
<th>Particles</th>
<th>Size</th>
<th>Density (kg/m³)</th>
<th>Specific heat (kJ/kg.K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>40</td>
<td>3900</td>
<td>0.728288</td>
<td>11.7</td>
<td>99.5</td>
</tr>
<tr>
<td>Al2O3 (alfa)</td>
<td>40</td>
<td>3700</td>
<td>0.833092</td>
<td>30</td>
<td>99.8+</td>
</tr>
<tr>
<td>ZnO</td>
<td>40</td>
<td>5606</td>
<td>0.496315</td>
<td>21</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Appendix E: Risk assessment for 2.4 kW PEMFC experimental study

Table E.1 Risk assessment for 2.4 kW PEMFC

<table>
<thead>
<tr>
<th>RISK ASSESSMENT DOCUMENT</th>
<th>Details/Title</th>
<th>Number:</th>
<th>Photo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name(s): (of assessors; include name and position) Mohammad Rafiqul Islam (S3407409), PhD Student</td>
<td>Date: 11 Nov. 2013</td>
<td>Figure 1: Stack structure of PEMFC with cooling plates</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>2.</td>
<td>3.</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>5.</td>
<td>6.</td>
<td></td>
</tr>
<tr>
<td>School: SAMME</td>
<td>College: SEH</td>
<td>Location: Bundoora East Campus, RMIT University</td>
<td></td>
</tr>
</tbody>
</table>

**DESCRIPTION OF PROCESS/EQUIPMENT:** Using Nano-Fluids for Proton Exchange Membrane Fuel Cell (PEMFC) Cooling in Automotive Applications.

![Figure 1: Stack structure of PEMFC with cooling plates](image1)

![Figure 2: H₂ storage tank](image2)
The aim of this project is to investigate the use of nano-fluids in PEMFC cooling systems with a particular emphasis on automotive applications. The project will investigate the advantages and challenges associated with using nano-fluids for fuel cell cooling. It will model, characterise and optimise automotive fuel cell cooling systems using nano-fluids as coolants. It will identify the characteristics of the most suitable types of nano-fluids that can be employed by the fuel cell cooling systems used in automotive applications. Last but not the least, it will experimentally investigate the advantages and challenges of using nano-fluids as coolants in fuel cell cooling system and validate the results suggested by the theoretical model.

**MATERIAL SPECIFICATIONS**

The following modules are used in developing the optimal cooling system for PEMFC cooling:

<table>
<thead>
<tr>
<th>Equipment/Material</th>
<th>Description</th>
<th>Applicable Hazard Nos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Exchange Membrane Fuel Cell (PEMFC) Figure 1</td>
<td>2.4 kW Fuel Cell stack; 27-cell configuration.</td>
<td>4, 8, 10.4, 12.1-12.4, 12.6</td>
</tr>
<tr>
<td>H₂ storage tank. Figure 2</td>
<td>Metal hydride low-pressure hydrogen storage cylinder. Maximum operating pressure 1MPa (10 bar).</td>
<td>3, 4, 8</td>
</tr>
<tr>
<td>Ultrasonic Homogenizer (Sonicator). Figure 3</td>
<td>Ningbo Scientz Biotechnology Co. Ltd. (China) JY98-IIIDN homogenizer, Capacity:50-1000ml.</td>
<td>11.8, 11.10,</td>
</tr>
<tr>
<td>Electrical Conductivity Meter (ECM). <strong>Figure 4</strong></td>
<td>BOQU Instrument Co. Ltd. DDG-3080 Industrial Conductivity Meter; Range: 0.01μS/cm-600μS/cm.</td>
<td>11.10</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Hydrogen flow meter. <strong>Figure 5</strong></td>
<td>Sierra SmartTrak 100 Series Flow meter and Controller capable to measure up to 1000 slpm.</td>
<td>-</td>
</tr>
<tr>
<td>Water pump. <strong>Figure 6</strong></td>
<td>General purpose water pump of 0.5 HP 370W; Head maximum 36 m, Flow maximum 36 l/min.</td>
<td>-</td>
</tr>
<tr>
<td>Heat Exchanger/Radiator. <strong>Figure 7</strong></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Air Drier Powder</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Nano-Particles</td>
<td>Skyspring Nanomaterials Inc. USA</td>
<td>1, 3</td>
</tr>
<tr>
<td><strong>Product #</strong>: 1330DL</td>
<td>Aluminum Oxide (Alumina, gamma-Al2O3, 99.9%, 20 nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Product #</strong>: 1319NH</td>
<td>Aluminum Oxide (Alumina, alpha-Al2O3, 99.0+, 40 nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Product #</strong>: 2810NH</td>
<td>Copper Oxide Nanoparticles (CuO, 99+, 40 nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Product #</strong>: 7910DL</td>
<td>Titanium Oxide Nanoparticles (TiO2, anatase, 99.5%, 10-30 nm)</td>
<td></td>
</tr>
<tr>
<td><strong>Product #</strong>: 8410DL</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5**: Sierra SmartTrak 100 Flow measure and controller.

**Figure 6**: Water pump.
Zinc Oxide Nanoparticles (ZnO, 99.8%, 10-30 nm)

Product
Diamond Nanoparticles (C, 55-75 %, 4-15nm)

#: 0512HZ

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Will be bought from local market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-Ethylene glycol (EG)</td>
<td>Will be bought from local market</td>
</tr>
<tr>
<td>Hand Glove Box. Figure 8</td>
<td>Will be bought from local market</td>
</tr>
<tr>
<td>Container for Nano-fluids. Figure 9</td>
<td>Will be bought from local market</td>
</tr>
</tbody>
</table>

Table 1. Modules used on the project

Fabrication Work
Fabrication of mechanical parts; such as FC, motor, air compressor, pump, etc. mounting brackets, are required for this project. Machining of mechanical parts will be carried out by RMIT workshop staff. Fabrication of simple mechanical parts; e.g. drilling holes, hacksawing, etc. may be performed by the student team members.

Fabrication of electronic components and electrical harnessing are not required for this project as the existing electronic equipment for 1.2kW fuel cell will be used.

Test Protocols
The fuel cell and electronic/electrical drivetrain components will be bench-tested prior to fitting to the test rig. Bench tests will be conducted in Renewable Energy Lab (REL), building 258, Bundoora East Campus, RMIT University.

The REL is fitted with a high-pressure hydrogen supply from a compressed-gas cylinder in an external cupboard, a fume...
cupboard with forced extraction system, an interlocked hydrogen safety control system and hydrogen detectors which automatically shut off the hydrogen supply when leakage is detected.

**Operator Training**

FC Manufacturer will organize a quick start service to rapidly ramp-up fuel cell integration capability through a four-hour long supporting introductory knowledge transfer session via web conferencing. This will help the engineers and the engineering teams to rapidly and effectively integrate the fuel cell product with minimal hurdles.

The student team has been briefed in operation of the hydrogen safety interlock system and in operation of the high-pressure laboratory hydrogen supply in the REL.

**Material safety and MSDS**

No hazardous substances/dangerous goods are used in the project. MSDS sheets have been inspected for Hydrogen and Nano-particles. These are discussed below and the MSDS sheets included with this document.

**Hydrogen**

Hydrogen is a clear, odourless gas. It is non-toxic, but does represent a risk of fire, explosion or suffocation. Risk reduction measures are outlined in the following sections to address these risks. The self-ignition temperature for hydrogen is 565.5°C, which is considerably higher than petrol (280°C). The highest possible temperature in the FC is around 55°C, and there are no naked flames or arcing (sparking) under operation condition.

**Water-Ethylene Glycol mixture**

Ethylene glycol is an organic compound used as antifreeze formulations in industrial application. It is an odourless, colourless, syrupy, sweet-tasting liquid. Ethylene glycol is only weakly toxic, but cases of poisonings are not uncommon.
However, it is diluted with 50% water; therefore the toxicity and poisonous effect will be reduced largely.

**Surfactant**

The surfactant/surfactants is a blend of surface active agents. Surfactants are compounds that lower the surface tension or interfacial tension between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

**Project & Applicable Hazards**

Tables 2 & 3 show a list of the planned activities for the project, indicating the applicable hazard numbers for each activity. The highlighted activities will be performed by or under from supervision from RMIT workshop staff as well as from manufactured expertise.

**Table 2: Activities of FC start-up**

Manufacturer will present a “Quick-Start” service in front of our research team in which we will meet with a highly knowledgeable engineer for an intensive introduction to FC. The session will include a review of key topics, including:

- Product overview
- Operating conditions
- Safety considerations
- System design
- Mechanical interfaces and packaging
- Material selection
- Electrical interfaces
- Hydrogen delivery design
- Air delivery and ventilation design considerations
- Cooling system design considerations
- High voltage and low voltage design consideration
- Control system strategy
- Fault monitoring strategy
- Failure modes and methods to mitigate
- Diagnostics and troubleshooting
- Maintenance requirements

Moreover, FC start-up will be as follow:

<table>
<thead>
<tr>
<th>Nos</th>
<th>Activity</th>
<th>Aims</th>
<th>Location, Method &amp; Equipment</th>
<th>Hazard Nos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Test of Fuel Cell (FC) operation</td>
<td>Verify FC is operational. Characterise FC.</td>
<td>Bench test in REL fume cupboard.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Compare results to characterisation undertaken in 2011, to identify any degradation and estimate remaining FC operational lifetime.</td>
<td>REL fume cupboard, hydrogen supply, power supplies and electronic load, Digital Multi-Meters (DMM’s).</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Test of FC electrical system</td>
<td>Test and verify FC correct operation with voltage regulator and output dc-dc converter</td>
<td>Bench test in REL fume cupboard.</td>
<td>3a-3f</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>REL fume cupboard, hydrogen supply, power supplies, electronic load, DMM’s and oscilloscope.</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Test of FC hydrogen system</td>
<td>Test and verify correct operation of the fabricated hydrogen supply system</td>
<td>Bench test in REL fume cupboard.</td>
<td>3b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>REL fume cupboard, filled metal-hydride fuel canister, power supplies, electronic load, DMM’s.</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Assemble FC sub-system to test article</td>
<td>Mount FC sub-systems; i.e. water pump, radiator, air compressor, H₂ cylinder, etc. on the test rig</td>
<td>General Student Workshop. Assembly with general hand tools: - Spanners, screwdrivers, electronic test equipment.</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>FC system test</td>
<td>Test and verify correct operation of the FC system mounted in the test rig</td>
<td>REL, Bundoora</td>
<td>3a-3f</td>
</tr>
<tr>
<td>6</td>
<td>Characterise initial performance</td>
<td>Measure the FC operation by using the deionized water as the coolant. Measure the FC operation by removing de-ionizing unit and replacing the deionized water by nano-fluids.</td>
<td>Partly assembled test article (with FC sub-system mounted to test rig), DMM’s.</td>
<td>2, 3a-3f</td>
</tr>
<tr>
<td>7</td>
<td>Prepare test article</td>
<td>Clean the FC by de-ionizing water during using each type of nano-fluid.</td>
<td>General Mechanical tools: - spanners, screwdrivers, etc.</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Electrical/electronic fabrication</td>
<td>Build voltage regulator modules for the FC sub-systems. Build wiring harness for power and data.</td>
<td>General electronics tools: - screwdrivers, pliers, soldering station. Electronics fabrication is conducted off-site at student’s premises.</td>
<td>3d</td>
</tr>
<tr>
<td>9</td>
<td>Mechanical fabrication</td>
<td>Mounting plate to fit pump, air compressor, radiator, etc. to the test article. Mountings and fittings for electrical equipment and FC.</td>
<td>Metal component fabrication by Workshop staff. Simple fittings fabricated by student team using general student workshop tools.</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 3: Nano-fluids preparation**
Nano-fluids will be prepared in two step methods; purchasing nano-particles and then dispersing the nano-particles into water-ethylene glycol mixture using sonication. The sonication process is given as follows:

<table>
<thead>
<tr>
<th>Step</th>
<th>Activity</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Sonication probe</td>
<td>Select the appropriate probe from several probes based on the job. Choose the correct sonication probe tip. Screw on required probe. Place tube/beaker holding fluid to be sonicated. Immerse probe in solution, adjust platform so end of probe is ½-way down into the solution. Switch power on.</td>
</tr>
<tr>
<td>11</td>
<td>Sonicating water bath</td>
<td>Take the required and optimum amount of liquid in the sonicating bath for avoiding spreading. The sonicating water bath should contain water to at least 5 cm depth. Place beaker in the water bath and switch on the power.</td>
</tr>
<tr>
<td>12</td>
<td>Nano-fluids preparation</td>
<td>To prepare high thermal conductivity coolant. REL, Bundoora. Appropriate amount of water-EG, nanoparticles. Sonicator probe,</td>
</tr>
<tr>
<td>13</td>
<td>Disposal</td>
<td>Avoiding any harm to the skin. Used hand gloves. Any spills agents must be handled carefully.</td>
</tr>
<tr>
<td>14</td>
<td>Repairs</td>
<td>Avoiding any damage and/or accident. Ensure the sonicator is in good working order before using it.</td>
</tr>
<tr>
<td>15</td>
<td>Relevant MSDS</td>
<td>Avoiding any kind of hazard. Understood the MSDS for any chemicals used in the solutions.</td>
</tr>
</tbody>
</table>

1. IDENTIFY THE HAZARDS
<table>
<thead>
<tr>
<th></th>
<th>(“Yes” indicates potential hazards.)</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHEMICALS CLASSED HAZARDOUS SUBSTANCES/ DANGEROUS GOODS (DG) - List each Hazardous Substance/Dangerous Goods to be used and provide a MSDS – refer to risks of each chemical and of the chemical process to be used. Note: If the project consists only of chemical reactions conduct a Chemical Risk Assessment.</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>GENERATED MISTS, FUMES, DUSTS- Does the process generate mists, fumes or hazardous dusts? i.e. explosive conditions. Refer to MSDS.</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Can suffocation result due to lack of oxygen if a leak occurred? Could gases displace the oxygen?</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>COMPATIBLE CONTAINMENT – If decanting chemicals are the containers to be used, chemically resistant? (e.g. fuel can to store fuel)? Ensure you label all containers with Hazardous Chemicals and Dangerous Goods class the same as the original container. Is there adequate bunding or a spill kit available for the quantity of chemicals to be used in the area?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>HIGH or LOW TEMPERATURE – Does the process involve a high or low temperature hazard? i.e. above 40C and below 10C</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Can anyone be injured by unintended fire or naked flames?</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>Is there a possibility of an explosion intentionally or otherwise?</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>5</td>
<td>IONISING RADIATION - Are X-Rays, Alpha, Beta, Gamma or other energetic sub-atomic particles being used in this operation? Check equipment operation manuals and refer to Radiation Officer.</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>6</td>
<td>NON-IONISING RADIATION - Are Radio waves, microwave, infrared, visible or ultra violet used at harmful levels? Check equipment operation manuals and refer to Radiation Officer.</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>7</td>
<td>LASER RADIATION - Are collimated beams (e.g. laser pointers) of energy used in its operation? Check equipment operation manuals and refer to Radiation Officer.</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>PRESSURE or VACUUM – Does the process apply pressure or vacuum to cylinders, vessels, or connecting lines?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------------------------------------------------------------------------------------------------------</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>8.1 High pressure fluid e.g. Hydraulic lines used?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>GAS CYLINDERS – Are any gas cylinders used in the process? What size?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>ELECTRICAL - Can anyone be injured by electricity due to:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1 When moving or operating equipment can parts of the equipment contact live electrical power supplies inside or outside buildings</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2 Overloading of electrical circuits? i.e. piggy backed power boards</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.3 Damaged or poorly maintained electrical leads, switches and cables? Visual inspection.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.4 Water near electrical equipment? i.e. sinks near power outlets or rigs with heaters in water (FC produces water &amp; Nano-fluids)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.5 Exposed power or lack of isolation? Visual inspection by an authorized Technical Staff member for any possibly hazardous wiring. Check for Electrical Emergency Stops on equipment and be aware of them. Note: For low voltage wiring, insulation must be used for electrical work which are below the low voltage limits and above 60V DC and 80V AC – check with the authorised Technical Staff member</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.6 Electrical items not tested and tagged [T&amp;T] (all mains powered equipment needs testing and tagging)? List all electrical equipment to be used and ensure you check for T&amp;T labels before operation List any new equipment requiring T&amp;T. or any equipment past the due date (as indicated on the T&amp;T label)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1. IDENTIFY THE HAZARDS (continued)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>MANUAL HANDLING - Can anyone using equipment or performing a task be injured due to:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.1 Uneven or slippery work surfaces?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.2 Poor housekeeping e.g. obstacles or waste being placed in a work space?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.3</td>
<td>Lack of proper work platform, stairs or ladders?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.4</td>
<td>Lack of guard rails or other suitable edge protection on equipment as necessary?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>Unprotected holes or gaps?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.6</td>
<td>Steep walking surfaces?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.7</td>
<td>Collapse of the supporting structure?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.8</td>
<td>Repetitive or sustained postures, movement or forces?</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.9</td>
<td>Lifting and moving around of heavy items during testing or construction</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.10</td>
<td>Other manual handling risks (Sonicator, Electrical conductivity Meter)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>11.11</td>
<td>Poor ergonomic design of equipment when operating?</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

Note: Conduct a manual handling risk assessment if there is a potential for musculoskeletal injury. (Use Manual Handling Risk Assessment Form) (see RMIT website: Staff: Health & Safety: Policies & Procedures: Personal Health & Safety: Manual Handling procedure>Supporting documents tab: Manual Handling Risk assessment form) and attach to this Risk Assessment

| 12   | MECHANICAL - Can any person or body part be physically injured by: |
| 12.1 | Hair, clothing, gloves, jewellery, limbs, rags or other materials become entangled with moving parts? | X |
| 12.2 | Being trapped or sheared between parts of the equipment or between the equipment and structures/work pieces? | X |
| 12.3 | Material falling off equipment or work pieces being ejected? Excessive vibration causing failure of parts or control? | X |
| 12.4 | Uncontrolled or unexpected movement? Mobility of equipment e.g. uncontrolled vehicle? | X |
| 12.5 | Equipment/process unable to be slowed stopped or immobilised (e.g. when no emergency stop button is fitted)? | X |
### 12. IDENTIFY THE HAZARDS (continued)

| 12.6 | The equipment tipping or rolling over? For rotating parts could they be unbalanced? | X |
| 12.7 | Parts of the equipment/object collapsing in operation? | X |
| 12.8 | Being thrown off or under? | X |
| 12.9 | Coming into contact with sharp or flying objects? | X |
| 12.10 | The equipment, parts or work pieces disintegrating? | X |
| 12.11 | Being burned by friction due to contact with moving parts or surfaces, or material produced by a process? | X |
| 13 | NOISE- Will the process produce noise at a hazardous or uncomfortable level? i.e. above 80dB | X |

Note: Conduct a noise risk assessment if there is a potential for injury due to noise. (Use Noise Risk Assessment Form) (see RMIT website: Staff: Health & Safety: Policies & Procedures: Personal Health & Safety: Noise Management Procedure:>Supporting documents tab: Noise \management Risk assessment form) and attach to this Risk Assessment

| 14 | INDUCTION/TRAINING – Do you require induction in the safe use of the laboratory in this area?  
Do you require training to use the specific equipment as required? | X |
| 15 | OTHER - Please specify: | X |
## 2. ASSESSING THE RISK

<table>
<thead>
<tr>
<th>No.</th>
<th>Describe the Hazard (Number as per section 1 and list the hazards identified that require control)</th>
<th>Identify the Risk / Outcome (injury, illness e.g. Crushing)</th>
<th>Risk Assessment Equipment or process with current (standard) controls in place (Use risk score matrix found below this table)</th>
<th>Risk Score CxExP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogen is classed as a dangerous good 2.1, and is a simple asphyxiant. (Activities 1, 3, 4, 5, 6)</td>
<td>Extremely flammable gas, may explode if heated. Exposure to moderate concentrations may cause dizziness, headache, nausea and unconsciousness. Under fault conditions leaking hydrogen may accumulate in the atmosphere, leading to asphyxiation.</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>2a</td>
<td>Titanium (IV) Oxide Nano-powder is classed as Xn Harmful. (Activities 7, 11, 12, 13)</td>
<td>Harmful by inhalation. Irritant to skin and mucous membranes. Irritating effect on the eye.</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>2b</td>
<td>Copper (II) Oxide Nano-powder is classed as XI Irritant. (Activities 7, 11, 12, 13)</td>
<td>Irritating to skin, eyes and respiratory system Acute toxicity Subacute to chronic toxicity</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>2c</td>
<td>Alluminum Oxide (gamma) Nano-powder is classed as XI Irritant. (Activities 7, 11, 12, 13)</td>
<td>Irritating to skin, eyes and respiratory system Acute toxicity</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>2d</td>
<td>Alluminum Oxide (alpha) Nano-powder is classed as XI Irritant. (Activities 7, 11, 12, 13)</td>
<td>Irritating to skin, eyes and respiratory system Acute toxicity Subacute to chronic toxicity</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Effects</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>Zinc Oxide powder is classed as Xn Harmful. (Activities 7, 11, 12, 13)</td>
<td>Harmful by inhalation.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Irritant to skin and mucous membranes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Irritating effect on the eye.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>Diamond Powder. (Activities 7, 11, 12, 13)</td>
<td>Irritating on the eye</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>The fuel cell uses hydrogen fuel.</td>
<td>Under fault conditions leaking hydrogen may accumulate in the atmosphere, leading to asphyxiation or explosion.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Moderate concentrations within an enclosed environment may cause dizziness, headache, nausea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>The fuel cell uses hydrogen fuel.</td>
<td>Under fault conditions leaking hydrogen may ignite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>or accumulated leaking gas may explode above concentrations of 4%.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>This may cause burn injuries or death from explosion.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>The fuel cell uses hydrogen fuel.</td>
<td>Under fault conditions leaking hydrogen may ignite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>or accumulated leaking gas may explode.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>This may cause burn injuries or death from explosion.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>Burns from contact with the tip of a soldering iron during electronic assembly. (Activity 8)</td>
<td>Possible minor injury such as skin burns.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen fuel is stored at high pressure (13MPa) in compressed-gas cylinders. The high-pressure storage is outside of the REL in a locked supply cabinet.</td>
<td>Rupture of a high pressure storage vessel may cause injury or death from metal shrapnel or explosion.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3e</td>
<td>The fuel cell reacts hydrogen fuel with atmospheric oxygen, producing water. (Activities 1, 3, 4, 5, 6)</td>
<td>Water may come into contact with DC electric power cables, with consequent risk of minor (ELV) electric shock.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3f</td>
<td>The high frequency sound during sonication. (Activities 10, 11, 12, 14)</td>
<td>The high frequency sound emitted by the sonicator can damage the hearing.</td>
<td></td>
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</tr>
<tr>
<td>4a</td>
<td>Sonicating water bath by splitting water may cause hazards. (Activities 11)</td>
<td>By splitting water or liquid, working place may become slippery.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>Sonicator Probe may cause injury and damage. (Activities 10, 14)</td>
<td>Without proper screwed probe can make damage. Bigger probe more than requirement can break the container.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|   |   |   |   |   |   |
|---|---|---|---|---|
|   | 50 | 3 | 0.5 | 75 |
|   | 15 | 3 | 1 | 45 |
|   | 5 | 6 | 1 | 30 |
|   | 1 | 1 | 3 | 3 |
|   | 1 | 3 | 3 | 9 |