Electrodeposited Metal Nanostructures Fabricated by Dynamic Hydrogen Bubble Templating

A thesis submitted in the fulfilment of the requirements for the degree of

Doctor of Philosophy (Applied Chemistry)

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BSc (Applied Sciences) (Honours)

BSc (Applied Sciences)

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November 2016
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.

Daniel Oppedisano

November 2016
Acknowledgements

There is a great number of people who I must thank for all their guidance, help, support and encouragement throughout this research.

To start with I would like to greatly thank my senior supervisor Dr. Lathe Jones, for his guidance, knowledge, insight, help and support throughout this research. He has been responsible for teaching me the workings of electrochemistry and has given me tonnes of advice from the commencement of this degree and hopefully into my developing career.

I would like to thank Prof. Suresh Bhargava for giving me the opportunity to undertaken this degree. By allowing me to be a part of the Centre for Advanced Materials and Industrial Chemistry (CAMIC) has giving me great access to excellent facilities and highly knowledgeable researchers. I would also like to thank his for this enthusiasm and support since my undergraduate study and into this post-graduate research.

Dr. Selvakannan Periasamy wealth of knowledge in the fields of surface analysis and catalysis have been greatly helpful in understanding XRD and XPS. It is always a pleasure going to discuss my work with Kannan, and receiving a great range of useful ideas, and ways to strive to make my research better. Thank you for all your support and guidance, especially in the later stages of my research.

Very special mentions to my peers come brilliant young professionals Dr. Fiona Charalambous, Dr. Blake Plowman and Dr. Rahul Ram. Each in their own way have been there to improve, encourage and support my research throughout its development. They are always available for a discussion or to review piece of work and to impart their experience and knowledge.
At RMIT, I have been privileged to have excellent access to specialised scientific instrumentation. The RMIT Microscopy and Microanalysis Facility (RMMF) has been valuable with special thanks in particular to Mr. Phil Francis and Dr. Matthew Field. I would also like to thank the building 3 facility and Mr. Paul Morrison (ICP-MS) and Mr. Frank Antolasic (XRD).

This research would not have been possible without the excellent laboratories at RMIT and those who manage their day-to-day operations. Thanks to Mr. Karl Lang, Mrs. Nadia Zakhartchouk, Mrs. Zahra Homan, Mrs. Ruth Cepriano-Hall and all the prep-room staff for their expertise and friendliness, allowing our research to run as smooth as possible.

I would also like to thank the financial support from RMIT’s School of Graduate Research for the scholarship I received to undertake my studies.

In my time at RMIT I have met many people who I now call my friends. I would like to thank my close friends Bebeto Lay, Dr. Melissa Kelson and Dr. Katie Tur for all the fun and for being there for both the good times and for those frustrating times. I would also like to thank my peers come friends Amanda Abraham, Yunnita Francesca, Victoria Coyle, Vishal Minstry, Dr. Scott McMaster, Dr. Aaron Raynor, Baiyu Ren, Qing Loh, Dr. Andrew Basile, Dr. Vivian Li and Sam Jackson. I would also like to thank the other great people I who have helped me along the way. Thanks to Dr. Ben Alford, Dr. Steve Priver, Dr. Ilija Najdovski, Dr. David Yao and Ms. Manika Mahajan.

I wouldn’t have been able to do it without the support and encouragement from my friends outside of the university, so thank you to Daniel, Lauren, Jenette, Nicole, Brad, Melissa, Christina and Jenifer.
I also appreciate my ever reliable and understanding work place Coles, where I have some
great bosses who have allowed the flexible work and study arrangement.

I finally would like to thank my family. My parents Michael and Sharon have been the
greatest support throughout my entire university studies, always showing their enthusiasm
and love unconditionally. All of my grandparents, especially my grandmother, Judith, who
was always so generous, loving and proud, unfortunately didn’t get to see me finish this
thesis but you will always be remembered.
In loving memory of my grandmothers

Francesca Maria Oppedisano (1927-2013)

Judith Wright (1938-2016)
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<td>a.u.</td>
<td>Arbitrary Units</td>
<td></td>
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<td>Ag/AgCl</td>
<td>Silver/Silver Chloride reference electrode</td>
<td>+0.210 V vs. SHE</td>
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<td>C&lt;sub&gt;dl&lt;/sub&gt;</td>
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<tr>
<td>FCN</td>
<td>Hexacyanoferrate (III) or Ferricyanide</td>
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<tr>
<td>H&lt;sub&gt;ads&lt;/sub&gt;</td>
<td>Hydrogen Adsorption</td>
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<tr>
<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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<tr>
<td>Hys Cycle</td>
<td>Hybrid Sulfur Cycle</td>
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<tr>
<td>i</td>
<td>Current</td>
<td>A / mA</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectroscopy</td>
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<tr>
<td>IHP</td>
<td>Inner Helmholtz Plane</td>
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<tr>
<td>j</td>
<td>Current Density</td>
<td>A cm&lt;sup&gt;2&lt;/sup&gt; / mA cm&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Exchange Current Density</td>
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<tr>
<td>η</td>
<td>Overpotential</td>
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<td>OCP</td>
<td>Open-circuit potential</td>
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<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
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<td>Proton Exchange Membrane</td>
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<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
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<td>Roughness Factor</td>
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<td>Sodium Borohydride</td>
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<td>Scanning Electron Microscopy</td>
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<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode $E^0 = 0.0 \text{ V}$</td>
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<tr>
<td>SSA</td>
<td>Specific Surface Area $m^2/g$</td>
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<tr>
<td>STS</td>
<td>Sodium Thiosulfate</td>
<td></td>
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<tr>
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<td>X-ray Diffraction</td>
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Abstract

The thesis describes the preparation of a range of nanostructured films utilising electrodeposition at high overpotentials, where metal deposition is accompanied by the evolution of hydrogen (H₂) bubbles, by a method termed Dynamic Hydrogen Bubble Templating (DHBT). The DHBT method provides a versatile route to a range of nanostructured, highly porous, high surface area metallic materials through the use of H₂ bubbles as a template. Materials can be produced with controlled surface properties including morphology, composition, porosity and electronic environment.

It has been shown through the use of electrodeposition by the DHBT method, how changing simple deposition parameters including the applied potential, deposition time and electrolyte composition can be used to control the properties of the materials deposited. The two factors that are important in controlling morphology are the H₂ bubble behaviour and the metal nucleation and growth during electrodeposition.

It was shown that changes in the hydrodynamic conditions during electrodeposition can be used to force metals with slow deposition kinetics into diffusion limited growth regimes. Ruthenium, a metal with slow deposition kinetics was electrochemically deposited as dendrites for the first time. The turbulent conditions caused by the H₂ bubbling compresses the diffusion layer, which when combined with the high overpotential, allowed access to Ru with a dendritic morphology. The oxidation state of these Ru materials were controlled to yield ruthenium dioxide (RuO₂), which is an important for capacitance and catalysis applications.
The DHBT method reliably formed a porous gold (Au) nanostructured honeycomb film, which was directly compared with model Au nanoparticles for activity towards the sulfur dioxide (SO₂) oxidation reaction. It is shown that DHBT allowed a morphology active for electrocatalysis to be accessed. When compared to low index Au nanoparticles, the dendritic morphology of the Au honeycomb showed a lower overpotential for SO₂ oxidation. This showed how the films made by this method could be used as an active alternative to supported nanoparticles.

The DHBT method was used to prepare multimetallic films that are candidates for a large number of catalytic reactions. Deposition under diffusion limited regimes by DHBT overcomes kinetic limitations that arise when depositing metals with different deposition rates, which allowed for control over the noble metal content in multimetallic structures. The facile fabrication of multimetallic films occurred with the addition of small amounts Au and palladium (Pd), and Au to a copper (Cu) electrolyte. It was shown how very small amounts of noble metals could significantly change the morphology and composition, while affecting the crystal lattice of Cu. High specific surface area films were prepared with less than 5% of noble metal content, sufficient to exhibit optimised catalytic activities. The films were found to be a solid solution, where the Cu acted as the host in which the noble metals were dissolved. The films displayed surfaces enriched with noble metals, which is desired for catalytic applications and allows for expensive noble metals to be placed at the surface where they are most effective. It was found that Au enriched over Pd and Cu due to surface strain, and because of Pd catalysed electroless deposition of Cu. It was shown that the synergism obtained by the combination of three metals (e.g. CuAuPd), was effective at increasing the catalytic activity, particularly for the hydrogen evolution reaction (HER).
The CuAuPd films were optimised by changing the electrolyte composition, where the morphology and surface chemistry were affected. For HER reaction, it was found that whilst increased noble content for the CuAu20Pd10 film had the highest reaction rate, the CuAu10Pd10 proceeded with a much lower onset potential without significant rate loss. Therefore, an increased noble metal content was not required for optimisation of the film properties.

Films with the addition of Au and Pt to Cu were prepared, with their catalytic activity tested for model reactions and the sodium borohydride electrooxidation reaction for the direct borohydride fuel cell. The small amounts of noble metals caused drastic changes to the morphology and properties of Cu based films. Au and Pt both surface enrich to a greater extent in the bimetallic films than in the trimetallic film, with CuAu having a greater noble metal content than CuPt. However, in the trimetallic films, the Pt content in the surface was greater than Au, due to the interchangeability of Pt with Cu at the surface rather than a surface strain effect. The trimetallic films were more effective for model catalytic reactions compared to bimetallic films, even with lower noble metal contents.

These porous nanostructured films are ideal for possible alternatives to nanoparticles that are currently used for fuel cell reactions. They are conveniently prepared by electrodeposition in a single step procedure. The CuAuPt films were applied towards the electrooxidation of NaBH₄, where surface properties are critical for activity and to the reaction pathway taken. This was a demonstration of how films prepared by the DHBT method could be used as an alternative to supported nanoparticles. CuPt10 was the most active for the direct oxidation pathway, but was also active for the indirect hydrolysis pathway. The combination of CuAuPt was able to reduce the hydrolysis pathway, whilst
allowing the direct oxidation pathway to proceed at a lower reaction potential. The stability at a constant operating potential was improved on a trimetallic film compared to a bimetallic films.

The thesis has studied the fabrication of a range of surfaces by DHBT, and shown that DHBT can be used to access a wide variety of different metallic nanostructures in a simple and controlled manner using H₂ bubbles produced at high overpotential. These materials have good chemical and structural stability, which present themselves excellent candidates for applications in reactions where catalysts based on supported nanoparticles have suffered from long term stability problems. Studies on the effect of experimental conditions on the morphology and structure of the films obtained has greatly increased our understanding of the factors that control the properties of films made by this method, and have opened the path for a greater range of films to be made in future work with superior control.
Chapter 1

Introduction
1.1 Background

As the world we live in grows and becomes more advanced, with more people to feed, transport and entertain, so too does our energy requirement. The energy demand is expected to increase by one third of the current demand by 2040.[1] Energy generation and storage are intense areas of research as there is always an increasing demand for more power and ways in which to store it. One of the main issues surrounding energy is our reliance of fossil fuels and limitations to current technologies. The uncertainty in remaining fossil fuel reserves such as coal, oil and natural gas is one of the main driving forces behind investigation into new technologies.[2] Oil is predicted to be the first fossil fuel to be exhausted, with coal having the largest and more stable reserve quantity.[3] The other main issue is the overwhelming acceptance among the scientific community (97 % of climate scientists) that climate change is real, and that the release of greenhouse gasses due to human activity, including the burning of fossil fuels, is a significant contributor to global warming.[4] Therefore cleaner, greener and renewable fuels are required for future energy needs. Alternative fuels include hydrogen and small organic molecules including methanol and ethanol, which all can be obtained from sustainable, renewable sources.

Generation of energy from alternative fuels generally requires materials called catalysts. At the core of emerging energy technologies are metal nanoparticles and nanostructured materials,[5] with a particular focus on utilising noble metals including platinum (Pt),[6, 7] ruthenium (Ru),[8] palladium (Pd),[9] and gold (Au).[10] The advantage of noble metals are that they are highly stable and are very active for the catalysis of important reactions whilst being resistant to chemical attack and wear. Therefore they are in high demand, which, when coupled to their low abundance, results in their high cost that has limited their
economic use. Pt in particular is highly sought for its nobility, being extremely chemically and thermally stable, as well as its high catalytic activity. Due to its versatility and use in a number of application and its low earth abundance, Pt is the second most expensive metal, the most expensive being Au.[11] Therefore there is an inherent need to reduce the reliance on these precious metals by restricting the amount we use in applications, or to find alternatives.

1.2 Applications of Electrodeposited Metal Nanostructures

Nanostructured metal materials are at the core of new technologies for production and storage of energy,[12, 13] as well as for applications such as sensing.[14-16] Metal nanoparticles and nanostructures can be implemented as electrocatalysts in fuel cells. Fuel cells are able to convert chemical energy of renewable fuels to electrical energy more efficiently, and with lower emissions, than current fossil fuel burning technologies.[17] As for the storage and delivery of this energy, super or pseudo-capacitors are high-capacity electrochemical capacitors capable of delivering more power faster and for more cycles than many currently available technologies.[18]

1.2.1 Catalysis

Catalysis, in its simplest terms, is the broad area of study that involves increasing the rate of a chemical reaction. The key is for the catalyst material to increase the reaction rate or selectivity, but not be consumed during the course of the reaction. Catalysts provide alternative pathways for reactions, usually occurring at lower activation energy, improving the reaction kinetics for the desired process. Catalysts can either be homogeneous or heterogeneous, however, due to ease of separation from the reaction mixture,
heterogeneous catalysts are preferred. Bimetallic catalysts have been shown to increase the stability, selectivity and activity of reactions due to a combination of one or more of the three synergistic effects: the third-body effect, bi-functional mechanisms or electronic effects.

Model catalytic reactions are a useful way to pre-screen and characterise suitable catalytic materials. A model reaction must be one which satisfies three main criteria:

- The reaction must be well-controlled and proceed directly without any by-products or side reactions
- It must not proceed, or only proceed to a negligible extent, without the presence of a catalyst
- It must be performed under mild conditions at mild temperatures and solvents.[19]

A model reaction that can be used to evaluate the catalytic properties of a material under ambient conditions at open-circuit potential (OCP) is the reduction of hexacyanoferrate(III), also termed ferricyanide (FCN), by sodium thiosulfate (STS).[20-23] This reaction is performed at room temperature in water, with the reaction monitored easily by UV-Visible Spectroscopy (UV-Vis). It is a redox reaction where the two half reactions are the oxidation of \(S_2O_3^{2-}\), and the reduction of \(Fe(CN)_6^{3-}\), and proceeds according to Equation 1.1.

\[
2[Fe(CN)_6]^{3-} + 2S_2O_3^{2-} \rightarrow 2[Fe(CN)_6]^{4-} + S_4O_6^{2-} \quad (1.1)
\]

The catalyst surface is required to act as a proxy to ferry electrons from thiosulfate across to reduce FCN. The reaction proceeds to a negligible extent, \(-2.50 \times 10^{-6} \text{ s}^{-1}\),[24, 25] without a catalyst, therefore satisfying the final criteria point, ensuring its suitability to act as a model
for insights into the catalytic function of a material. As the reaction occurs at the surface of the catalyst, the surface properties can be studied and compared.

### 1.2.2 Electro catalysis

Electrocatalysis is an extremely important area of research, especially in regards to energy generation. Unlike conventional catalysis, electrocatalysis involves an electrochemical reaction at a polarised electrode, and requires the application of a potential to drive the reaction, resulting in a current. Fuel cell reactions usually consist of two redox reactions, one at the cathode and one at the anode. The oxidation at the anode is typically of small organic molecules such as methanol,[26] ethanol,[27] or formic acid,[28] which all require a electrocatalyst to proceed, as their rate is too slow in the absence of a catalyst to make fuel cells viable. A basic proton exchange membrane fuel cell (PEMFC) schematic is displayed in Figure 1.1. The cell consists of two electrodes, an anode and a cathode, separated by a polymer electrolyte membrane, or proton exchange membrane (PEM) as it is also called, that only allows the conduction of protons.[17] Currently, fuel cells utilise supported Pt nanoparticles as electrocatalysts on both the anode and the cathode.[17, 29]

Fuel cells utilising hydrogen gas and air are starting to become commercially available, and so called Fuel Cell powered Vehicles (FCV) are on the market today.[30-32] However, their purchase costs are high, partly due to the 10 g of expensive, pure Pt particles loaded onto porous carbon supports used for the electrodes,[33] and issues surrounding hydrogen production and storage for these fuel cells has limited their adoption. An alternative fuel cell under heavy development is the Direct Methanol Fuel Cell (DMFC).[26, 34] It uses liquid methanol, which is sourced from renewable resources and is easily stored and transported by existing infrastructure. There are a number of other fuel cells under development,
including Direct Formic Acid Fuel Cells (DFAFCs),[35] Direct Ethanol Fuel Cells (DEFCs),[27, 36] as well as lesser known fuel cells including the Direct Borohydride Fuel Cell (DBFCs).[37] Notably the latter involves an Anion Exchange Membrane instead of a Proton Exchange Membrane that is used for the other fuel cell types mentioned, however the same working principles apply.

![Figure 1.1 Proton Exchange Membrane Fuel Cell Schematic.](image)

There are other important electrocatalyst reactions, such as Sodium Borohydride (SBH) oxidation for Direct Borohydride Fuel Cells (DBFCs),[37] the Hydrogen Evolution Reaction (HER), Sulfur Dioxide (SO$_2$) Oxidation,[38] Oxygen Reduction Reaction (ORR),[39] and the Oxygen Evolution Reaction (OER).[40] These reactions, regardless of whether they are anodic and cathodic, use Pt for a catalyst, which is usually in the form of supported Pt nanoparticles to minimise Pt usage and maximise activity.

There are a number of challenges pertaining to all fuel cells with regards to both the PEM and the electrode catalysts. In regards to the electrocatalysts, there are issues due to activity, stability and cost. There are large overpotentials involved in most fuel cell reactions
that significantly reduce their efficiencies, which acts as an impediment to their practical use. These are related to the energy requirements for breakage of the chemical bonds in the fuel on the anode and the O=O bond on the cathode, which usually occurs through complicated, multi-electron mechanisms. Adsorption and desorption of reactants and products is another factor that may poison the catalyst surface and result in large overpotentials.[7] Thus far, nanoparticles containing Pt are the most efficient towards catalysing reactions, however there is a significant cost element in regards to both the fabrication of the catalysts and high cost of the metal, as well as issues regarding prolonged stability and activity. While nanoparticles have high activities, there are difficulties in stabilising them.[21, 41] They can also suffer poisoning through the strong adsorption of intermediates. The combination of two or more metals has been found to improve stability and activity issues,[40, 42] but despite growing research alternative cheaper materials have not quite matched the activities of noble metals.

It has been shown that the method of preparation of electrocatalytic materials directly effects their performance.[43] Studies are often focussed on finding improvements into catalyst fabrication methods with the aim to improve activity, stability and selectivity. Improvement in activity can be demonstrated by reducing the onset or reaction potential for an electrochemical reaction to proceed, and/or to enhance the rate of reaction, i.e. increase the operational current density. Any energy input that is required over the standard reduction potential, \( E^0 \), is designated as an overpotential, \( \eta \). Overpotentials in redox reactions can add significant operational costs to a cell and reduce cell performance.
Butler-Volmer theory relates electrode kinetics of electron transfer to the activation energy, $E_a$, and the electrode potential, $E$. It accounts for both anodic and cathodic reactions (Equation 1.2).[44]

$$j = j_a + j_c = j_0 \left[ \exp\left(\frac{\alpha_a nF\eta}{RT}\right) - \exp\left(-\frac{\alpha_c nF\eta}{RT}\right)\right] \quad (1.2)$$

Where:

- $j_a$ and $j_c$ = the current density at the anode and cathode, respectively
- $j_0$ = the exchange current density
- $\alpha_a$ and $\alpha_c$ are the charge transfer coefficients at the anode and cathode, respectively
- $n$ = number of electrons
- $F$ = Faraday's constant (96500 C mol$^{-1}$)
- $\eta$ = overpotential where $\eta = (E - E^0)$
- $R$ = the gas constant (8.314 J K$^{-1}$ mol$^{-1}$)
- $T$ temperature in Kelvin

$j_a$ and $j_c$ are related to the standard rate coefficients, $k_a$ and $k_c$, for the anodic and cathodic reaction, respectively. As the potential is changed, $k_a$ and $k_c$ are influenced in an exponential fashion as shown in Equation 1.2.[44]

The Butler-Volmer equation (Equation 1.2) describes a situation where the charge-transfer step is responsible for exclusively determining the rate of reaction and does not take into account mass transfer phenomena such as migration and diffusion, which would become important at higher overpotentials. $j_0$, the exchange current density, is an indication of the intrinsic rate of a redox reaction. If $j_0$ is small, a large overpotential, $\eta$, is required to obtain an appreciable current density. By applying a large $\eta$, cathodic or anodic currents will flow. If
an intermediate η is applied, both currents will flow. The larger the \( j_0 \) is, the higher the current obtained at lower overpotentials. Electrocatalytic activity is thus demonstrated by the reduction in overpotential to achieve a desired current density.[45]

As the current state-of-the-art of electrocatalysts thus far consist of supported nanoparticles, an active area of study is to devise new ways to make metal materials of high surface area that are active electrocatalysts. Stability over a longer time scale, without the complications of a support that is necessary for nanoparticles, is desirable, with the long term view of implementation in fuel cells and other energy related devices.

### 1.2.2.1 Hydrogen Evolution Reaction (HER)

A well-studied, documented and accessible model electrochemical reaction is the Hydrogen Evolution Reaction (HER). It is a surface based reaction that involves the combination of hydrogen ions (H\(^+\)) at an electrode interface, and the passage of electrons to form hydrogen (H\(_2\)) bubbles, which then detach and evolve into the electrolyte as H\(_2\) gas.

Generally HER proceeds in three steps in both acid and alkaline solutions.[46, 47]

1) Electrochemical hydrogen adsorption according to the Volmer reaction:

\[
H^+(aq) + M + e^- \leftrightarrow MH_{ads} \tag{1.3}
\]

2) Followed by Electrochemical desorption according to the Heyrovsky equation:[48]

\[
MH_{ads} + H^+(aq) + e^- \leftrightarrow M + H_2(g) \tag{1.4}
\]

3) Chemical desorption according to the Tafel reaction:

\[
2MH_{ads} \xleftrightarrow{\ k_3\ } 2M + H_2(g) \tag{1.5}
\]

The reaction rate for H\(_2\) evolution can be compared amongst different materials using the exchange current density, \( j_0 \). Plots of \( j_0 \) with respect to the Metal-Hydrogen (M-H)
chemisorption energy or $\Delta E_H$ exist in the form of volcano plots (Figure 1.2) that visually layout metals side by side.[49, 50]

![Figure 1.2](image)

*Figure 1.2 Experimentally measured exchange current, $\log(j_0)$, for hydrogen evolution over different metal surfaces plotted as a function of the calculated hydrogen chemisorption energy per atom, $\Delta E_H$ (top axis). Reprinted with permission from ref [49].*

The chemisorption energy, $\Delta E_H$, is an important factor as it describes how well hydrogen binds to the surface of the metal. Metals with a weak interaction do not allow sufficient time for the transfer of electrons to take place, while those with an interaction that is too strong, cause the hydrogen to ‘stick’ too well to the surface causing difficulty in releasing hydrogen. The bottom portion of Figure 1.2 compares the Gibbs energy. It shows that Pt (and Ir) are the closest metals to being thermoneutral, which reflects their high $j_0$, compared to the other metals on the arms of the volcano curve. The rate of HER on various metals is thus directly determined by comparison of the $j_0$ and the M-H interaction.
1.2.2.2 The Hybrid Sulfur (HyS) Cycle and Sulfur Dioxide (SO₂) Oxidation

The study of the oxidation of sulfur dioxide (SO₂) is not a new topic, however it is still not well understood. The first electrochemical study was performed in 1953 by Rozental and Veselovsky,[51] with mechanistic and speciation studies being performed since the 1960s.[52, 53] The SO₂ oxidation reaction is of great importance, both for fundamental and applied areas of electrochemistry. In the 1980s, the reaction was the focus for desulfurisation and removal of SO₂ from flue gases. SO₂ is one of the most hazardous pollutants that enters the atmosphere from industrial feeds.[54] In the past ten years, the SO₂ oxidation reaction has seen renewed interest for its application towards water splitting for the production of hydrogen in the Hybrid Sulfur Cycle (HyS cycle), otherwise known as the Westinghouse Cycle.[55-58]

The HyS cycle is a large scale thermochemical cycle used to split water to produce H₂. The ‘thermo’ part of the name, coming from the thermal degradation of sulfuric acid to produce SO₂, and ‘chemical’ involving the electrochemical oxidation of SO₂ (Figure 1.3). The source of heat for the degradation step can either be nuclear or solar.[59] The electrochemical process occurs in a cell called an electrolyser. The electrolyser is a Proton Exchange Membrane (PEM) Fuel Cell, consisting of two compartments separated by the PEM, similar to that in Figure 1.1.
The key reactions occurring in the reaction are the reduction of H\(^+\) at the cathode (Equation 1.6) and the oxidation of SO\(_2\) at the anode (Equation 1.7) that yields the overall reaction in Equation 1.8

\[
2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^0 = 0.00 \text{ V} \quad (1.6)
\]

\[
SO_2(aq) + 2H_2O (l) \rightarrow H_2SO_4(aq) + 2H^+(aq) + 2e^- \quad E^0 = 0.157 \text{ V} \quad (1.7)
\]

\[
SO_2(aq) + 2H_2O (l) \rightarrow H_2SO_4(aq) + H_2(g) \quad E^0 = 0.157 \text{ V} \quad (1.8)
\]

H\(_2\) evolution occurs close to thermodynamic predictions, however the anodic oxidation of SO\(_2\) has a large overpotential. This is believed to be due to kinetic limitations and electrodes that have varying catalytic abilities.[59] The reaction mechanism, and the effect of the electrode on catalysis is still not well understood.

The reason why the HyS cycle is so attractive lies in the ability of SO\(_2\) to split water (Equation 1.8) at significantly lower potentials than by water electrolysis (Equation 1.9).

\[
2H_2O (l) \rightarrow H_2(g) + O_2(g) \quad E^0 = 1.229 \text{ V} \quad (1.9)
\]
The proposed conditions for the cycle involve high temperatures (\textsim 80^\circ C) and high acid concentration (> 6 M) which are required for the acid electrolyser to achieve optimal cycle integration and to reach the performance goal of 500 mA cm\(^{-2}\).[56] The main cost of the cycle lies with the acid electrolyser. An improvement would result in a 60 % decrease in the electrolyser area and significantly reduce electrolyser capital cost. 500 mA cm\(^{-2}\) was proposed for an applied voltage of 0.6 V.[56] So far, the achieved current density at 0.6 V for an aqueous feed is 200 mA cm\(^{-2}\).[59] It has been demonstrated that half of the applied voltage results in anodic overpotential.[53] To reduce the reaction overpotential further and thus improve the cycle efficiency are the key aims.

The primary electrodes used for the study of SO\(_2\) oxidation are either Pt or Au, with a significant portion of the literature for this reaction performed on Pt electrodes.[53, 54, 61-72] A few other electrodes have been studied, and for a time it was Pd that was considered to have the best activity, until it was discovered that corrosion of the electrode was occurring.[67, 73] Carbon and carbon based materials have also been employed, however they showed limited activity. Only through the addition of noble metals was any significant activity attained, as they perform better kinetically.[74] The most investigated material is Pt as it has the highest activity, however, there was a call for a significant change to the electrode surface for any further improvement in reaction overpotential or kinetics to be made.[75] There is a gap in the literature on the effect of morphology of noble metals on the oxidation of SO\(_2\), with only flat polycrystalline electrodes having been studied up until now.
1.2.2.3 Sodium Borohydride Electro-oxidation Reaction

Borohydrides are a valuable source of energy, either indirectly for hydrogen storage, or for the direct borohydride fuel cell (DBFC).[76] One of the main issues surrounding the use of hydrogen proton exchange fuel cells is the storage of gaseous hydrogen. Sodium borohydride, NaBH₄, is an excellent hydrogen storage material in a non-gaseous form, with a capacity of 10.8 wt % H, with H₂ accessible through the reaction with water.[77] However, NaBH₄ can also be used for energy generation when directly fed to a fuel cell anode of a DBFC. The DBFC is one of the lesser studied fuel cells that has been investigated even though it has a high theoretical cell voltage of 1.64 V, which is significantly higher than that of other fuel cells using hydrogen (1.24 V) or methanol (1.19 V).[76, 78]

Even though it was first proposed in the 1960s,[79] there has been a loss in momentum behind its development. This is partly due to the significant complexity in determining the mechanism of borohydride oxidation, which is a complex multi-electron process.[80] There are two proposed mechanistic pathways for the anode oxidation reaction. Equation 1.10 is the ideal reaction involving the direct eight electron oxidation pathway.[81] The indirect pathway involves hydrolysis and a four electron process as shown in Equation 1.11.[79] Because the hydrolysis reaction for hydrogen production has received more attention, the eight electron pathway is often overlooked.[82]

\[ BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \] (1.10)
\[ BH_4^- + 4OH^- \rightarrow BO_2^- + 2H_2 + 2H_2O + 4e^- \] (1.11)

The requirement for DBFCs is the eight electron oxidation process where NaBH₄ is used directly as the fuel, and whereby the high cell voltage of 1.64 V is obtained with a theoretically high anodic specific capacity of up to 5.7 Ah g⁻¹.[83]
Equation 1.11 is a simplified half reaction and a range of studies have revealed the four electron reaction pathway to be more complex. [81, 84-86] Borohydride initially undergoes hydrolysis, which results in the production of hydrogen according to Equation 1.12. However, this is an unwanted side reaction in this fuel cell as it limits the coulombic efficiencies and may prevent the direct eight electron process.

\[
BH_4^- + H_2O \leftrightarrow BH_3OH^- + H_2 \quad (1.12)
\]

The hydroxide species in Equation 1.12 gives way to the following two reactions in Equation 1.13 and 1.14, giving the release of four electrons and overall another mole of H\(_2\), bringing the total to two moles.

\[
\frac{1}{2}H_2 + OH^- \rightarrow H_2O + e^- \quad (1.13)
\]

\[
BH_3OH^- + 3OH^- \rightarrow BO_2^- + \frac{3}{2}H_2 + 2H_2O + 3e^- \quad (1.14)
\]

When the eight electron reaction proceeds and is combined with the cathodic reaction in Equation 1.15 it yields the overall reaction in Equation 1.10, which gives the high theoretical voltage of 1.64 V. [76, 78]

\[
2O_2 + 4H_2O + 8e^- \rightarrow 8OH^- \quad (1.15)
\]

\[
BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad (1.16)
\]

As borohydrides are usually associated with hydrogen storage rather than its direct use as a fuel, the initial primary objective was finding electrode materials with activity towards the catalysis of the hydrolysis reaction (Equation 1.12). [81, 84] Au is considered to be non-catalytic with regard to the hydrolysis reaction whereas Pt is known to be catalytic. Pt is also active for the eight electron oxidation. There are however, very limited studies on either Au or Pt materials.
To drive the eight electron direct oxidation pathway, it is essential to prevent the hydrolysis of borohydride from occurring. Working in alkaline solution significantly improves this, however it does not stop the hydrolysis completely. It has been shown that for the eight electron pathway to take precedence it is important to have the OH⁻/BH₄⁻ concentration ratio above 4.4.[81] Gyenge, and Martins et al. have investigated the use of thiourea (TU) to suppress H₂ evolution in favour of the direct oxidation pathway.[80, 87]. Pt has been shown to be the most active towards the eight electron oxidation and has been used, despite its high cost. Au, while being inactive for the hydrolysis reaction, is active for the eight electron oxidation.[82] Efforts have been previously made to reduce the Pt loading by combining it with Cu which had a reasonably good activity for the direct BH₄⁻ oxidation compared to bulk Pt.[78] Carbon supported CuPd nanoparticles have also been studied for their activity towards NaBH₄ electro-oxidation. It was found that the Cu addition was beneficial from both a cost and activity perspective.[86] PtAu catalysts have also been investigated, combining Pt’s high activity towards the four electron hydrolysis and Au’s direct eight electron process to drive the eight electron reaction at a faster rate.[88]

1.2.3 Capacitance

Energy storage is another area of energy research, and it concerns the preparation of suitable materials that are able to store and deliver power. Current battery technology, such as Nickel-Cadmium and Li-ion, have limitations in delivery of large bursts of power, and long-term cycling. Electrochemical supercapacitors solve issues the of power density, charge/rate and longevity,[89, 90] however, low energy density and high production costs are the major issues surrounding these technologies.[91]
Electrochemical supercapacitors have gained interest in the last few years for their applications, including peak-power sources for electric vehicles, back-up storage for calculators, lightweight electronic fuses, and starting power for fuel cells.\[92, 93\] There are two types of charge storage mechanisms, those based on double-layer capacitance and those based on pseudocapacitance.\[94\] Electrochemical double-layer capacitance involves the separation of charge at an electrode/electrolyte interface. Pseudocapacitance occurs due to fast, reversible faradaic processes at solid electrodes. For both mechanisms, accessible and active surface area of electrodes must be maximised.\[92\] The capacitance from reversible redox processes gives them high-energy and high-power densities due to their fast charge/discharge capacity.\[95, 96\]. Noble metal oxides have been identified as being ideal materials for supercapacitors as they are able to take part in fast faradaic reactions. Electrode materials are often made from metals with multiple oxidation states.\[92, 93, 95\]

### 1.3 Fabrication of Metal Nanostructures

Nanoparticle and nanostructure material synthesis is a very active area of research. Fabrication can be carried out via wet chemical synthesis methods, such as chemical reduction[6] and sol gel methods,\[97\] as well as physical methods such as physical and chemical vapour deposition,\[98\] and through electrodeposition.\[99\]
The methods for preparation of metal nanoparticles and structures (catalysts/electrocatalysts) can be separated into four main areas.[98]

- Wet chemical synthesis, such as sol-gel (colloidal) processes and surfactant based shape directional templating[97, 100-103]
- Impregnation,[104-106]
- vacuum and thermal decomposition (physical and chemical vapour deposition),[107-110]
- electrochemical methods.[111-114]

The wet chemical methods, such a sol-gels (colloids) and microemulsions,[115] usually require the use of additional capping, stabilising and shape directing agents.[97] They are often performed at elevated temperatures and pressures to attain varying degrees of control during fabrication. Sol-gel processes are complicated and the shape of the resulting materials are not well controlled.[92, 116] The requirement of surfactants and protecting agents in colloidal methods adds impurities, which are not easily removed. If they are able to be removed, changes to the nanostructure shape and surface will most commonly follow. Regardless, the additional agents can significantly affect the surface properties.[116]

The impregnation method is one of the simplest and most used methods. The support acts as the basis for the chemical process to take place, where the reactants are adsorbed and converted, however there is very little control of the size and morphology, with the nanoparticles being governed by the support.[98] Impurities are also a common problem.[104] To prevent impurities in the final deposit, high purity reagents are used, increasing the fabrication cost. Deposition methods are the favoured methods, as they can produce higher purity materials with a degree of control. Physical and chemical vapour
deposition methods require the use of high temperatures and pressures, as well as specialised equipment to produce high purity materials, but often involve difficulties in establishing uniform particle sizes.[98]

Electrochemical methods are the simplest of all the previously described methods, often employing deposition from simple and cheap aqueous salt solutions, with the deposition controlled by the applied current or potential. Electrodeposition is thus one of the most attractive methods for deposition of various particles and structures, due to its simplicity and versatility in controlling morphology.[99, 117-120] Electrodeposition will be discussed further in Section 1.4.

1.3.1 Morphology Control: The Effect of Shape, Size and Crystallography

Precise control is required to produce materials with advantageous properties of size, shape, morphology, crystallography and increased specific surface area.[43] By controlling key properties, materials can be tuned to obtain the greatest activity and functionality,[116] which is essential in being able to reduce noble metal loadings and increasing the specific surface area. Specific surface areas (SSAs) can be enhanced by increasing the active surface area in comparison to the amount of material physically being present in a film or material. The unit of measurement of specific surface area is m²/g. Specific activity is also an important parameter, especially in electrocatalysis, where the efficiency is measured as current vs. surface area, (i/cm²) also known as current density, j. However, efficiency can also be measured by current vs. weight of active material (i/g). In capacitance studies, the usual measure of effectiveness is the capacitance (Farads, F) per gram of active material, F/g.
Nanoparticles have been at the forefront in increasing our understanding of the effect of morphology on catalytic activity, elucidating reaction mechanisms and offer a technique to reduce noble metal loadings.[7, 43] Nanoparticles are useful tools for investigating the properties of reactions as a function of morphology, and there are numerous and well-documented fabrication studies producing particles of different size,[121] shapes,[6] and crystal orientation.[122, 123] Morphological features can profoundly affect the function and activities of nanoparticles and materials.[116, 124, 125]

Due to their small size, nanoparticles have a large surface area to volume ratio,[126] with high surface energies leading to shapes with irregular and specific orientations.[116] For example, it has been found with regard to the Oxygen Reduction Reaction (ORR) that there is a definite relationship between mass activity, dispersion and particle size.[127] There is a limit to effective nanoparticle size, and having nanoparticles that are too small can lead to a ‘negative’ particle size effect, whereby small particles are too small to contribute to catalysis and have a greater susceptibility to poisoning.[128]

Fundamental studies on single crystal structures have been able to show how specific crystal facets or specific shapes can have significantly different activities.[23, 123, 125, 129] Studies of such nature often involve the exploration of important catalytic reactions and the different activities achieved on each of the different crystal facets.[125, 130] For example, the shape of Pt nanoparticles, or more specifically the low index planes of Pt used, greatly affects the efficiency of methanol electrocatalysis, with results showing Pt (111) is more active than Pt (110), with Pt (100) being the least active facet.[45] It is therefore necessary to have control over fabrication of specifically shaped nanoparticles, as this leads to control
over orientation (which facets are exposed to solution) allowing identification and exploitation of active properties that are susceptible to surface crystallography.[129]

From a practical point of view, there are often activity losses due to instability and agglomeration of nanoparticles, leading to their necessity to be supported, usually on high surface carbon networks.[41] Nanoparticles, due to their size and specific crystal facets, are inherently very active, and this causes difficulties in regard to stabilising them, preventing agglomeration and minimising loss due to dissolution from supporting substrates.[23, 41, 131] Agglomeration and Ostwald ripening results in the loss of the desired shape, and hence loss of active sites and specific surface area. Dissolution and detachment is a significant issue on its own, leading to material loss, reduction to the surface area and a drop in performance.[41] The nanoparticles can be embedded or deposited elsewhere in a cell, such as the membrane, thus causing damage and even perforation leading to cell failure. Investigations into support material consumes a large part of the literature, especially in regards to stability for long term activity.[127, 128, 132-134] As such, the supporting material must be taken into account when considering the effectiveness of a nanomaterial.[6, 127] Difficulties can arise in regards to the support with conductivity and interconnectivity, surface area, hydrophobicity and porosity.[133] There are often difficulties in achieving loaded nanoparticles deep within (porous) carbon networks.[98, 99]

As highlighted above, there are a range of concerns and issues when using supported nanoparticles as electrocatalysts. As nanoparticles are often fabricated by wet chemical methods and then drop cast or fused onto an electrode, there are opportunities for issues to arise with regard to stability and loss of preferential size, shape and morphology upon agglomeration. To avoid some of the issues associated with nanoparticles, there have been
numerous studies looking at unsupported or self-supported nanostructured networks and films.[135, 136] Micro- and nano-structures can address the stability issues associated with the use of nanoparticles whilst still exhibiting specific surface properties comparable or better than those of nanoparticles.[120, 135, 136] Micro- and nano-metal structures can provide self-supported alternatives to nanoparticles, with acceptably high activities, whilst decreasing instability issues, fabrication and operation costs.[137] There are two distinct areas, smooth and rough structured materials. Smooth materials are usually thin single orientated 1-D and 2-D films, which aim to increase the activity without using larger quantities of noble metals and avoiding stability issues that arise with nanoparticles. Rough nanostructures take advantage of different shapes and morphologies, maximising the numbers of active sites, which increases the accessibility and results in large, stable specific surface areas.

Electrodeposition offers an attractive way to produce electroactive materials in an ‘in-situ way’ that avoids stability issues that can occur with nanoparticles, with excellent access to an array of active sites and large surface areas. 3-D porous materials can satisfy the need for economical use of materials while providing access to a range of different active morphologies. It has been shown that 3-D porous structures are able to stabilise active sites and allow for better reagent dispersion and accessibility.[138] The porous nature allows for better accessibility to active sites over 2-D counterparts, resulting in significantly improved activities.[118, 139] Shown in Figure 1.4 is a comparison of a porous Pt honeycomb material compared with flat 2-D Pt polycrystalline (poly) electrode for methanol oxidation Figure 1.4 B, and carbon monoxide (CO oxidation) Figure 1.4 D. It was shown that a better current density for methanol oxidation and an improved oxidation potential for CO was
discovered when using a porous Pt honeycomb due to a larger number of exposed active sites.[118]

![Figure 1.4 Comparison of a 3-D Pt honeycomb vs. 2-D Pt polycrystalline electrode for B) methanol oxidation in N₂ purged 1 M MeOH – 0.5 M H₂SO₄ and D) CO stripping voltammogram in N₂ purged 0.5 M H₂SO₄. CO was adsorbed at a dosing potential of −0.1 V vs. Ag/AgCl in CO saturated 0.5 M H₂SO₄. Reprinted with permission from ref [118].](image)

Once the morphology and surface chemistry that leads to increased catalytic activity is established, materials with high surface area can be designed and prepared where the nanostructure and ‘active sites’ for catalysis are part of a bulk film, as opposed to supported nanoparticles. This allows for more efficient use of expensive noble metals allowing for metal loadings to be reduced. Another outcome can be insight into reaction mechanisms, allowing for further studies into other suitable materials, with the key properties being discovered and implemented. Identification of Ideal surface properties can help to find alternative catalyst materials, although it must be noted that reaction mechanisms can differ on different material surfaces.[80]

### 1.3.2 Porous Materials

Controlled synthesis of porous materials remains important for applications in diverse areas such as catalysis,[138] including electrocatalysis,[140] energy,[12, 13] and
sensing.[16] Porous materials have many useful properties and benefits over flat 2-D structured materials.[13] Hierarchical porous structures have morphologies that allow for easy surface access of analytes or reactants, yielding fast mass transport and high sensitivities.[15, 138, 141] 3-D porous structure fabrication considers the effects of morphology, including pore size and distribution, specific surface area and surface roughness. The fabrication of porous materials can be attained in a number of ways; electrochemically (discussed in Section 1.4) and through other methods, including self-assembly, templating (including hard and soft templating, biological foams and shape directional agents) and selective leaching methods such as dealloying.[141, 142] For the fabrication of electrocatalyst materials, selective de-alloying and electrodeposition offer the most convenient methods of preparation.

Dealloying involves the fabrication of an alloy or co-deposited bimetallic films, usually a combination of a noble and less noble metal. The less noble metal, often a base metal such as copper, is dissolved in a secondary step. Removal of the less noble metal leaves behind a framework of the desired noble metal that may be nanostructured with controllable pore size. These porous structures can then be modified through galvanic replacement or further deposition steps to modify the electrode surface, further changing the surface composition, morphology and activity.[143] Erlebacher et al. gave a detailed and insightful explanation into the dealloying process. The process starts with the dissolution of a single atom of the less noble metal and leads on to the creation a series of defect sites that are susceptible to further dealloying (Figure 1.5 b), which continues until a layer of only noble metal ad-atoms remain. The metal ad-atoms coalesce and form clusters exposing more non-noble metal, allowing the dealloying process to continue (Figure 1.5 c). As the process goes on and as
more non-noble metal is removed, a network of noble metal nanostructures is left behind across the surface (Figure 1.5 d).[144] This is an effective technique to create porous metal structures, but is somewhat limited as there is almost always small quantities of the less noble metal remaining in the final structure, which is an impurity.

Figure 1.5 Simulated evolution of porosity formation for Au 10% Ag 90% a) the initial condition is a surface fully passivated with gold except within a circular region. b) After 1 s, the pit has penetrated a few monolayers into the bulk. There are fewer gold clusters near the side wall than at the centre of the pit. c) After 10 s, a gold cluster has nucleated in the centre of the pit. d) At 100 s, the pit has split into multiple pits; each will continue to propagate into the bulk to form a porous structure. Reprinted with permission from ref [144].
1.3.3 Multimetallic Electrocatalysts – Synergistic Effects

Surface morphology is not solely responsible for catalytic activity; surface composition also has a direct effect.[128, 145] It has been well established that electrocatalysis reactions are highly dependent on the chemistry of the surface.[146] Electrocatalytic surfaces can be improved greatly by tuning physical and chemical properties through the combination of a secondary or tertiary metal with one already active metal. A broad range of properties can be accessed in relation to morphology,[147] and surface states, including a controlled composition formed through segregation,[148] and alloying,[149] which impart variable electronic properties on the surface.[28, 150] Many different metals are active on their own, however improvements to cost, activity and stability can arise from combining two or more metals together.[115] Combining a less noble, and significantly cheaper, metal such as copper with a noble metal instantly reduces the cost.[86] Another advantage of using copper, over carbon, is the increases to activity that it can bring.[40, 42] Two or more noble metals may be combined to take advantage of each metals individual properties and to promote favourable morphological and electronic properties leading to increased activity, in a synergistic approach.[122, 146, 151] A prime example is the bimetallic platinum-ruthenium (PtRu) catalyst used for methanol oxidation.[34, 152] It has been discussed previously that Pt surface suffers poisoning from strong binding of reactants or intermediates. In the case of the DMFC, methanol oxidation proceeds through a pathway producing carbon monoxide, which blocks the surface active sites and reduces the activity of the catalyst. The addition of Ru is able to provide an oxidation pathway necessary for the complete the conversion of carbon monoxide to carbon dioxide, effectively removing carbon monoxide from the surface, leaving the Pt active sites available for further
Another example is the study whereby nano-NiO was deposited on Pt for formic acid oxidation. Pt is required, however did not facilitate the direct oxidation pathway until the nano-NiO was added, thus showing how synergistic effect of the two metals was able to improve the activity (and stability) and drive the direct desired pathway.[155] Trimetallic Co-Ru-B has been proven to enhance both the catalytic activity and stability towards sodium borohydride hydrolysis compared to binary equivalents,[156] whilst a Pt-Co-Cr trimetallic alloy catalyst was found to double the activity compared to monometallic Pt towards ORR.[157] As these combinations of two or more metals and/or noble metals have proven effective, there are many other examples in the literature where two or more metals have been combined to increase the desired outcome in various applications.[158-161]

There are three main effects linked to increased activity when two or more metals are combined; the third-body effect, bi-functional mechanism and the electronic effect. For the third body effect, also known as the geometric or ensemble effect, the additional metal causes the blocking or disruption of continuity of a surface that would normally result in the binding to a poisoning species.[35, 105, 155] The bifunctional mechanism relates to two different parts of a surface having distinct and different roles in a reaction mechanism. E.g. PtRu catalysts for alcohol oxidation; the adsorption of CO takes place on the Pt surface, while the Ru provides the necessary hydroxyl species to complete the oxidation to CO$_2$.[154] And finally, the electronic effect is a result of an additional metal modifying the electronic properties of the surface compared to the original metal.[162] This change in electronic properties can alter the bond strengths and interactions for a particular reaction mechanism, effecting the efficiency of the reaction.[162] A practical example is the 2009
study by Bogdanovskaya et al. showing how the electronic environment was changed around Pt after alloying with Co and Cr, resulting in a reduction in surface interactions and surface poisoning of oxygen containing species, thereby increasing the interaction with molecular oxygen, thus increasing the ORR activity compared to pure Pt.[157] In another example in 2007, Stamenkovic et al. showed how Ni able was able to induce changes to the Pt (111) crystal facet, increasing its activity and stability towards the ORR due to changes in the surface structure and electronic properties.[130]

1.4 Electrodeposition

Electrodeposition is by far one of the simplest and fastest methods for fabrication of metal nanoparticles and structures.[163] The process involves using the passage of charge to reduce metal ions dissolved in an aqueous solution or ionic liquid, onto a substrate (Equation 1.17). This results in the formation of metal species in their ground or elemental state, but depending on the deposition parameters applied, different oxidation state species such as oxides can also be formed.

\[ M^{n+}(aq) + ne^- \rightleftharpoons M(s) \]  

(1.17)

Electrochemical deposition offers many advantages over the other methods mentioned in Section 1.3, including:

- A high rate of deposition
- The use of simple experimental steps
- Utilisation of lower purity reactants
- Fabrication of high purity materials
• Ease of morphological control through changes in the:
  ▪ Applied Potential
  ▪ Bath composition (acid and metal salt concentrations)
  ▪ Deposition Time
  ▪ Substrate properties
  ▪ Temperature

To add to the above physically defined parameters, a range of different techniques in electrochemistry can be implemented, such as potentiostatic, galvanostatic and voltammetric control (discussed in Section 2.1), which can yield different final morphological and compositional properties in deposits.

Electrodeposition occurs at the metal-solution interface. The metal-solution interface in its simplest form was theorised by Helmholtz, describing a finite charge excess at a metal surface attracting the opposing charged ions directly from the adjacent solution. However other models such as Gouy-Chapmans have adapted Helmholtz’s original model and described the interface as being more dynamic, taking into account charge distribution as a function of distance from the electrode, thermal motion and concentration gradients. Stern elaborated on the Gouy-Chapman model, combining it with the Helmholtz model to explain how ions are not single point charges and that mobility to the electrode is affected by size.[44]

The first region, the compact region at the metal-solution interface is known as the Inner Helmholtz Plane (IHP). The IHP describes a metal electrode with an excess (negative) charge directly that has ions from a solution specifically adsorbed adjacent to metal surface with an opposing (positive) charge of that of the metal electrode. This region is known as the double
layer.[164] Moving a further distance out from the electrode is the Outer Helmholtz Plane (OHP), which refers to the solvated ion species on approach to the IHP, where the (positive) charge is in excess and linearly reduces with distance from the electrode. Further out than this is the diffusion layer, sometimes called the Gouy-Chapman layer, which is the region with lower ion species concentration than the bulk, with delocalised charge where ions either transfer from the bulk solution on toward the inner planes (Figure 1.6).[164] This region is important as it controls the supply of species to the inner planes of the metal-solution interface.

During electrodeposition, ions travel to the metal-solution interface from the bulk solution or IHP where charge transfer occurs and ions are reduced to their ground state form. This exchange can be measured as the current density, \( j \), which relates the measured current due to faradaic redox process at the surface area of the electrode.

![Diagram of Helmholtz Planes, Gouy-Chapman Layer, and Bulk Solution](image_url)

*Figure 1.6 The metal-solution interface.*
In order to deposit metal ions, the applied potential must be negative of that of the standard reduction potential of the metal and its oxidised species in solution. An excerpt from the electrochemical series is shown in Table 1.1 that shows the equilibrium potentials, $E^0$, under standard conditions for reductions relevant to this thesis. It is necessary to apply a cathodic overpotential, $\eta$, for deposition to take place.

Table 1.1 Standard electrode potentials (1 atm, 25 °C, 1 mol L$^{-1}$)[83]

<table>
<thead>
<tr>
<th>Half Reaction</th>
<th>Standard Electrode Potential, $E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$^{2+} + 2e^- \rightleftharpoons$ Pd</td>
<td>+ 0.915 V</td>
</tr>
<tr>
<td>AuBr$_4^-$ + 3e$^- \rightleftharpoons$ Au + 4Br$^-$</td>
<td>+ 0.854 V</td>
</tr>
<tr>
<td>PtCl$_4^{2-} + 2e^- \rightleftharpoons$ Pt + 4Cl$^-$</td>
<td>+ 0.758 V</td>
</tr>
<tr>
<td>Cu$^{2+} + 2e^- \rightleftharpoons$ Cu</td>
<td>+ 0.340 V</td>
</tr>
</tbody>
</table>

Metal deposition rates can vary due to different reduction kinetics for the deposition of different metals, which may be expressed as an exchange current density for a particular redox reaction, $j_0$. A higher $j_0$ value indicates that the kinetics for the redox reaction are fast, and a smaller overpotential is required to drive the reaction. A smaller $j_0$ value, common for complex, multi-electron mechanisms, indicates a larger overpotential is required to drive a redox reaction at an acceptable rate.

The bath composition i.e. the species in the electrolyte used for the deposition, is directly responsible for the species deposited and the morphology and structure. It is convenient to relate metal deposition kinetics in terms of electrochemical equivalent rate measurements, such as those listed in Table 1.2, which practically measure the deposition kinetics. It can be seen that the metals Pd and Pt have faster deposition rates than Au, Cu and Ru.
Table 1.2 Electrochemical Equivalent Metal Reduction Rates[164]

<table>
<thead>
<tr>
<th>Metal</th>
<th>$k$ (volume) cm$^3$/A-h</th>
<th>$k$ (mass) g/A-h</th>
<th>$k$ (thickness) µm/(A-h/dm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (III)</td>
<td>0.127</td>
<td>2.45</td>
<td>12.7</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>0.1326</td>
<td>1.186</td>
<td>13.26</td>
</tr>
<tr>
<td>Pd (II)</td>
<td>0.1651</td>
<td>1.985</td>
<td>16.51</td>
</tr>
<tr>
<td>Pt (II)</td>
<td>0.1696</td>
<td>3.640</td>
<td>16.96</td>
</tr>
<tr>
<td>Ru (III)</td>
<td>0.1017</td>
<td>1.257</td>
<td>10.17</td>
</tr>
</tbody>
</table>

These kinetic rates are dependent on a number of factors, including:

- The nature of the substrate, i.e. the material used, the roughness and presence of insulating and active sites will affect the deposition kinetics.[165]
- The composition of the electrolyte and the competition with other electroactive species will also affect the deposition kinetics and therefore the resulting deposit.
- The potential or current density applied.

The rate of a redox reaction at an electrode will increase with the applied potential. The application of a small potential i.e. a small deviation from the equilibrium potential, $E^0$, results in a process controlled by charge transfer i.e. kinetic limitations.[164] If the applied potential is large, the deposition process becomes limited by the rate of diffusion of ion species to the substrate, which is a combined effect of species mobility, overpotential and the concentration gradient between surface and bulk (diffusion limited). As the electrodeposition rate increases with the application of a large overpotential there is a deficiency in the available ions, therefore the rate/deposition process becomes reliant on the transport or diffusion of ions to the substrate. This change to diffusion can result in a
drastic change in the resulting deposits in terms of size, shape and morphology. The nature of the growth is dependent on the diffusion rate of the metal ion species to the electrode. The composition of the electrolyte is also important as it can affect the conductivity and therefore the final deposited structures.[164]

When considering the electrodeposition of multimetallic films, the relative rates of each reduction species must be considered. Partial curves can relate the deposition current, $i$, of a metal (e.g. metal A or B) relative to applied potential, $E$, thus determining the rate of deposition (Figure 1.7). Different metals have different kinetic rates of deposition (see Table 1.2) which are dependent on the $E$ used.[164] Deposition can occur under two regimes, being either kinetically limited or diffusion limited. At low $E$, the deposition of each metal A and B is determined by its kinetic rate, as described by its partial curve. Metals A and B would deposit together at their relative kinetic rates. Increasing $E$ to the point where the A and B overlap, would see metal A depositing under a diffusion limited regime, with B still depositing with regard to kinetics. At high $E$, multiple metals would deposit under diffusion limited regimes, which allow for the different morphologies such as dendrites to be accessed.[164, 166]

![Figure 1.7 Partial Curve describing the i vs. E relationship for two metal species.](image)
These partial curves can be altered with changes to the deposition electrolyte, either by the addition of other metals, stabilising additives or capping agents.[167]

Electrodeposition involves a phase change at the metal-solution interface from aqueous solution to a solid or gaseous form via nucleation and growth mechanisms. Nucleation is the first stage of deposition, which refers to the beginning of metal deposition where atoms collect (reduce) to form stable clusters across the substrate surface. There is a critical size that clusters must reach to be stable.[44] The high overpotentials which are routinely used in electrodeposition reduce the critical size of clusters allowing nucleation to be rapid.[164] The stability of clusters is a function of the surface energy and overpotential.[44, 168] Nucleation sites act as seeds for subsequent metals ions to reduce and grow. The shape and orientation of these seeds is dependent on the composition of the electrolyte, substrate and composition of the electrolyte, which causes variations in the seeds to arise.

The growth of the metal film may follow kinetic or diffusion growth limitations. Growth on a nucleated surface is dependent on geometric and energetic parameters.[168] Metal deposition is a dynamic processes where the electrodeposition site geometries are changing as deposition time proceeds, and this can also effect the electrodeposited structures. When comparing the deposition of different individual metals, growth patterns will differ from one another due to differences in kinetics and surface energies.

As nucleation subsequently controls the growth of the electrodeposited material, the dependence on the surface energy and its ability to be altered by potential, charge and composition can enable the control of final morphological structures of the metal deposits.
The use of electrodeposition at high overpotentials allows for rapid nucleation on the substrate, evenly coating the surface with seeds that are able to create sites for further deposition of structures to occur. An evenly coated surface allows for even charge to be applied across the whole modified substrate and uniform deposits to be obtained.

In this thesis, the above concepts are taken into account, by looking at the application of a large overpotential to a metal electrode substrate immersed in an acid based electrolyte. This combination induces hydrogen evolution and electrodeposition of a metal simultaneously and is known as the Dynamic Hydrogen Bubble Templating (DHBT) method, which will be discussed in Section 1.5.

1.5 The Dynamic Hydrogen Bubble Template (DHBT) Method

A method to reliably fabricate porous metal nanostructures in a clean, easy and fast manner is the method termed the ‘dynamic hydrogen bubble templating’ (DHBT) method. Studies involving the deposition of structures and films using DHBT date back to the first studies in the 1970s, however it has been used for more intense research since it was brought to the forefront by Marozzi and Chialvo between 2000-2001.[169, 170] Since then, there have been a number of recent examples of porous film fabrication by this method reported in the literature.

In electrochemistry it is usually desirable to work within the potential window of the supporting electrolyte, be it an acid, base or ionic liquid. This is to prevent the breaking down of the electrolyte causing detrimental results when studying electrochemical processes or disruption of the growth of films. For the growth of films, electrodeposition
usually occurs at less than half of the limiting current to avoid unstable formations or protrusions, such as dendrites.[164] The DHBT method, however, involves working at extreme overpotentials that forces the electrolyte, usually an aqueous solution containing acid, to break down and evolve hydrogen bubbles that serve to shape and form films with porous, high surface areas. Due to the large overpotentials utilised, a co-reduction process occurs where metal ions in the electrolyte are reduced at the same time as $H^+$, a process where Equations 1.18 and 1.19 occur simultaneously.

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s) \quad (1.18)$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad (1.19)$$

Hydrogen ions supplied by the supporting electrolyte are reduced, to form micro-bubbles on the electrode surface. Bubble formation on an electrode surface involves three key steps: nucleation, growth and detachment.[171] Due to the high overpotentials used by DHBT, super saturation of $H_2$ in the solution near the electrode causes heterogeneous nucleation of bubbles at the surface. Small bubbles coalesce to form larger bubbles and continue to grow, as long as they are attached to the surface, until they reach a critical size, known as the ‘bubble break-off diameter’. The break off diameter is related to the ability of a bubble to coalesce and its residence time on the surface. These factors are dependent on the surface energy and morphology of the surface at which reduction is taking place on.[168, 172, 173]

The bubbles attached to and detaching from the surface of the electrode disrupt the surface, affecting the subsequent co-reduction of metal ions from the same electrolyte. The role of these bubbles are critical, and their behaviour directly affects the metal deposition. Hydrogen bubbles insulate and block surface sites on the substrate, which would otherwise
be available for reduction of incoming metal ions, forcing the ions to instead seek out sites around the bubbles.[171, 174] At a critical size, the bubble breaks away from its occupancy site on the electrode surface, leaving behind a void. The growing metal surface will thus have to grow around these bubbles, which act as a dynamic template. Depositing for longer times usually results in an increase in the size and thickness of the metal film, with relatively small pore sizes at the surface of the film which gradually increase in a ‘stack up’ model approach, as shown schematically in Figure 1.8.

![Figure 1.8. Schematic of the Dynamic Hydrogen Bubble Templating Method.](image)

The behaviour of hydrogen bubbles, including the kinetics (exchange current density) of hydrogen evolution on metal sites, effects the rate of bubble formation and the break-off diameter, which leads to differences in the size of the resulting pores. [172, 175] The exchange current density, $j_0$, or the rate of hydrogen evolution per unit area of surface differs for each metal.[49, 50] This has been described previously in Section 1.2.2.1 and
shown through the use of volcano curves that relate the metal-hydrogen chemisorption energy to exchange current density (Figure 1.2). The \( j_0 \) for \( \text{H}_2 \) evolution have been determined for Au (10\(^{-5.4}\) A cm\(^{-2}\)), Cu (10\(^{-5.37}\) A cm\(^{-2}\)), Pd (10\(^{-3}\) A cm\(^{-2}\)) and Pt (10\(^{-3.1}\) A cm\(^{-2}\)),\(^{[49, 50]}\) indicating a significantly faster \( \text{H}_2 \) evolution rate off the electrodepositing Pt or Pd compared to either Cu or Au. A faster rate means shorter residence times of bubbles on the surface, leading to a smaller break off diameter, reducing the amount of time available for coalescences to occur. Less time for coalescence means smaller bubbles are formed, that are directly linked to pore size in the final deposit.

Natural convection of species to an electrode occurs in any electrodeposition process, which causes the formation of a diffusion layer. Fick’s second law predicts that the diffusion layer thickness increases relative to time, however by stirring the solution the diffusion layer is reduced in thickness.\(^{[164]}\) The rapid evolution of hydrogen bubbles upon the application of a large overpotential results in a turbulent environment that effectively stirs the solution resulting in compression of the diffusion layer. This compression changes the hydrodynamic conditions, and is able to override kinetic limitations that occur when depositing more than one metal, forcing multiple metals to deposit under a diffusion controlled regime.\(^{[172]}\) Compositions and morphologies of the deposits can be controlled through changes to the electrolyte composition and applied overpotential.\(^{[176]}\) Electrodeposition by DHBT has the advantage of producing materials with shapes and morphologies not afforded by other fabrication methods, and also not accessible by electrodeposition at lower overpotentials.\(^{[172]}\)

In other templating and fabrication methods leading to porous nanostructured materials, such as dealloying and soft/hard templating methods, it can be difficult to remove the
templating media, leading to impurities in the final product. DHBT templating avoids this difficulty, as the hydrogen evolved is cleanly removed from the surface. The method creates porous networked materials that are able to be utilised in a number of applications including sensing,[14-16] catalysis,[138] and energy.[12, 13] The porous networks provide enhanced stability while exhibiting large specific surface areas, allowing for better use of expensive noble metals and thus provides a method to fabricate high surface area bulk films that may be an alternative to supported nanoparticles.

This method has been applied to a number of different single metals, including copper,[175, 177, 178] silver,[179] tin,[15] gold,[120, 180] platinum,[118] nickel,[169, 170] and palladium.[181] It also has been applied to a number of bimetallic systems, such as CuAu,[182] CuPd,[183] CuAg,[184] AuPt,[141, 185] AgPd and AuPd,[186] NiCu,[187] and more. Recently, an extensive review on the DHBT method was carried out by Plowman et al. highlighting the influence of bubble behaviour and the range of metals that this method has been applied to.[172]

Generally, porous structures are obtained with the surface properties determined by the metal being deposited, the composition of the electrolyte and overpotential applied. For example, the deposition of multimetallic systems results in changes to the H$_2$ evolution rate, causing changes in fine surface structure and overall porosity.
1.6 Research Aims

There have been issues with the use of supported nanoparticles which has driven interest in using nanostructured metal materials for practical applications. However, issues in controlling the fabrication of these materials with wet chemical and physical deposition methods have arisen. An alternative technique that has been shown to reliably produce nanostructured metal materials is the DHBT method, which has been able to create an array of materials using electrodeposition with hydrogen evolution (Section 1.5). To fully take advantage of DHBT there are some aspects that require further understanding, including the deposition of metals with slow kinetics, as well as the factors that control the surface properties during the preparation of multimetallic materials. The effect on the parameters (e.g. applied potential, electrolyte concentration and time) for the deposition of multimetallic materials is not well understood. The properties of the material, including the morphology, composition and surface chemistry, can profoundly affect its activity.

The aim of this research is to fabricate porous nanostructured metal films in a fast, convenient way utilising the DHBT method described in Section 1.5, and to study the factors that control the morphology of these films. The DHBT method has been shown to reliably fabricate an array of different nanostructured materials by electrodeposition that occurs under diffusion limited regimes, which allow for access to morphologies not readily obtained by other methods. This method is advantageous as it can produce porous materials with morphologies that can be easily controlled through variations in experimental parameters, to fabricate and alter surface composition and morphology. These structures often show significant increases in specific surface areas over 2-D / planar
materials of similar composition. This increases the overall material utilisation, a desired goal whenever utilising noble metals associated with catalytic applications.

This research sets out to create an array of different metal structures suited to different end applications, illustrating how versatile and easy this method is to use, and how it can be applied to a broad range of applications that are not just limited to catalysis, but spread into capacitance as well. Control of the surface properties is demonstrated by changing simple deposition parameters. The method offers an alternative to others at a fundamental level, but there is also the capacity to upscale for large scale production.

Ru has slow deposition kinetics and therefore DHBT may allow access to controlled morphologies that are not attained by other deposition methods. As DHBT can produce porous networks, it is applied to Au to fabricate a honeycomb structures that can be used in a case study towards the electrocatalysis of the SO$_2$ oxidation reaction. The DHBT method capability will be also extended to investigate the fabrication of trimetallic catalyst materials, where the properties affecting morphology and catalytic activity will be explored.

1.7 Thesis Outline

The experimental section, Chapter 2, describes the chemical and electrochemical methods used in this thesis, as well as an overview of all the methods used for characterising the materials during this research.

The project first sets out to apply the method of dynamic bubble templating to the electrodeposition of Ru (Chapter 3), an important metal for both catalysis and capacitance.
Ru is known for its very slow deposition kinetics, which has hampered the formation of Ru surfaces with morphological features. Given that the extreme conditions electrodeposition via DHBT affords, it was applied to Ru for the first time to see if we could force dendritic growth, which has not been seen before.

Chapter 4 is a study on the DHBT method to benchmark traditional nanomaterials, such as Au nanoparticles, with porous materials obtained through the DHBT method. A porous Au surface was compared to a flat Au polycrystalline electrode, and three shapes of Au nanoparticles. Electrochemical techniques were used to probe the both the surface crystallography and the catalytic activity. The \( \text{SO}_2 \) oxidation reaction, an important reaction for the generation of hydrogen by the Hybrid Sulfur cycle, is used to compare surface reactivity of nanoparticles and a porous film. This reaction suffers from a large overpotential that hinders its further development. Polycrystalline Pt and Au are so far the two metals that are currently exclusively used for this reaction and studies typically look at the effect of preconditioning and temperature. The disparity in surface reactivity between common nanoparticle shapes and porous films was directly contrasted in this chapter in a case study.

Chapters 5 and 6 apply the DHBT to the fabrication of trimetallic systems. Chapter 5 focusses on the CuAuPd system, and Chapter 6 on CuAuPt. The experimental factors that control the morphology and the pore size/surface area of porous films when noble metals are doped into a copper framework are poorly understood. In these chapters trimetallic materials of copper with two noble metals added in relatively small concentrations are studied, and experimental factors that lead to changes in morphology are studied. The electronic properties of these films are probed by a series of model reactions, such as hydrogen evolution and ferricyanide reduction, as a well as a potential catalyst for the
Direct Borohydride Fuel cell. These new materials are thus discussed as possible catalysts that may be more stable than supported nanoparticles in many applications.

1.8 References


Chapter 2

Experimental
2.1 Electrochemical Techniques

The general electrochemical set-up unless otherwise specified consisted of utilising a glass cell with an approximate volume of 20 mL, fitted with a Teflon cap that had holes in the top to allow for the connections to be made with the electrodes. Typical volumes used were between 10 - 15 mL and each time the solutions were purged with high purity nitrogen (N₂) gas for 10 – 20 mins to remove oxygen.

A typical three electrode setup was used consisting of a working electrode (WE), a counter electrode (CE) or auxiliary electrode and a reference electrode (REF) (Figure 2.1). The WE is the electrode of interest and this is electrode to which a potential or current is applied. The CE serves to allow a flow of current and be the reciprocal of the potential applied at the WE. It is important to measure the applied current or potential at the WE to be able to control and measure electrochemical processes. In two electrode setups, the applied potential is referenced to the CE, however there are great problems when large currents are being drawn at the working electrode. A three electrode setup allows for the CE and REF to be used independently, allowing for precise control and measurement of the applied potential at the WE.

The reference electrode used throughout this work was an Ag/AgCl in 3 M NaCl (RE-1B, ALS-Japan). This electrode consists of a silver (Ag) wire coated with a porous layer of silver chloride (AgCl), the wire is contained within a solution of 3 M sodium chloride (NaCl) and separated from the analyte solution by a glass frit. Due to its constant make up the potential is fixed at 0.210 V vs. the standard hydrogen electrode (SHE).
Figure 2.1 Three electrode electrochemical cell setup consisting of the working electrode (WE), a counter electrode (CE) and reference electrode (REF).

The CE varied depending on the electrochemical process and either a high purity (99.9 %, Sigma Aldrich) 0.5 mm platinum wire or an inert graphite rod (6 mm diameter, Johnson Matthey Ultra “F’ purity grade) were used as specified in each chapter.

Control of the cell was achieved using a CH Instruments 760D Bi-potentiostat attached to a Model 680 Amp Booster (CH Instruments) connected to a computer, allowing for electrochemical properties to be measured, analysed and controlled.
2.1.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is the most widely used and studied technique in the field of electrochemistry. It is a powerful analysis tool for investigating electrode processes and electrode kinetics. CV involves scanning the applied potential of an electrode from an initial potential, $E_1$, linearly to a secondary potential, $E_2$, over period of time. The length of this time period is determined by the scan rate, $\nu$, and usually has units of millivolts or volts per second (mV/s or V/s). At $E_2$ the potential sweep is reversed and the potential changes from $E_2$ back to $E_1$ in a reverse manner as shown in Figure 2.2. A recording of the current obtained from such sweeps is collected by the computer and displayed in a plot known as a voltammogram.

The potential for $E_1$ is usually chosen to be in a region where no electrode processes are occurring, but such that a process occurs during the potential interval between $E_1 \leftrightarrow E_2$, a potential interval where an either reduction or oxidation (or redox processes) can be observed. These redox processes are greatly affected by the range of the potential window and by the rate at which they are scanned. A wealth of information can be obtained from CVs, including information on potentials for redox processes, oxidation states of redox species, the number of electrons involved in redox reactions, the rate of electron transfer and chemical changes induced by electron transfer processes and adsorption effects.[1] Electrochemical reversibility and kinetics can also be obtained. A typical voltammogram for a reversible process is shown in Figure 2.3. The peak shapes can yield information regarding reaction kinetics.
The Randles-Sevcik equation (Equation 2.1) can be used to predict the magnitude of the peak current for a reversible electron transfer process.\textsuperscript{[1]} It is also extremely useful in determining unknown parameters such as number of electrons transferred, $n$, and diffusion coefficients, $D$. As the Randles-Sevcik equation is a relationship between peak current and scan rate, the scan rate can be altered yielding different peak currents, allowing for $I_p$ vs. $v^{1/2}$ to be plotted to yield $D$.

$$I_p = 0.446n^{3/2}FAc \sqrt{\frac{FvD}{RT}} \quad (2.1)$$

Where:

$I_p$ is the peak current

$n$ is the number of electrons transferred

$F$ is the Faraday constant

$A$ is the electrode surface Area

$c$ is the bulk concentration

$v$ is the scan rate

$D$ is the diffusion coefficient
R is the gas constant
T is the temperature in Kelvin

In this thesis, CVs are used in numerous ways including electrochemical surface cleaning, electrochemical surface area (ECSA) determination methods, and surface activity measurements including capacitive and catalytic ability. The wide range of applications that CV can be used for is thus evident in the results of this thesis.

2.1.1.1 Linear Sweep Voltammetry

Without the reverse sweep used for CV, the process is called Linear Sweep Voltammetry (LSV) i.e. \( E_1 \rightarrow E_2 \) OR \( E_2 \rightarrow E_1 \). LSV can be used to study the progress of electrode processes in one direction i.e. either reduction or oxidation. Such technique is used for the study of the electrocatalysis of the hydrogen evolution reaction (HER) and can yield information regarding the reaction onset potential, peak potential and peak current density the same as CVs.

2.1.2 Static Electrochemical Techniques

There are two techniques in electrochemistry that involve holding either the current or potential constant whilst measuring the opposing parameter as a function of time. Potentiostatic techniques involve applying a static potential to the working electrode as the current is measured with passing of time. Galvanostatic techniques involve applying a static current and measuring the potential as a function of time. The applied potential or current can be set to induce a series of redox processes to occur.

In this thesis, electrodeposition was performed using both the above methods as specified in each chapter. The monometallic studies involved the application of potentiostatic
techniques, where large cathodic overpotentials were chosen that induced rapid deposition of Ru and Au accompanied by hydrogen evolution. The Cu bimetallic and trimetallic films used the galvanostatic technique to drive the electrodeposition processes in a similar manner. An example of the voltammetric outputs are shown in Figure 2.3 a) Potentiostatic and b) Galvanostatic. These methods are not limited to bulk electrodeposition but can be used for other methods such as underpotential deposition (UPD).

UPD involves the deposition of a monolayer of a species, usually a metal or adatom such as hydrogen to an electrode surface through the application of a constant potential more positive than where bulk deposition occurs. This can yield useful information including surface state and surface areas explained in Section 2.2.1.[1, 2]

![Figure 2.3 Examples of static techniques a) Potentiostatic and b) Galvanostatic](image)

### 2.1.3 Chronoamperometry

Another useful electrochemical technique is the Chronoamperometric step technique that involves stepping the potential whilst measuring the current for a specified time. Usually the potential is stepped from a region where no redox processes are occurring, or the open-circuit potential (OCP), to a region where a redox process will occur. Chronopotentiometric techniques are similar, however involve stepping the current and monitoring the potential...
in relation to time. It is similar to the potentiostatic technique and is routinely used to electrodeposit materials or produce an electroactive product (such is the case in electrocatalysis) by stepping into a region where an electroactive species is reduced at the electrode surface.

In Chronoamperometry the decay of the current can be evaluated by the Cottrell Equation: [1]

\[
i = \frac{nFAC_0D^{1/2}}{\sqrt{\pi t}} \quad (2.2)
\]

In electrocatalytic studies the current, \(i\), can be measured when the potential is selected to drive a redox reaction. The behaviour of current, i.e. the rate in which it drops with time, can be used to evaluate the activity and stability of a material over long time periods. Another useful measure that is often described is the current density, \(j\). \(j\) is an effective measured of the amount of charge passed per unit surface area, usually in A/cm².

## 2.2 Characterisation

All electrodes require characterisation to determine their properties including morphological features such as size, shape, porosity and surface area; their chemical and electronic state including composition, crystal orientation, surface energy and capacitive/catalytic ability. In this section each will be described.

### 2.2.1 Electrochemical Surface Area Determination (ECSA)

Surface areas can be termed with regard to the geometric area, \(A_{\text{geometric}}\), or real surface area, \(A_{\text{real}}\). \(A_{\text{geometric}}\) is the assigned area related to a smooth 2-D area of an electrode surface. However, in reality even smooth electrode surfaces have a degree of roughness due
to defects on the surface. Therefore the $A_{\text{real}}$ will be higher than $A_{\text{geometric}}$ with the difference known as a roughness factor, RF (Equation 2.3).

$$(RF) = \frac{A_{\text{real}}}{A_{\text{geometric}}} \quad (2.3)$$

The porous materials that have been developed in this thesis are far from smooth. Therefore it was necessary to measure $A_{\text{real}}$ of the electrodes and electrodeposited films to identify the actual surface area that a material has.

Electrochemical surface areas (ECSAs) can be used to measure $A_{\text{real}}$ of an electrode or material surface. The determination of the ECSA gives the most effective measurement on the number of electro active sites accessible to an analyte or reaction species. There are a number of electrochemical methods that can be used to determine electrochemical surface area, with a few listed below.[2] They all work on the principle of known charge-to-surface area responses, so that the charge measured, $Q$, can be compared to the known charge, $Q^*$, to obtained the surface area, $A$, as in Equation 2.4:

$$A = \frac{Q}{Q^*} \quad (2.4)$$

2.2.1.1 ECSA by Hydrogen Adsorption

For platinum (Pt) based materials the ECSA can be determined from the relationship for hydrogen adsorption ($H_{\text{ads}}$) on Pt surface sites. It works on the principle of adsorption of hydrogen before hydrogen evolution. The voltammetric peaks in the region of $H_{\text{ads}}$ can be integrated to get the total charge (in coulombs, C) as a result of $H_{\text{ads}}$. This method relies on the principle that one hydrogen attaches to each available Pt site on the material surface.
(Equation 2.5). The charge obtained can be related to the surface area by dividing it by the accepted value of polycrystalline Pt of 210 µC cm$^{-2}$.

$$Pt + H^+ + e^- \rightarrow PtH_{ads} \quad 210 \, \mu C \, cm^{-2} \quad (2.5)$$

The ECSA for Pt surfaces were obtained through cycling between 0.0 and 1.4 V vs. SHE in 1 M H$_2$SO$_4$ at a scan rate of 50 mV/s for 10-20 cycles until a stable response was obtained. The peak area was measured for the region between 0.0 and 0.4 V vs. SHE. The charge was calculated by dividing the peak area by the scan rate. By dividing the charge by 210 µC the surface area in cm$^2$ was obtained.[2]

### 2.2.1.2 ECSA by Oxide Stripping

Similar to the method applied to Pt, the ECSA of Au surfaces can be determined by forming an oxide on the surface. A monolayer of oxide forms on Au surfaces when scanned in the anodic direction, which is reduced on a reverse CV scan. The charge required to strip the oxide layer off the surface can thus be integrated. This is a two electron process therefore the charge related to the surface area is higher, at 400 µC cm$^{-2}$.

$$AuO_{ads} \rightarrow Au + O^{2+} + 2e^- \quad 400 \, \mu C \, cm^{-2} \quad (2.6)$$

The ECSA for Au surfaces were obtained through cycling between 0.0 and 1.6 V in 1 M H$_2$SO$_4$ at a scan rate of 50 mV/s for 10-20 cycles until a stable response was obtained. The peak area was measured for the region on the cathodic sweep between 0.7 and 1.2 V vs. SHE. The charge was calculated by dividing the peak area by the scan rate. By dividing the charge by 400 µC, the surface area in cm$^2$ was obtained.[2]
2.2.1.3  ECSA by UPD of an adatom

The above methods are not always suitable as on some metal electrode surfaces the regions of \( H_{\text{ads}} \) or oxide stripping are not well defined. Ruthenium electrodes in particular have no definable hydrogen or oxygen region due to overlap. The principle of UPD is somewhat similar to the above methods, whereby an adatom (usually Cu or Ag)[2] is adsorbed onto the electrode surface creating a monolayer, usually with a 1:1 relationship with the exposed surface sites of the electrode. For example Cu can form an UPD layer on Ru, and when this layer is stripped, the charge under the peak can be used to determine the area, as seen in Equation 2.7:[3-5]

\[
Cu_{\text{upd}} \rightarrow Cu^{2+} + 2e^- \quad 420 \, \mu C/cm^2 \quad (2.7)
\]

The exact procedure used is described and developed in Section 3.3.1 to determine the ECSA of electrodeposited Ru surfaces.

2.2.1.4  ECSA by Double Layer Capacitance (\( C_{\text{dl}} \))

The materials prepared with copper (Cu) presented another challenge with regard to the measurement of the real surface area. Unlike Pt and Au that have well defined surface area determination methods, Cu and Cu multimetallic materials have a unique electrochemical surface that prevents accurate ECSA determination via these methods.

An alternative method using the double layer capacitance, \( C_{\text{dl}} \), was used to determine the real surface area.[6, 7] \( C_{\text{dl}} \) was measured in the ideally polarisable range of each film where no faradaic processes were occurring, over a range of scan rates. The perchlorate ion (\( \text{ClO}_4^- \)) is chosen as the electrolyte of choice for this type of measurement due to its limited specific adsorption on solid electrodes.[7-9] Adsorption of the electrolyte, such as that which occurs
with $\text{SO}_4^{2-}$, is a problem, as redox process may be induced therefore causing faradaic responses interfering with the accurate measurement of $C_{dl}$.

The ECSA for the films prepared in Chapters 5 and 6 was determined by measuring the $C_{dl}$ in potential range between -0.35 and -0.15 V vs. Ag/AgCl in 0.1M HClO$_4$. The range was dependent on each film, determined from a series of initial CVs at 0.1 V/s in 0.1 M HClO$_4$ to reach initial stable responses. Once the potential range was determined, CVs were performed in the range at scan rates of 0.02, 0.05, 0.1 and 0.2 V/s for 10 cycles with the final cycle used as displayed in Figure 2.4 a). The slope from the plot of scan rate vs. $C_{dl}$ (Figure 2.4 b) was divided by the average $C_{dl}$ value of 28 $\mu$F cm$^{-2}$, which is the estimated value relating the charge (in $\mu$F) per unit surface area (cm$^2$) for copper, platinum and gold and a host of other metals.[7]

![Figure 2.4 Example of the CV response in 0.1 M HClO$_4$ for a porous film the measure of $C_{dl}$ and b) the plot of scan rate, $v$, vs. $C_{dl}$.](image)

65
2.2.2 Model Catalytic Reactions

2.2.2.1 Hydrogen Evolution Reaction (HER)

The HER is important when considering water splitting reactions or counter cathodic reactions to anodic oxidation processes in aqueous solution. The reaction on various materials can be related by the exchange current density, $j_0$, and the M-H interaction, which are dependent interactions at the electrode surface as described in Section 1.2.2.1.

The HER was performed in N$_2$ purged, 1 M H$_2$SO$_4$ via linear sweep voltammetry (LSV) from 0.1 to -0.7 V (vs. SHE) at a scan rate of 0.01 V/s. The catalysts can be directly compared for activity by measuring the current density at a voltage of -0.6 V vs. SHE for the HER, which can be used to compare the effects of surface morphology and composition. Another parameter that was measured to determine activity is the onset potential for the beginning of H$_2$ evolution. This relates the surface effectiveness to reduce the overpotential required to initialise H$_2$ evolution. The onset potential was defined as the potential at which 3 % of the current at -0.6 V is reached.

2.2.2.2 The Ferricyanide (FCN) Reduction Reaction

The reduction of ferricyanide (FCN) by sodium thiosulphate (STS) is a model reaction that can be used to probe the surface activity of the films as a useful predictor of heterogeneous catalysis in aqueous solution when the surface is not polarised, and thus can be used to screen potentially useful classes of catalysts. Uncatalysed, the solution is very stable and reacts only at a negligible rate of $-2.50 \times 10^{-6} \text{ s}^{-1}$. [10, 11] This is a useful reaction that allows the catalytic activity to be studied under diffusion control. It has been observed that this reaction is dependent on the specific shapes and crystal facets,[12] therefore allowing the
effect of different morphological features to be probed. It is a surface based, diffusion controlled, electron-transfer reaction, where the surface shape, composition, accessibility and area are important factors in determining the reaction kinetics. STS is in excess and therefore the reaction is assumed to be pseudo first order. The STS binds to the surface of the catalyst preventing the FCN reacting with the surface and allowing for electron transfer to occur.[12, 13] The catalyst surface acts as a mediator/proxy to transfer electrons between FCN and thiosulphate.[11]

The reduction of 1 mM hexacyanoferrate(III), \(K_3[Fe(CN)]_6\), by 0.1 M \(Na_2SO_4\) was undertaken in a flask with a total volume of 24 mL. The sample was fixed to the side of the flask and the solution was stirred at a constant velocity throughout the experiment. The progress of the reaction was monitored by UV-Vis Spectroscopy, by taking aliquots every min for 15 mins and placing them into a quartz cuvette with 1 cm path length to analyse the absorbance at 420 nm.

### 2.2.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is an imaging technique that allows high magnification electron imaging to capture fine surface morphological features. Unlike typical optical techniques that use light to capture the image, SEM images through the use of electrons. Electrons are fired from an electron gun, in a high vacuum environment, down a column consisting of a series of focussing lenses onto the samples. The electrons interact with the sample causing production of secondary electrons that are collected by the detector and processed to yield electron images of the sample. As the name mentions electrons are
scanned across a sample to build up a data set that is processed into an electron image.[14, 15]

The imaging conditions that were used are was observed by Scanning Electron Microscopy (SEM, FEI Nova 200 SEM) under high vacuum using an accelerating voltage of 10 kV with a spot size of 3.0.

### 2.2.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is another technique, like SEM in Section 2.2.3, that uses a beam of accelerated high voltage, high speed electrons, which are fired from an electron gun, down a column, passing through a number of electromagnetic lenses and stigmators and through a sample that allows particles or structures to be imaged. However, unlike in SEM which uses secondary electrons to generate an image, TEM uses ‘transmitted’ electrons, i.e. electrons that pass through a specimen to be detected and processed that allows for ultra-high resolution images (10\(^{-10}\) m) to be captured at high magnifications. As this technique relies on transmission of electrons, it is limited to thin samples (usually no thicker than 100 nm).

The nanoparticle solutions were drop cast onto copper grids and imaged by Transmission Electron Microscopy (TEM) on a JEOL 1010 TEM at a 100 kV accelerating voltage.

### 2.2.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a powerful ultra-high vacuum (UHV) technique able to characterise the surface of a material through the use of photoelectrons. The
technique is based on the photoelectric effect, where the binding energy of a core electron is overcome by the energy of an x-ray photon, whereby the core electron is ejected and its kinetic energy is measured by an electron spectrophotometer. The characteristic of the orbital from which the photoelectron originates is responsible for the binding energy that can be measured.[16]

Survey scans broadly view the peak intensities and qualify which elements are present. High resolution core-level scans specific to regions for elements of interest can be performed to obtain specific peak binding energy information.

Chemical analysis of the surface was undertaken under ultra-high vacuum using X-ray Photoelectron Spectroscopy (XPS, Thermo K-alpha X-ray Photoelectron Spectrophotometer) with an Al Kα (1486.6 eV) X-ray source with a spot size of 400 μm. Binding energies were calibrated to C 1s at 284.6 eV.

2.2.6 X-ray Diffraction (XRD)

Metals can exist in a range of different crystal orientations. The crystal orientation of a material can affect the properties of a material including growth mechanisms, adsorption/desorption behaviour and catalytic activity (including electrocatalysis). X-ray Diffraction (XRD) is a useful technique that can identify the crystallographic properties of a material. XRD is a useful tool involving the collection the diffraction patterns of species that can afford crucial information such as the nature in which the noble metals are incorporated into the film (i.e. alloy formation or surface segregation), crystallite orientation and crystallite size.
X-rays are produced in an x-ray tube when high speed electrons remove K, L or M inner electrons from a target atom (e.g. copper) causing the outer electrons of the target atom to fill the empty orbitals, causing a release of energy in the form of x-rays. These x-rays form a beam and are directed onto a sample of interest to determine its crystal lattice properties. The crystal lattice of atoms in a material can reflect the x-ray beam when Bragg’s Law (Equation 2.8) is satisfied.[17, 18]

\[ n\lambda = 2d \sin \theta \]  

(2.8)

Where \( n \) in an integer called the order of reflection, \( \lambda \) is the wavelength of the x-ray beam, \( d \) is the inter-planar spacing within a crystal and \( \theta \) is the angle between the planes. Bragg’s law determines the angle at which diffraction peaks will be observed, which depends on the d-spacing between planes of atoms within a crystal lattice.[17, 18]

Another useful equation is the Scherrer equation (Equation 2.9) that can be used to calculate the crystallite size of particular crystal planes:[19]

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  

(2.9)

where \( \tau \) is the mean size of ordered crystalline domains, \( K \) is a dimensionless shape factor with a typical value of 0.9, \( \lambda \) is the x-ray beam wavelength, \( \beta \) is the line broadening determined to the peak full width at half maximum (FWHM) and \( \theta \) is the Bragg angle.

Diffraction patterns were obtained using a Brüker D4 Endeavour diffractometer operating at 40 kV and 35 mA, fitted with a Cu Kα radiation source (\( \lambda = 1.5406 \ \text{Å} \)), incident beam monochromator and LYNXEYE detector. A 1° divergence slit was used to analyse between the 2θ range 10-90° with a step size of 0.02° 2θ and counting time of 43 s/step.
2.2.7 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is a powerful characterisation technique for quantitative identification of elements within a sample matrix. It includes identification of both metals and non-metals. It involves the introduction of a dissolved aqueous sample through a nebuliser into an electromagnetic high temperature plasma. The plasma consists of ionised helium or argon gas with a temperature between 6,000 and 10,000 Kelvin. The plasma ionises the sample species to their ionic form, usually with a +1 charge, where they are detected at a quadrupole mass spectrometer that separated ions on the basis of mass-to-charge (m/z) ratio able to identify the individual elements. At present 65 elements can be detected.[20]

The bulk elemental analysis was undertaken by ICP-MS (Agilent 7700 ICP-MS) using a helium gas plasma. Films were prepared for bulk analysis by carefully mechanically removing them from the copper substrate and then dissolving in aqua regia, before dilution and analysis in a 2 % HCl matrix. 1000 ppm standards for ICP-MS were purchased from Fluka Analytical.

2.2.8 Ultraviolet-Visible Spectroscopy (UV-vis)

UV-visible Spectroscopy involves passing the spectrum of UV and visible light through a sample. There are two modes in which the spectrometer can operate; transmission and absorbance mode. For transmission mode, light is passed through the sample, which can induce electronic transitions inside molecules of a sample to a higher energy state. Upon relaxation to their original state, energy is released in the form of light and can be measured as a percentage transmitted, T %. In absorbance model, an incident wavelength of light, I₀, is passed through the sample. The sample may absorb this light, I, and the absorbance, A, is
measured which allows the absorptivity to be calculated using the Beer-Lambert law (Equation 2.10):

\[ A = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot L \]  

(2.10)

\( \varepsilon \) is a measure of the absorptivity, called the extinction coefficient, \( c \) is the concentration of the sample and \( L \) is the path length.[21] A Cary 60 UV-Visible Spectrophotometer was used for all UV-Visible Spectroscopy measurements, with samples placed into a quartz cuvette with a path length, \( L \), of 1 cm.

### 2.3 Materials

#### 2.3.1 Chemicals

All solutions were made up with high purity Milli Q water (Millipore) (Resistivity >18.2 M\(\Omega\).cm at 22 °C). Ruthenium chloride (RuCl\(_3\).xH\(_2\)O, Ru 40-43 %), potassium tetrachloroplatinate (K\(_2\)PtCl\(_4\)) (Precious Metals Online, Wollongong), chloroauric acid (HAuCl\(_4\)), tetrabromoaurate (KAuBr\(_4\)), palladium nitrate (Pd(NO\(_3\))\(_2\).xH\(_2\)O), hexacyanoferrate(III), (K\(_3\)[Fe(CN)\(_6\)]), cetyltrimethylammonium bromide CTAB, ((C\(_{16}\)H\(_{33}\))N(CH\(_3\))\(_3\)Br), cetyltrimethylammonium chloride, CTAC, ((C\(_{16}\)H\(_{33}\))N(CH\(_3\))\(_3\)Cl), L-ascorbic acid, Nafion, (Sigma -Aldrich), sulfuric acid (H\(_2\)SO\(_4\)), sodium sulfite (Na\(_2\)SO\(_3\)) (Merck), Perchloric acid (HClO\(_4\)), sodium borohydride (NaBH\(_4\)), lead nitrate (Pb(NO\(_3\)\(_2\)) (BDH Chemicals), copper (II) sulfate (CuSO\(_4\)) (Asia Pacific Chemicals (APS), sodium hydroxide (NaOH) (Ajax), hydrochloric acid (HCl) (Rowe Scientific) and sodium bromide (NaBr) (Acros) were all used as received.
2.3.2 Electrodes

Evaporated gold (Au) films were prepared by e-beam evaporation using a Balzers system, providing a 10 nm Ti adhesion layer to a clean Si (100) wafer (Montco Silicon Technologies), followed by 150 nm of Au. These surfaces were then cut as required and cleaned using acetone, ethanol and Milli Q water, after which they were thoroughly dried under a stream of nitrogen. In order to control the exposed geometric areas of these films, the substrates were masked using polyimide tape (Kapton tape), to expose reproducible geometric electrode areas.

Glassy carbon plates (Sigradur G, HTW) were cut in house, with reproducible surfaces obtained by polishing the smooth faces on a polishing pad (Microcloth, Buehler) with an aqueous 0.05 μm alumina slurry. These surfaces were then thoroughly washed with Milli-Q water and dried under a stream of nitrogen. Reproducible geometric surface areas were again obtained by masking with Kapton tape.

Polycrystalline Au and Pt electrodes (BAS) were cleaned using the same procedure as described for glassy carbon surfaces, with separate polishing pads used for each material in order to avoid cross-contamination. The geometric area of the polycrystalline electrodes was maintained by the electrode casing material, with an exposed diameter of 1.6 mm.

Copper foil (ChemSupply) was treated by immersion and agitation in 10 % HNO₃, to remove surface contaminants, then rinsed with ultrapure Milli-Q water, acetone and ethanol before finally being dried in a stream of N₂ gas. Reproducible geometric areas were again obtained by masking with Kapton tape.
2.4 References


Chapter 3

Ruthenium Electrodeposition

Sections of this work have been published in the following peer-reviewed journal article:

3.1.1. Introduction

Ruthenium (Ru) is an extremely important precious metal due to its wide use in a range of different applications. Ru is a transition metal that can cycle through many different stable oxidation states, -II to +VIII.[1, 2] It falls into a class of metals known as platinoids or platinum-group metals (PGMs), which also includes the metals platinum, palladium, rhodium, osmium and iridium.[3] They all share similarities in key properties including remarkable stability, durability and resistance to wear and chemical corrosion, which means that they are highly reusable and not often consumed in reactions. They occur in low abundance in nature and tend to be found together in deposits.[4] Platinum (Pt) is very well known and extremely widely studied for use in a number of applications including catalysis and electrocatalysis.[5, 6] As such, it is in high demand, which is reason for its ever increasing cost. However, it has another major drawback that it can be easily poisoned and deactivated, reducing its overall efficiency in catalytic applications. Like Pt, Ru is also a relatively scarce metal, hence has an elevated price over more abundant earth metals, however still is around 20 times cheaper than Pt.[7] Yet Ru yields some comparable abilities to Pt, such as providing favoured mechanistic pathways towards catalysis of the oxygen reduction reaction,[8, 9] as well as corrosion resistance and some other of the PGMs ideal properties described above. There is thus a continued reason to study Ru in conjunction with, and possibly as a replacement for applications that currently use Pt. The use of Ru in commercial applications is growing. It is currently produced at a rate of 12 tonnes per year with roughly 5,000 tonnes in reserve.[10] It is most commonly used on an industrial scale as a major catalyst component for dimensionally stable anodes in the Deacon Process for the production of chlorine through the oxidation of hydrochloric acid.[10] Another major
application is in the electronic industry, where Ru is alloyed with Pt to harden it, which is then used for electrical contacts.[10] Ruthenium alloys (and multimetallics) are also used for catalysis, both at the fundamental and industrial level. Fundamentally, there are many articles which combine Ru with other transition metals for use in catalysis applications for fuel cells,[11-13] such as oxygen reduction[8] and oxygen evolution.[14] Among them, the most commonly studied is the PtRu alloy as the anode catalyst for methanol and other small alcohol fuel cells. This combination has been shown to significantly improve activity and longevity of platinum fuel cell catalysts.[15-18]

Ruthenium and its oxides are widely studied for catalytic, electrocatalytic and capacitive applications. Over (2012) presented an excellent review detailing synthesis methods and a range of applications regarding RuO$_2$.[1] Ruthenium oxides (RuO$_2$ or RuO$_x$H$_y$) have widely being studied as materials for a new class of electrochemical capacitors known as pseudo- or super-capacitors.[1, 19-23] Electrochemical capacitors store energy through the separation of charge at the interface between the solid electrode and the electrolyte. Pseudocapacitor capacitance comes from reversible redox processes, which gives them high-energy and high-power densities.[24] The capacitance of ruthenium oxides can vary and are dependent on the preparation method of the material. In electrocatalysis, Ru is used in conjunction with Pt (PtRu and derivatives) in the all-important Direct Methanol Fuel Cell (DMFC).[25-29] Pt on its own is an excellent catalyst but is expensive and easily poisoned. Through synergistic incorporation, Ru is able to prevent of carbon monoxide (CO) poisoning of a Pt catalyst due to strong CO adsorption. CO binds strongly to Pt, where Ru is able to provide the pathway to completely oxidise the CO, through the actions of the bi-
functional mechanism and electronic effects leaving the Pt sites once again free to react with methanol.[30, 31]

For the control of Ru morphology, there are a number of parameters that require further development. It is important to further understand properties such as the deposition mechanism and its effect on the morphology, which should also lead to optimisation of the specific surface area for efficient use of Ru. Electrodeposition offers an easy way to fabricate and study Ru for a range of morphologies. This is not the first time that Ru has been electrodeposited. Previous authors have used potentiostatic,[32-35] galvanostatic,[36-41] or cyclic deposition methods,[42-45] where it has been shown that the electrode potential is critical to the composition of the electrodeposited Ru or RuOx. Throughout the literature there are few studies that have been able to establish morphological control of Ru surfaces and make uniform structures. Electrodeposited Ru has exhibited an array of structures such as plates,[46], thick cracked mud,[47] round and roughened particles,[19] but very few can claim complete control over morphology with a uniform surface. There are many articles that are focussed on the deposition of films, which often show cracks. The films can be split into two groups, both with cracked mud morphologies, the first being smooth films,[36, 44, 48-50] and the second being relatively rough films.[35, 38-40] There are few materials that are electrodeposited that show porosity[51] and of those, the ones to show large open microporous structures are co-deposited with other metals such as copper and iridium. [34, 42, 43] Ionic liquids have also been used to deposit Ru at relatively high overpotentials due to the larger operating window of these solvents, which has proven useful where thin layers are required.[52, 53] There are two previous works which have shown open flower and spiked microporous Ru structures. One work focussed on the co-electrodeposition and subsequent de-alloying of copper to obtain structures that showed similarities to flower-like
blossoms.[34] The other makes use of flame pyrolysis to create highly-branched and connected networks of ruthenium dioxide (RuO₂).[54] However, there currently is not a single step process that results in porous and dendritic ruthenium and/or ruthenium oxides from an aqueous solution. The working electrode potential will determine whether oxides or pure metal are likely to form on the surface, and electrode potential ranges have been elucidated for acidic solution.[44, 55]

### 3.1.2. Current Techniques for Preparation of Ruthenium and its Oxides

Numerous studies have investigated different methods to prepare Ru for practical use. Compared to other noble metals such as Au and Pt, the advancement of methods to control the morphology and maximize surface area of Ru deposits is underdeveloped. The current methods for preparation of ruthenium/ruthenium dioxides can be set into four main areas.[56] They include: sol-gel processes (wet chemical methods),[23, 46, 57] thermal decomposition,[58-61] vacuum deposition methods (atomic layer deposition, physical vapour deposition and chemical vapour deposition)[22] and electrochemical methods.[35, 62-64]

Sol-gel preparation has been successfully studied to prepare RuO₂ powders with intent for the application of pseudo-capacitors. It was Zheng, Cyang and Jow (1995)[23, 57] that showed that hydrous RuO₂ could be prepared by a sol-gel method. It was found that these materials, when pressed into an electrode pellet, were able to produce the highest achieved capacitances of 720 F/g. However, it has been noted that sol-gel processes require a number of process steps in a complicated preparation process that is not easily
controlled. Other preparation methods as described in Section 1.3 can be used, however they each have their imperfections. Electrodeposition offers an attractive preparation process for fabrication of Ru structures. 3-D morphologies of Ru have been attained using electrodeposition including distorted honeycomb, cracked mud, dense packed films or thin films which have nano-sized particles on the surface.

### 3.1.3. Applications of RuO$_2$

One of the most notable properties of Ru is its ability to form stable oxides. There are numerous studies on Ru in its +IV oxidation state, RuO$_2$, especially in relation to electrical capacitance. The hydrous form, RuO$_2$.xH$_2$O, has been targeted for capacitive materials as they have achieved highest the capacitances of 400 – 1100 F/g [24, 57, 66-69]. The ability to be highly capacitive is due to its ability to be a mixed electron-proton conductor. Anhydrous RuO$_2$ is just a metallic conductor (electrons only), and has much lower capacitances of usually under 50 F/g [66] Capacitance and high charge storage is linked to the facile transport pathways for both protons and electrons [67, 69]. This can be facilitated by developing materials that have suitably large specific surface areas. Protons and electrons interact with hydrous ruthenium oxides according to the Equation 3.1: [61, 66, 67]

$$RuO_x(OH)_y + \delta H^+ + \delta e^- \leftrightarrow RuO_{x-\delta}(OH)_{y+\delta} \quad (3.1)$$

Proton mobility is dependent on the amount of water chemically and physically bound to RuO$_2$, which allows protons to permeate into the material [24, 67]. Anhydrous RuO$_2$ is an ordered, crystalline structure and in the absence of adsorbed water molecules, is unable to accept protons [23, 46]. Therefore capacitance in crystalline RuO$_2$ is only due to electronic conductivity. Proton mobility has been strongly correlated to water content. Water content,
electronic conductivity and crystallinity are all a function of annealing temperature (Figure 3.1).[61, 66]

As surface interactions are the key to efficient use, it is crucial that high specific surface areas for these materials are obtained, whilst adhering to the necessary surface oxide state and hydration level of the Ru material to maximise its capacitive ability.

![Image](image_url)

*Figure 3.1 Specific Capacitance of RuO$_2$.xH$_2$O as a function of annealing temperature and water content. Reprinted with permission from ref [66].*

In catalysis the more surface area that is available, the larger the number of electrochemical active sites for the species to interact with the surface and for reactions to take place. For capacitance, a large surface area increases the number of surface sites for redox reactions or double layer charging to occur and hence increases the specific capacitance.[70] The efficiency of a pseudocapacitor is determined by capacitance per gram (F/g). The surface interaction with the oxide is crucially important to changes in the activation, therefore affecting the catalytic effectiveness.[71] It is essential that as much of the material as possible contributes to the overall specific surface area. Another drive to increase the surface area is to maximise the material utilisation. Even though Ru is cheap compared to Pt, it is still an expensive material when compared to common materials such as carbon.
3.1.4. Research Aims of Chapter

The main research aim of this chapter is to establish the electrochemical deposition conditions using DHBT that lead to high surface area Ru, and study the surface and physical properties of the films thus formed, in order to assess the potential usability of the material obtained in a range of applications.

A key aim is to prepare open 3-D structured materials of Ru with high specific surface areas, showing how electrodeposition can be controlled through use of the DHBT method. The novelty of the chapter lies in the fact that because of the slow deposition kinetics of Ru, a direct electrochemical method to deposit high surface area Ru materials has not been developed before. Increasing the specific surface area is key for implementation of Ru based materials into energy applications such as capacitance and catalysis, where a high specific surface area is desired, as activity is confined to the surface.

In this work it is proposed that pure Ru will be directly deposited using the DHBT method in a single step process. The aim of this research on the electrodeposition of Ru is to investigate the morphology of 3-D structures through variations in deposition conditions, until a material with high specific surface area is obtained. This will increase our understanding of how DHBT can be applied to a metal that is difficult to deposit with a high surface area. Bath compositions will consist of ruthenium chloride, RuCl$_3$.xH$_2$O and perchloric acid, HClO$_4$.

As ruthenium dioxide (RuO$_2$) is the most useful form of ruthenium, this chapter will also investigate the ability to oxidise the surface of the deposited Ru, as well as look at the properties of its hydrous form, especially in regard to capacitive applications. Surfaces will therefore be oxidised electrochemically, annealed and studied by X-ray Photon
Spectroscopy (XPS) to characterise the surface properties. Surface capacitance of the oxidised surface will also be studied.

3.2. Results and Discussion

To develop materials that have suitable specific surface areas that may allow for the implementation of Ru to become more widespread, it is necessary to address the key experimental variables. There are many advantages to using electrodeposition over the other methods as described in Section 1.4 which allow for control over metal deposition to be obtained.

3.2.1. Electrodeposition of Ruthenium

The DHBT technique involves the co-reduction of a metal salt, $M^{n+}$, and $H^+$ at extreme overpotentials (see Section 1.5). In this chapter, $Ru^{3+}$ and $H^+$ are the two species of concern. Cathodic electrodeposition by potentiostatic deposition of Ru onto an evaporated Au substrate (described in Section 2.3.2) was performed using electrolytes containing ruthenium chloride, $RuCl_3.xH_2O$ in perchloric acid, $HClO_4$. Immediately before deposition the substrates were cleaned by agitation in a 1 M HCl/1 M HNO₃ solution for approximately 10 s, rinsed with Milli-Q water, ethanol and then sonicated in ethanol for 2 mins at 25 °C. The substrate was then dried in $N_2$ gas ready for deposition. Electrodeposition was performed in a conventional three electrode cell, with the working electrode being the evaporated Au substrate masked to geometric surface area of 0.049 cm² with Kapton tape. The counter electrode was a platinum wire and an aqueous Ag/AgCl reference electrode was used. All potentials in this chapter, unless specified otherwise, are referenced to SHE.
It became apparent early in this study that there was a difference in the electrochemical deposition process involving Ru in comparison with other metals that had been previously electrodeposited. This is due to the sluggish electrodeposition kinetics for Ru$^{3+}$ reduction that prevents easy control of morphology when compared to other metals such as copper and gold. However, palladium,\[72\] and platinum,\[73\] both which have been classified to have slow electrodeposition kinetics (or low melting point metals by the Winand classification), can still be generated as highly porous materials.

The assessment of a suitable material will be determined by the uniformity of the surface, as well as examination of porosity, specific surface area and stability. Further assessments will look at the ability of the materials to be manipulated by oxidation and annealing processing in the goal of enhancing/controlling specific capacitance.

3.2.2. Effect of Deposition Voltage and Time

The effect of deposition voltage and time was the first deposition parameter examined. From the previous work, and through work done by Kim et al.\[50\] the voltage needed for rough surface formation would probably have to be more cathodic than -2.8 V (-3 V vs. Ag/AgCl), as at -2.8 V only shiny, smooth deposits were formed. Two voltages were of focus, -3.8 and -4.8 V (-4 and -5 V vs. Ag/AgCl), and the features of the deposit were examined and screened using SEM imaging. The deposition time of 300 s was a sufficient time to grow a significant deposit off the surface of the substrate. Using DHBT for other metals such as copper, a shorter deposition time of 15 s is sufficient to grow interconnected honeycomb networks. Due to the sluggish kinetics described above, the deposition time needed to be significantly increased to obtain acceptable film growth from the aqueous Ru solution. The first observations involving the effect of applied potential demonstrates the
initial differences that are possible due to changes in deposition conditions. Figure 3.2 shows the effect of deposition at applied potentials of either -3.8 V or -4.8 V. The deposited film at -3.8 V shows large cracks and a not so uniform surface, with large densely packed particles, compared to a more uniformly packed surface with smaller surface structures that were obtained using -4.8 V. The finer and more uniform surface of Figure 3.2 b) more closely represents the ideal surface, and therefore -4.8 V is the potential that was used for further study.

![Figure 3.2 Effect of Deposition Voltage a) -3.8 and b) -4.8 V 25 mM RuCl₃ₓH₂O in 0.2 M HClO₄ for 300 s.](image)

### 3.2.3. The Effect of Acid Concentration

Aqueous RuCl₃ solutions are capable of precipitating ruthenium hydroxides at a pH above 4, necessitating the use of acidic conditions to maintain the Ru(III) salt in solution.[44] This becomes more important because of the significant cathodic potential applied, which results in the vigorous evolution of hydrogen due to the rapid reduction of H⁺ ions. The consumption of H⁺ ions results in an increase in the pH both local to the working electrode, and over time in the bulk solution. The acid concentration also effects the deposition process as DHBT is sensitive to the concentration of hydrogen ions available in the acid.
electrolyte. The acid concentration is responsible for the availability of H\(^+\) ions. Hydrogen bubbles during DHBT are rapidly formed through the reduction of H\(^+\), and the properties of these bubbles including the size, residence time and rate of evolution will directly influence the morphologies of Ru deposits obtained. The hydrogen bubbles play a key role, as they have the ability to block the substrate from incoming, co-depositing metal ions forcing the Ru\(^{3+}\) to seek vacant (bubble free) sites to be reduced. The bubble behaviour has a profound effect on the morphology, and is dependent on a number of factors. For example, the exchange current density for H\(^+\) evolution, the surface energy, and the morphology of the deposition site will affect the residence time and bubble break off diameter. Due to the large overpotential of -4.8 V used, the H\(_2\) evolution rate is rapid, and therefore the solution adjacent to and near the electrode surface is turbulent. This turbulence causes compression of the diffusion layer that increases the availability of H\(^+\) and Ru\(^{3+}\) ions from the bulk solution. As the increase in acid concentration will increase the H\(^+\) ion availability, the turbulent nature of deposition increases causing changes to the morphologies obtained. Therefore there is an ideal ratio between the acid concentration, and concentration of the Ru\(^{3+}\) ions in the solution for suitable deposits to be obtained. This ratio is investigated in this section and in Section 3.2.4.

Perchloric acid, HClO\(_4\), was chosen to be the most suitable acid to use as there is less interference due to the weak adsorption of the perchlorate (ClO\(_4\)^-\) ion compared to other anions,\(^{[74, 75]}\) which results in better repeatability of deposition. The concentration range of perchloric acid investigated was between 0.1 and 0.5 M. Smooth films of Ru were formed with 0.1 M HClO\(_4\), which were not sufficiently stable to adhere to the Au surface, suggesting the H\(_2\) was not acting as a template under these conditions. The concentration range of
0.2-0.5 M HClO₄ became the focus for further experiments. The optimum RuCl₃.xH₂O concentration was approximately 25 mM, so therefore this was the concentration used for initial experiments, as well as 50 mM for comparison. Figure 3.3 shows the effect on morphology with two acid concentrations, at the two different Ru³⁺ concentrations. The top two images in Figure 3.3 correspond to deposits using a Ru³⁺ concentration of 25 mM. The deposits change from being open, slightly porous and relatively uniform, (Figure. 3.3 a) to being larger and smoother structures in Figure 3.3 b. The bottom images of Figure 3.3 use a Ru³⁺ concentration of 50 mM. The 0.5 M deposit (Figure. 3.3 d) shows particles that are much more closely packed, which seems to induce cracking.

*Figure 3.3 Effect of perchloric acid concentration a and c) 0.2 or b and d) 0.5 M HClO₄ for RuCl₃.xH₂O 25 (top) or 50 mM (bottom).*
Figure 3.4 shows images at a higher magnification to better compare the morphology of structures obtained at different acid concentrations. The two lower concentration ranges of 0.2 and 0.25 M (Figure 3.4 a and b) show similar growths that are of ‘cauliflower’ shaped 3-D buds with an observable height off the substrate. The comparatively ‘smooth’ particles in Figure 3.4 c) were obtained using 0.5 M, and the surface seems to be flatter with compacted growth. The observable morphology differences between the concentration of 0.2 and 0.25 M HClO₄ exist in the porosity or openness. The surface of the films obtained using 0.25 M HClO₄ (Figure. 3.4 b) have structures that are slightly finer and more open. Therefore 0.25 M HClO₄ best represents an acid concentration that yields the highest surface area structures and therefore is the most suitable acid concentration for further study. This also shows the significance in the delicate balance between H⁺/Ru³⁺ ratio, and the how small changes in acid concentration can yield significant changes to morphology.

The increasing H₂ evolution rate changes the hydrodynamic environment, causing a reduction in the diffusion layer thickness. This increases the availability of the Ru³⁺ ions near the electrode available for electrodeposition,[76] and also affects the ability of the nucleating Ru metal to template around the bubbles as they release from the growing surface. This may explain the more densely packed and larger particles observed at higher acid concentration.
3.2.4. Effect of Metal Salt Concentration

The other parameter that can be controlled in the bulk electrolyte is the concentration of the Ru$^{3+}$. Shown initially in Figure 3.3, there are distinct differences observed due to the effect of concentration of the RuCl$_3$.xH$_2$O salt. Using a constant acid concentration of 0.25 M, the effect from changing the Ru$^{3+}$ concentration was investigated using three selected concentrations of 15, 25 and 50 mM. The SEM images in Figure 3.5 result from the use of these different concentrations. It is seen that the two lower concentrations in Figure 3.5 a and b), give smaller, more open structures. Whereas the 50 mM deposit, Figure 3.5 c, shows a large single, dense and rough particle (at the same scale) with no porosity. The 15 mM therefore represents the optimal concentration of all three deposits when material utilisation is considered, and will be further compared in Section 3.3.
3.2.5. Effect of Time and Pulse Sequencing

During investigations on the effect on morphology of different acid and ruthenium chloride concentrations, it was consistently observed that whilst microstructures with excellent roughness and porosity were prepared, the overall uniformity of the deposit was poor. Imperfect surfaces were obtained like that seen in Figure 3.6 a). To combat the imperfect surfaces, implementation of a pulse sequence was used to nucleate initial Ru sites onto the substrate. Following the pulse sequence, the deposition at -4.8 V was performed which yielded defect-free uniform surfaces over several mm. The pulse sequences involved switching between two current densities, between -1 Acm$^{-2}$ for 0.05 s, then 0.2 Acm$^{-2}$ for 0.05 s, repeated for 120 cycles (12 s total), which resulted in a stabilisation of the surfaces on the macro-scale in the final deposit (Figure 3.6 b). The pulse sequence allows for small amounts of Ru to evenly nucleate across the Au surface, setting up initial nucleation sites, allowing for a uniform final deposits to grow,[77] which also enhanced the repeatability of the deposits both on the micro and macro scale.
3.2.6. Dendrite Formation and Summary

It has been shown in the above sections that the morphology of electrodeposited Ru can be controlled through changes in the experimental conditions. Through the stepwise identification of the ideal deposition conditions, the morphology that represented an optimal morphology was identified as an electrolyte containing 15 mM RuCl$_3$.xH$_2$O in 0.25 M HClO$_4$. To ensure a uniform surface, the deposition step was proceeded by a pulse sequence of (-1 Acm$^{-2}$ to 0.2 Acm$^{-2}$) 0.05 s for 120 cycles (12 s total), then an immediate deposition step of -4.8 V for 300 s.

Closer inspection of the film surfaces produced under the conditions described above showed a very interesting and substantial finding. This was the first evidence of electrochemically deposited Ru dendrites, as shown in Figure 3.7.
As has been previously described, Ru has slow deposition kinetics relative to other metals such as copper (Table 1.2), which readily form dendritic structures, and this limits the ability to control the morphology of electrodeposited Ru. The conditions used have thus allowed the growth of dendrites of Ru for the first time due to a combination of factors. The rapid evolution of H₂ bubbles affects the hydrodynamic conditions near the substrate surface, compressing the diffusion layer and causing a localised increase in the current density, which is exacerbated by the insulating bubbles on the surface. This allows the effective current density, and thus rate of Ru electrodeposition to be high enough to lead to a diffusion limited growth regime, which favours the formation of dendrites (Figure 3.8 a).[78]

However, further out from the initial substrate as the surface area is increased, the current
density of deposition decreases. This prevents the kinetic limitations from being overcome, and the regime returns to being controlled by kinetics. This is shown in the scheme in Figure 3.8 b, which relates the morphology seen in previous SEM Figures to the growth regimes leading to dendritic and compact growth.

Figure 3.8 The scheme showing the regimes in which Ru is deposited both under a) diffusion limited growth near the substrate at high current density and b) compact growth due to kinetic limitations further away from the substrate.

3.3. Characterisation of Ru Deposits

With the ideal deposition conditions optimised, further quantitative analysis of the Ru surfaces was undertaken, which involved looking at key film parameters including surface area, mass, oxidation state and the capacitance of oxidised and thermally treated surfaces.
3.3.1. Quantitative Determination of Electrodeposited Ru Films

The three important parameters in determining the material utilisation are the weight, surface area and most importantly the specific surface area (SSA) of the Ru deposits. The determination of Ru surface area is not straightforward, unlike the relatively simple methods that are routinely used for electrochemical determination for other noble metals such as Pt and Au (Sections 2.2.2.1 and 2.2.2.2). For Pt, it is as simple as integrating the charge of the hydrogen adsorption/desorption region which is easily observed by cyclic voltammetry (CV). This method relies on the principle that one monolayer of hydrogen adsorbs to the Pt surface in a well characterised region of electrode potential, allowing determination of the electrochemically active surface area (ECSA). Integrating of the charge responsible for the hydrogen adsorption process and dividing it by 210 µC cm$^{-2}$, the surface area of deposit can be obtained. A similar method can be performed on an Au surface, but by utilising the charge required for the reduction an electrochemically formed Au oxide monolayer.

Due to the overlap of the hydrogen and oxygen adsorption/desorption regions on Ru surfaces, these methods cannot be used. An alternative method for investigating the electrochemical surface area of metals other than Pt and Au, uses a reversible redox couple in solution (such as the ferricyanide/ferrocyanide couple) and the Randles-Sevcik equation (Equation 2.1). The method relies on diffusion to the surface allowing for the estimation of surface area. However, this method assumes diffusion to a flat surface and as the Ru films have a significant roughness, errors would be significant.

Surface area determination was thus undertaken by under potential deposition (upd) of copper (Cu). This method has proven to be the most suitable for Ru, and was
described in a two-part research paper by Green and Kucernak,[81, 82] which showed an excellent comparison with other methods including N₂, BET physisorption, and CO chemisorption. The method works on the principle of the adsorption of a complete monolayer of Cu, which means for each Ru atom at the surface, one atom of Cu will adsorb.[87] This is suitable due to the atomic radii size similarities between Cu and Ru, being 0.128 and 0.134 nm, respectively. The relationship between the Cu stripping charge and surface area is described in equation (2):[81]

$$Cu_{upd} \rightarrow Cu^{2+} + 2e^- + 420 \mu C cm^{-2} \quad (3.2)$$

Figure 3.9 shows the stripping peak for Cu upd for a pure Ru and an oxidised Ru film surface. Cu was observed in Figure 3.9 b) to be unable to deposit on an oxidised Ru surface. This was in agreement with observations made by Green and Kucernak. It however has been disputed that this method in not limited to Ru metal and in fact is applicable to the oxide form as well.[86] Green and Kucernak used a relatively flat surface compared to those analysed in this work. Their maximum surface area was mentioned to be 0.633 cm², and used preconditioning times (the time the potential was held for the upd of Cu) of 60-100 s. It was stated that it may be necessary to precondition for longer times for materials with larger surface areas. The preconditioning time was determined to be a significant factor in the true determination of the surface area and preconditioning times of over 3000 s or more were required to form a complete monolayer.[86]

The deposited Ru films were placed in a 0.1 M H₂SO₄ blank solution and bubbled with nitrogen gas for 10 mins, after which time a linear scan voltammogram (LSV) from 0.2 to 0.8 V at 10 mV/s was performed. It was important to not to go above 0.8 V to prevent oxidation for the Ru surface. This linear scan was used as a background for the Cu upd and
stripping runs. The stripping runs used a solution of 2 mM CuSO₄ in 0.1 M H₂SO₄. It has been identified that there are slow uptake kinetics between Ru and Cu,[86] therefore the Ru electrode was left in the Cu containing solution overnight with slow N₂ bubbling. The sample was preconditioned at 0.3 V to deposit a monolayer of Cu, followed by linear sweep 0.3 to 0.7 V at 10 mV/s to strip the Cu. The blank is subtracted from the stripping run to obtain the peak area of the Cu stripping peak. Given that a 1:1 monolayer is assumed, the peak area should be relative to the area of the active Ru sites. Dividing the sum of charge by the relationship in Equation 3.2 (420 µC cm⁻²) gives the area in cm².

For this present work, various preconditioning times were examined. Figure 3.9 a) shows an example investigation into optimising and increasing the preconditioning times on an electrodeposited Ru surface. It is not until a repeatable maximum is observed that a complete Cu monolayer is assumed to have been formed, and a complete 1:1 coverage of the Ru surface by Cu is confirmed. The peak area was obtained by integration of the Cu stripping peak after background subtraction using the previously measured blank.

![Figure 3.9 Cu Stripping at various preconditioning times on a) Ru metal surface and b) an oxidised Ru surface.](image)

The peak maximum was found to occur between 10800-14440 s (3-4 hrs), which had repeatable responses with acceptable experimental error (Figure 3.10). The range of the
surface areas obtained is shown in Table 3.1. The surface area values are much larger than those determine in works performed by Kucernak \((0.633 \, \text{cm}^2)\),\cite{81,82} explaining the requirement for significantly longer preconditioning times. The surface area varied across different samples was 39-72 cm\(^2\). This is a much greater area than what was used for the original method and it was concluded that the preconditioning time required is greater for the surfaces prepared by DHBT than general flat polycrystalline electrodes.

![Graph](image)

*Figure 3.10 Example Cu stripping voltammogram used for the determination of Ru surface area, showing a stable, repeatable peak area after 10800 s preconditioning time.*

The weight of Ru deposited on the substrate was determined by anodic dissolution in 0.1 M NaOH at + 1.4 V for 60 s, which dissolved the entire Ru film leaving the bare Au substrate. A sample of solution from this anodic dissolution was then diluted in a 2 % HCl matrix, and Ru concentration was determined by ICP-MS, allowing the original weight of the deposit to be calculated. The results are tabulated (Table 3.1) for four representative materials.
Table 3.1 Direct Comparisons of four Ru films

<table>
<thead>
<tr>
<th>Film</th>
<th>[Ru] mM</th>
<th>[HClO₄] M</th>
<th>ECSA cm²</th>
<th>Mass gᵇ</th>
<th>SSA m²/gᶜ</th>
<th>RFᵈ</th>
<th>Faradaic Efficiency %ᵉ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>0.25</td>
<td>16.83</td>
<td>8.95 x 10⁻⁵</td>
<td>18.8</td>
<td>343</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>0.25</td>
<td>16.42</td>
<td>1.54 x 10⁻⁴</td>
<td>10.6</td>
<td>335</td>
<td>2.22</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>0.50</td>
<td>6.22</td>
<td>1.48 x 10⁻⁴</td>
<td>4.2</td>
<td>127</td>
<td>0.91</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.25</td>
<td>23.46</td>
<td>2.77 x 10⁻⁴</td>
<td>8.5</td>
<td>479</td>
<td>2.95</td>
</tr>
</tbody>
</table>

a) Electrochemical surface area determined (ECSA) by Cu upd stripping.
b) Determined by ICP-MS after anodic dissolution.
c) Specific surface area (SSA).
d) Ratio of Electrochemical surface area (determined by Cu upd) to geometric surface area.
e) Percentage of charge attributed to Ru reduction during electrodeposition.

There are several important points to take from the data in Table 3.1. The largest surface area is observed with film 4, and can be attributed to the large rough particles which resulted in a denser growth (Figure 3.5 c), but the SSA is significantly lower. The SSA looks at the utilisation of Ru by comparing the mass used to the active surface area obtained. The ECSA of 15 and 25 mM Ru (film 1 and 2 in Table 3.1) is very similar, but the surface produced from 15 mM Ru has a higher SSA (more efficient use of Ru). The SSA of Ru (expressed as m²/g), is highest for those samples where the morphology appears more open in the SEM images (Figure 3.5 a and b). The highest SSA (film 1) is from the film that showed dendritic growth of Ru for the first time, which is a recognised high SSA morphology.

The last column of Table 3.1 shows the faradaic efficiencies for the materials deposited. Faradaic efficiency was calculated by integrating the current to obtain the charge passed during potentiostatic electrodeposition of each surface, Q_Total. The equation used was faradaic efficiency = Q_Ru/Q_Total. Q_Ru was determined from the weight of Ru deposited,
assuming a three electron reduction from RuCl\textsubscript{3} to Ru. For all of these structures, over 97\% of the charge passed is due to H\textsubscript{2} evolution, which is not surprising given the high acid concentration and significant overpotential employed. This is a faradaic efficiency far below that for bubble templated Cu deposition where honeycomb-like structures were formed from aqueous solution (faradaic efficiency around 30\%),[88] or NiCo electrodeposition by a similar procedure (faradaic efficiency > 20\%),[89] and is another indication of the difficulty and difference in handling a metal that has very slow deposition kinetics.

3.3.2. **Increase in Substrate Size**

It is likely that the size of the Ru electrodes would have to be increased if real world applications were studied. To investigate the scale-up ability, the size of the masked area of the substrate was increased from (0.049 to 0.49 cm\textsuperscript{2}). The same optimal conditions of electrodeposition were adhered to with an electrodeposition bath of 15 mM RuCl\textsubscript{3}·xH\textsubscript{2}O in 0.25 M HClO\textsubscript{4}, an initial pulse sequence of (-1 A cm\textsuperscript{-2} to 0.2 A cm\textsuperscript{-2}) 0.05 s for 120 cycles (12 s total) then an immediate deposition step of -4.8 V for 300 s. The resulting deposits are shown in Figure 3.11. On a larger surface area, it is seen that the optimised conditions give rise to high surface area “tree-like” structures. There was slight variance observed in the surface area obtainable with the areas being between 39-72 cm\textsuperscript{2} that resulted in SSAs of the films to increase to between 19-44 m\textsuperscript{2}/g, which is in very similar in range to film 1 in Table 3.1. In fact on these larger surface areas, maximum SSAs were obtained, as the compact growth regime proposed in Figure 3.8 is not entered. It is these films that are used in the following sections for studies of surface properties.
3.3.3. Surface Oxidation State

Due to the large cathodic overpotential and the sufficiently acidic electrolyte utilised in the deposition of Ru, the deposited species is Ru metal (Ru\(^0\)). However, it is the oxide species, RuO\(_2\).\(x\)H\(_2\)O,[23, 57, 90] that has been identified as the species that is responsible for capacitive and catalytic properties.[11-13, 91] Figure 3.12 shows a CV of an ‘as deposited’ Ru surface. Although the range of oxidation processes are not particularly well resolved at this scan rate, the overlapping oxidation processes have been described adequately by previous workers.[92-94] It is confirmed that the acidic solution used has been sufficient to prevent precipitation of Ru hydroxides, and that significant Ru oxide formation has not occurred. Figure 3.12 shows a broad hydrogen adsorption/desorption region between 0.0 and 0.2 V, and shows oxide formation from ca. 0.8 V. This is typical of pure metallic Ru surface.[92]
3.4. Surface Treatment

To further probe the surface characteristics, oxidation and annealing of the Ru deposits was performed by electrochemical oxidation and heat-treatment in air to generate RuO$_2$ species. As RuO$_2$ materials are known to have capacitance properties, the specific capacitance was used to compare how each of the oxidation and annealing steps affected capacitance of the materials.

The specific capacitance, $C_s$ (Farad), of oxidized Ru surfaces was estimated by voltammetry in 1 M H$_2$SO$_4$. The current was integrated over the discharge time ($\Delta t$) for a specific voltametric potential window ($\Delta V$) to obtain the charge, $Q$ (C) passed per unit volt (V), giving F (Farad). The equation then used was $C_s = C/m$, where $m$ is the mass of the Ru deposit. A feature-less ‘rectangular’ shaped CV is indicative of a constant charge exchanged between an electrode and an electrolyte,[23] and the retention of the rectangular shape over increased scan rates are ideal for capacitive materials.[95, 96]
The first step in making the materials suitable for capacitance studies is to oxidise them. This was performed electrochemically. Oxidation was examined by two methods in a 1 M H₂SO₄ electrolyte. First by holding at an oxidising potential of 1.4 V for 300 s, which causes the slight evolution of oxygen but did not degrade the surface, and secondly by constant cycling between 1.0 – 1.5 for 40 – 60 cycles at a scan rate of 20 mV/s. Figure 3.13 shows an as-deposited sample that has been cycled under capacitive conditions and a sample cycled comparatively after oxidation. There is a reduction the voltammetric features and an enhancement in the rectangular shape after the oxidation procedure. Upon multiple sweeps the voltametric response changes until it stabilises, with the change being observed by the broadening of features from the as-deposited film (Figure 3.12 compared to Figure 3.13). This indicates that there is a formation of surface RuOₓ. Another method for oxidation was performed by CV between 1.0-1.5 V at a rate of 20 mV/s for 10 sweeps.

Figure 3.13 Capacitance Cyclic Voltammogram of ‘as deposited’ Ru and ‘after oxidation’ Ru in 1 M H₂SO₄ at scan rate 20 mV/s.
Previously Ru oxides prepared for capacitive purpose have achieved the best capacitance values when annealed between 150 – 200 °C. The times of annealing vary throughout the literature, with annealing times in the range between 2-24 hrs. [23, 33, 34, 46, 57, 67, 97] The prepared Ru films were annealed at three temperatures of 150, 175 and 200 °C for 2 hrs to determine the optimum temperature. After each annealing step the capacitance was measured from cyclic voltammetry sweeps shown in Figure 3.14.

Figure 3.14 Effect of Annealing temperature on Capacitance CVs of ‘after oxidation’ Ru in 1 M H₂SO₄ at scan rate 20 mV/s.

Figure 3.14 shows whilst the voltammetric response becomes more rectangular, indicating the evolution of the ideal constant charge/discharge properties, there is a reduction in the overall current upon annealing. In comparison to the literature, the capacitance was low, with the maximum always being observed for the unannealed (25 °C) state of the sample.
There was a significant loss in the capacitive ability after annealing, however the shape of the CV became more rectangular up to 200 °C. Table 3.2 shows the specific capacitances obtained after each treatment step, all measured at a scan rate of 10 mV/s.

Table 3.2 Capacitance and Annealing Results for the different treatment conditions. Specific Capacitance F/g measured at a scan rate of 10 mV/s.

<table>
<thead>
<tr>
<th>Film</th>
<th>Treatment</th>
<th>Capacitance and Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AD</td>
</tr>
<tr>
<td>1</td>
<td>As Deposited (AD) and cycled for Capacitance</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Oxidation 1.4 V 300 s</td>
<td>103</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation by CV 1.0-1.5 V (60 scans)</td>
<td>127</td>
</tr>
</tbody>
</table>

Figure 3.15 Effect of increased scan rate, v (mV/s), on capacitance CVs of an oxidised and annealed Ru deposit in 1 M H₂SO₄.
Figure 3.15 shows the CV charge/discharge response at a range of scan rates of an oxidised and annealed Ru deposit over a potential window between 0 and 1 V, which is determined to be suitable for Ru materials.[44, 49, 61]. The ability of the electroactive oxyruthenium species to exchange protons results in the reversible redox wave in the CV.[44] Upon increasing the scan rate, the shape of the voltammetric response indicating the charge/discharge behaviour of the deposit remains constant even at faster scan rates, typical of pseudocapacitive behaviour.[95, 96, 98]

Figure 3.16 shows the XPS analysis of an as-prepared Ru surface, and a surface that had been annealed at 200 °C for 2 hrs in air to observe the change in surface chemistry. In scans of the Ru 3d orbital, peaks appear as a doublet with a spin orbit splitting of approximately 4.17 eV.[99, 100] The binding energy of carbon (C 1s) impurities overlap with the Ru 3d_{3/2} peak and species were thus identified using the Ru 3d_{5/2} peak. Fitting was undertaken by considering three Ru binding energies at 280.0 eV, 280.8 eV and 281.8 eV. The lowest energy state at 280.0 eV is assigned to the metallic ruthenium, Ru⁰. The two higher binding energies are assigned to oxides formed on the surface, either through surface oxidation in the case of the as deposited film, or during the electrooxidation and annealing processes. The film in Figure 3.16 b) was obtained by electrooxidation via CV cycling between 1.0 and 1.5 V for 60 scans and annealed in air at 200 °C, and showed a significant shift to the higher binding energies indicating oxidation has occurred.[100] RuO₂ is the only oxide likely to form at the temperatures used in this work and not the higher oxidation states of RuO₃ or RuO₄.[69] The higher bonding energies of 280.8 and 281.8 eV can thus be assigned to RuO₂ species, with shifts in this region attributed to structural variations or hydration.[101]
absence of a significant Ru\(^0\) peak in the surface oxidized at 200 °C is seen in Figure 3.14, representing oxides that are electrochemically stable between 0 and 1 V.

![Figure 3.16 XPS analysis of a) an as-deposited and b) oxidised and heat treatment (2 hrs, 200 °C, air) Ru surface.](image)

Table 3.3 uses XPS peak binding energy information to semi-quantify the effects of different treatment methods and their resulting oxidation states. There are three main oxidation states of Ru detected by XPS at binding energies of 280.0, 280.8 and 281.8 eV, for
ruthenium metal (Ru⁰), ruthenium dioxide (RuO₂) and ruthenium dioxide,hydrate, (RuO₂·xH₂O), respectively. The versatility of the electrodeposited Ru material is shown by the ability to electrochemically oxidise and reduce the surface. Condition 4 is a film examined without any further treatment, or ‘as deposited’. 52.3 % of the signal comes from the peak at 280.0 eV (Ru⁰). Upon reduction (condition 5) this peak increases to 71.5 %.

Condition 1 shows an as-deposited film that has been cycled 10 times. As the scan range for capacitance CVs is between 0.2 and 1.2 V is it expected that the surface will oxidise, which was observed in condition 1 with the reduction in the Ru⁰ peak and increase in the binding energy peaks for RuO₂ and RuO₂·xH₂O. This has been seen previously by the difference in the shape between the CVs obtained for ‘as deposited’ and a sample after cycling (Figure 3.12 vs. 3.13). However, the Ru deposits can be purposely electrochemically oxidised (conditions 2 & 3), which is seen by the reduction of the Ru⁰ peak to < 10%.

Table 3.3 XPS peak binding energy (B.E) information for the different treatment methods of the Ru deposits, with percentage ratio of intensities.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Treatment</th>
<th>Ru 3d₅/₂</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ru⁰</td>
<td>RuO₂</td>
</tr>
<tr>
<td>1</td>
<td>Capacitance CVs and Annealed</td>
<td>280.0 (16.8 %)</td>
<td>280.8 (49.4 %)</td>
</tr>
<tr>
<td>2</td>
<td>Ox 1.4 V 300s</td>
<td>280.0 (9.6 %)</td>
<td>280.8 (46.1 %)</td>
</tr>
<tr>
<td>3</td>
<td>Ox CV 1.0-1.5 V (60 scans)</td>
<td>280.0 (7.3 %)</td>
<td>280.8 (53.6 %)</td>
</tr>
<tr>
<td>4</td>
<td>As deposited</td>
<td>280.0 (52.3 %)</td>
<td>280.9 (27.8 %)</td>
</tr>
<tr>
<td>5</td>
<td>Reduced (-1.8 V 300s)</td>
<td>280.0 (71.5 %)</td>
<td>280.8 (10.8 %)</td>
</tr>
</tbody>
</table>
As mentioned in Section 3.1.3, the capacitive properties of RuO$_2$ relies on the interconnectivity and proton permeability of the film. Even though these materials have well interconnected surfaces, with the majority of the surface oxidised to RuO$_2$ or RuO$_2$.$x$H$_2$O, the water content required for proton conduction was not sufficient to yield the high capacitance values obtained with materials prepared by sol-gel processes. It is Ru metal that is predominately electrodeposited initially, which limits the opportunities for water incorporation, unlike those prepared through sol-gel methods.[57, 91] As XPS is a surface characterisation method, it does not allow analysis of major bulk species, and therefore the high RuO$_2$ on the surface may not be translated into the bulk. Hence a Ru deposit was further oxidised in air at 400°C according to Zhitomirsky and Gal-Or,[64] where heating to this temperature was prescribed to change ruthenium metal to ruthenium oxide. However there was an extreme drop in the capacitive ability that suggests heating to 400°C only worked to decrease the water content further of these films

Nevertheless, RuO$_2$ has other applications in other energy related emerging technologies, where the surface states and morphologies are critical in determining the efficiency in desired applications. Such applications include cathode catalysts for oxygen evolution reactions (OER).[102] oxygen reduction reaction (ORR).[9] and the hydrogen evolution reaction (HER).[102, 103] in which controlled morphologies and large surface areas are desired.
3.5. Conclusion

This chapter shows how the dynamic hydrogen templating technique can be used to control the deposition of Ru, a difficult metal to work with due to its slow deposition kinetics. DHBT allows for relatively high surface area Ru films to be prepared, where the high overpotential, and hydrodynamic conditions at the surface of the electrode due to H₂ bubbling can force Ru dendritic growth, and allow large surface area Ru to be deposited in a reproducible way for the first time. Specific surface areas of up to 18.8 m²/g were obtained, and it was directly shown how morphology has a direct effect on obtained surface areas. It is shown how changes to deposition parameters can lead to deposition of controlled structures, avoiding the introduction of impurities that can occur when using sol-gels and complex fabrication steps, through deposition in a one step process.

The obtained Ru deposits can be further treated to alter the surface properties to probe the behaviour of the oxides formed on the surface. The maximum capacitance of 127 F/g obtained with these materials was not as high as those established under sol-gel methods. However through various treatments it can be shown how dynamic these material prepared by DHBT have the ability to be manipulated and to modify the oxidation states of the material through electrochemical and thermal procedures.

The high surface area, pure Ru film would be useful starting point for a range of applications, such as further surface decoration with other metals, conformal deposition with another material, or use of another established technique for adjusting the surface properties of a pure metal. The main outcome of this chapter is the study of conditions that lead to the reproducible preparation of high surface area pure Ru, including dendritic growth under controlled conditions for the first time.
3.6. References


72. Yang, G.-M., et al., Bubble dynamic templated deposition of three-dimensional palladium nanostructure catalysts: Approach to oxygen reduction using macro-


Chapter 4

Comparing the Shape and Morphological Effects of Different Gold Surfaces for the Sulfur Dioxide Oxidation Reaction.
4.1. Introduction

Gold (Au) honeycombs have been previously prepared in a fast and efficient way through the use of the DHBT, giving access to high surface energy crystal facets and active sites. The overall porous honeycomb morphology was built from highly-branched dendritic structures, which are responsible for the highly active surface.[1] In this chapter, the surface activity of an Au honeycomb surface will be compared to Au nanoparticles, to explore the differences in reactivity that may occur between specifically shaped nanoparticles and a nanostructured film surface created by the DHBT method.

The sulfur dioxide (SO₂) oxidation reaction will be used as a case study of an electrocatalytic reaction that is still quite poorly understood and of possible importance in the near future. The study will focus on how the morphology of the electrode surface can affect the reaction. Au nanoparticles (NPs) are easily fabricated and offer precisely shaped surfaces with exposed facets that can be well defined. Using the DHBT, Au honeycomb structures were fabricated, with surfaces built containing fine dendritic branched structures. The shape and morphology effects on the SO₂ oxidation reaction were examined. The SO₂ oxidation is of interest due to its involvement in the thermochemical cycle for the large scale production of hydrogen (Section 1.2.2.2). The electrode surface state is significant, with the parameters affecting the SO₂ oxidation reaction including the preconditioning procedures prior to oxidation, the lower potential limit, E_low, and the scan rate.

Section 1.3.1 highlighted the importance on shape, size, morphology and nature of the crystal phases in relation to the activity and functionality of material surfaces. Nanoparticles have proven to be active materials for catalysis and electrocatalysis, with composition, size and shape (which determines the orientation of the surface) having a critical effect on
electrocatalytic activity. [2-5] Au nanoparticles can now be reliably synthesized and used as models for catalytic reactions. [6-8] Long term use of nanoparticles is often hampered by problems with long term activity and stability. [9, 10] As such, the development of 3-D porous structures with highly active sites or morphologies in favourable surface orientations have been able to yield excellent results with regard to electrocatalysis and sensing applications. [1, 11] In this chapter, an Au honeycomb nanostructured film will be directly contrasted with pure Au nanoparticles to establish differences in electrocatalytic activity.

4.1.1. The SO$_2$ Oxidation Reaction

Section 1.2.2.2 describes the motive for the investigating the SO$_2$ oxidation reaction as being a crucial part of the Hybrid Sulfur (HyS) cycle for the large scale production of hydrogen. It has been detailed that there are two key parts to the cycle, with SO$_2$ oxidation making up the second, electrochemical part of the reaction. The reaction is thermodynamically favourable, but suffers from a large overpotential. [12]

The oxidation of SO$_2$ reaction has an interesting feature. Depending on the sweep direction, the oxidation occurs at different potentials. [12, 13] The oxidation of SO$_2$ has a theoretical $E^\theta = 0.157$ V (SHE), however experimentally the oxidation onset begins at a potential of 0.85 V (SHE) on a Pt electrode, a significant overpotential above 0.157 V. [14] The oxidation peak reaches a maximum current at a potential of 1.20 V. This large overpotential for the oxidation of dissolved SO$_2$ indicates a highly irreversible process. [12, 14, 15]

On the reverse scan, there is an additional anodic peak centred at 0.85V. [13, 16] Even though oxidation occurs in both scan directions, the forward scan is the only one examined in the most studies.
4.1.2. Improvements to the SO₂ Oxidation Reaction.

It was established very early on in studies of SO₂ oxidation on Pt electrodes that improved electro-oxidation was dependent on the preconditioning procedures which were responsible for ‘activating’ the electrode.[15, 17] Initially the activation was believed to be due to the creation and stripping of oxides off the Pt electrode surface. This involved holding or sweeping the electrode to high anodic potentials to form oxide species, then stripping the oxide layer off in a subsequent sweep to ‘activate’ the electrode.[15, 17] There was an optimum lower potential limit, \( E_{\text{low}} \), which was important in determining the stripping of the oxide. Going above or below the optimum potential resulted in a decrease in the voltametric response.[18]

However, it was Audry and Voinov [18] who also initially proposed that the ‘activation’ occurs through the formation of adsorbed sulfur species on the surface of the electrode, which occurs on both Pt and Au. Unanimously, it is now accepted that the reaction is enhanced by intermediate sulfur species from reduced SO₂ on the electrode surface.[12, 16, 19, 20] Sulfur species adsorption has been seen to readily occur on Pt and Au electrode surfaces by sweeping negatively or holding at a potential less than 0.5 V vs. SHE (Equation 4.1) to cause adsorption of reduced sulfur species in SO₂-containing solutions. [12, 16, 19, 21-23]

\[
SO_2 + 4H^+ + 4e^- \rightarrow S(s) + 2H_2O \quad E^0 = 0.449 \, V \quad (4.1)
\]

The \( E_{\text{low}} \) and preconditioning procedures determine the surface coverage of sulfur species. Both the presence and the extent of coverage of these adsorbed sulfur species affects the SO₂ oxidation reaction to a different degree on Pt and Au electrode surfaces. The adsorbed species tend to ‘stick’ more to a Pt electrode, taking up to five cycles to potentials past 1.5 V
(SHE) before a sulfur free surface is obtained. To remove the sulfur species off Au, only a single cycle is required. On Pt, the adsorption of sulfur species at different $E_{\text{low}}$ potentials has a more significant impact on the resulting $SO_2$ oxidation. Both Au and Pt have similar oxidation potential and current density when both are in an activated state.[15, 23] Therefore there is debate in the literature as to which electrode is more active. Quijada et al. have claimed that it is Au that is inherently more active, as it is not as reliant on the preconditioning procedures.[20, 24]

Studies have been limited to identifying differing electrochemical conditions on polycrystalline metal electrodes, without any development of new electrocatalytic materials, or control of morphology for this reaction.[12] In a study by Awad et al. that focussed on the phenomena of $SO_2$ poisoning on Pt electrodes for the oxygen reduction reaction, it was found that polycrystalline 2-D Pt was more susceptible to poisoning than electrodeposited Pt nanoparticles on a glassy carbon electrode.[25] Therefore this indicates that there is a morphological effect on $SO_2$ oxidation.

The most recent works by O’Brien et al. have looked at the effect of varying preconditioning potentials, and investigating the effect of acid concentration and temperature on the $SO_2$ oxidation properties on 2-D Pt and Au.[12, 22, 23, 26] To summarise the findings; different oxidation regions and scenarios were found to unfold as a result of preconditioning at lower $E_{\text{low}}$ limits. $SO_2$ oxidation is described to occur in either of two different regions (Figure 4.1):[12, 21]

Region 1 – the double layer region oxidation

Region 2 – the region involving platinum oxides.
In these regions, there are three different scenarios that can take place. The three scenarios that can result from varying $E_{\text{low}}$ potentials are:

Scenario 1: Limited response to catalytic oxidation (in Region 1)

Scenario 2: Activated response for catalytic oxidation (in Region 1)

Scenario 3: Inhibited response in Region 1 with a platinum oxide peak in Region 2. [12, 22, 23]

![Figure 4.1 Effect of sulfur coverage on oxidation scenario observed on Pt, 2 M $H_2SO_4$. Reprinted with permission from ref [12].]

From the most recent article published by the group, it was identified that a more drastic modification in the electrode was required for an overpotential improvement to occur. [23]

There has yet to be an investigation into the activity towards $SO_2$ oxidation on different morphological shapes. Thus it was decided to investigate the effect of morphology of Au
structures on the SO\(_2\) oxidation reaction. Three different specifically shaped nanoparticles with three different predominately exposed crystal facets, and an electrodeposited Au honeycomb will be used to study the SO\(_2\) oxidation reaction.

4.1.3. Research Aims of Chapter

In Chapter 1 it is described how the shape and size of catalysts can affect the electrocatalytic activity. It is therefore necessary to be able to reliably prepare and study nanoparticles and structures that are suitable to be used in catalytic applications.

In this chapter three shapes of Au nanoparticles will be fabricated and compared with an electrodeposited 3-D porous Au honeycomb film prepared by DHBT. The Au structures will be characterised electrochemically using a lead underpotential deposition technique, which is sensitive to the morphology of the surface.

The effects of morphology will be assessed by using an emerging, though not well understood electrocatalytic reaction involving the oxidation of SO\(_2\). The differences between nanoparticles and a porous nanostructured film prepared by DHBT will thus be identified. This will be a unique study, in which the effects of morphology on the activity towards the SO\(_2\) oxidation reaction will be investigated. Comparisons will be observed between specifically shaped Au nanoparticles, a 2-D Au polycrystalline disk and an Au honeycomb film prepared by the DHBT method.
4.2. Experimental

4.2.1. Preparation of Au Nanoparticles

Three shapes of nanoparticles were prepared via a seed mediated approach, designated cubic (NP\text{cube}), octahedral (NP\text{oct}) and rhombic dodecahedral (NP\text{rd}).

The seeds for the Au cubic nanoparticles (NP\text{cube}) were prepared by the reduction of 0.25 mM HAuCl\textsubscript{4} by ice-cold NaBH\textsubscript{4} (0.6 mM) in the presence of 0.075 M cetyltrimethylammonium bromide (CTAB) which was used 2 hrs after preparation. In the growth solution, 0.2 mM HAuCl\textsubscript{4} was reduced by 0.009 M L-ascorbic acid (L-AA) in the presence of 0.016 M CTAB, followed by the addition of the Au seed solution (1.25 \times 10\textsuperscript{-8} M). All the concentrations were the final concentrations. The solution was gently shaken after the addition of every component and was left to sit for 8 hrs. The solution containing cubic Au nanoparticles was centrifuged at 5000 rpm for 10 mins and rinsed with Milli-Q water (Resistivity >18.2 MΩ.cm at 22°C) three times.[6]

For the preparation of the octahedral nanoparticles (NP\text{oct}), a 20 mL seed solution consisting of 0.125 mM HAuCl\textsubscript{4} and 0.01 M CTAB was prepared first. A 100 µL solution of 0.1 M L-AA was added to the 20 mL solution. Finally, 100 µL solution of 0.1 M NaOH was quickly added. The colour of the solution changed to purple-red within 20 mins, indicating the formation of Au octahedral nanoparticles. The mixture was centrifuged at 7000 rpm for 20 mins and the solid was rinsed with Milli-Q water three times to remove the excess reactants.[8]

Rhombic dodecahedral nanoparticles (NP\text{rd}) Au seeds were first prepared by a 10 mL solution of 0.25 mM HAuCl\textsubscript{4} and 0.1 M cetyltrimethylammonium chloride (CTAC). To this solution, ice-cold NaBH\textsubscript{4} solution (0.45 mL, 0.02 M) was added whilst stirring. The resulting
brown solution was left for 2 hrs before use. Two vials labelled A and B were used for the growth solution. In each vial 250 μL of 0.01 M HAuCl₄ solution, 0.33 mL of CTAC, 10 μL of 0.01 M NaBr and 9.23 mL of Milli-Q water were mixed first. To both vials L-AA (150 μL, 0.04 M) was added and the solution became colourless. Afterwards, 25 μL of the Au seeds was added to vial A with shaking. The mixture in vial A turned light pink in 5 s. Then 25 μL of the solution in vial A was added to vial B. The solution in vial B was left to sit for 20 mins for the completion of the particle growth, and subsequently centrifuged at 4000 rpm for 10 mins and rinsed twice before collection of the nanoparticles.[7]

These prepared nanoparticles were used to modify glassy carbon (GC) electrodes. 4 μL of the nanoparticle solution was drop cast onto a GC substrate masked to an area of 0.049 cm² and allowed to dry in ambient conditions. Once dried they were stabilised by dropping a 4 μL layer of 0.5 wt % Nafion on top and again allowed to dry. These modified GC electrodes were then used for electrochemical analysis.

4.2.2. Preparation of Au Honeycomb by DHBT.

The dynamic hydrogen bubble templating (DHBT) method was used to fabricate an Au honeycomb material. Electrodeposition was performed at a constant voltage onto an Au evaporated Au wafer substrate (Section 2.3.2) in a conventional three-electrode cell consisting of an Ag/AgCl (3 M NaCl) (+ 0.210 V vs. SHE) reference electrode and a Pt wire counter electrode. All potentials have been adjusted to SHE. The electrolyte used for electrodeposition consisted of 10 mM KAuBr₄ (Sigma-Aldrich) in 1 M H₂SO₄ (Merck). The Au substrate was masked to an area of 0.049 cm² with Kapton tape and a potential of -3.8 V (-4 V vs. Ag/AgCl) was applied for 300 s. Prior to electrodeposition the Au substrate was
prepared by rinsing with acetone, ethanol and rinsing with Milli-Q water, then dried under a stream of nitrogen gas. The Au substrate was also electrochemically pre-treated using cyclic voltammetry (CV) between potentials of 0.2 V and + 1.6 V vs. SHE in 1 M H$_2$SO$_4$ at a scan rate of 50 mV/s for 50 sweeps or until a stable response was obtained.

4.2.3. Structural Characterisation

4.2.3.1. Lead Underpotential Deposition (Pb Upd)

Pb underpotential deposition (Pb upd) was used to probe the surface crystallography, due to the potential dependent Pb upd and stripping onto Au crystallographic planes.[3, 27-29] This allows for estimation of the exposed crystal facets for each structure, especially for the nanoparticles, which predominately have low index planes and thus give an uncomplicated response. Pb upd was performed in a solution containing 1 mM lead nitrate, Pb(NO$_3$)$_2$ in 0.1 M NaOH, via CV between -0.5 and 0.0 V at a scan rate of 50 mV/s for 50 sweeps.

4.2.4. Sulfur Dioxide Oxidation Procedure.

The method reported earlier for the analysis of the SO$_2$ oxidation reaction utilised a 1 M H$_2$SO$_4$ solution spiked with a 1 M Na$_2$SO$_3$ stock solution to give a final SO$_2$ concentration of 100 mM.[22] The 1 M H$_2$SO$_4$ solution was purged with N$_2$ gas before spiking. A Pt wire electrode was used as the counter electrode and was separated from the main electrolyte by a porous frit. The working electrode consisted of either blank Pt or Au polycrystalline disk electrodes, Au nanoparticles on GC substrates or electrodeposited Au honeycombs described in Sections 4.2.1 and 4.2.2. The polycrystalline electrodes were initially polished using a polishing pad and 0.5 µm alumina. The electrode was rinsed with Milli-Q water, and then sonicated in Milli-Q water before use.
CVs were initially performed in blank, N₂ purged, 1 M H₂SO₄ to electrochemically clean the electrode surfaces before analysis. Electrodes were immediately placed into the SO₂ containing solution where they were held at a pre-determined Eₗₒₜ₉ potential for 2 mins, then a five sweep CV was performed from Eₗₒ₉ to 1.6 V.

4.3. Results

4.3.1. Surface Characterisation

4.3.1.1. Morphological Imaging

SEM images of nanoparticles that had been drop cast onto GC substrates are shown in Figure 4.2 a-c). It is seen that an even coating of the nanoparticles occurs across the entire surface. The particles of each designated shape show excellent monodispersity, with good uniformity in size. Some differences arise with slight defects isolated to individual particles, as shown in the example TEM images (Figure 4.2 d-f) of individual particles. Figure 4.2 d) shows a cubic morphology with some truncation on the edges and sides. The TEM image presents a cube with an edge length of ca. 77 nm. Figure 4.2 e) shows triangular, quasi-square-bipyramidal shapes with slightly truncated vertices associated with octahedral particles with an edge length of ca. 27 nm. Figure 4.2 f) shows the shape identified as a rhombic dodecahedron. The edge length of the NPrd is ca. 75 nm. The NPCube and NPrd are similar in size compared to the NPoct which are slightly smaller. Overall the SEM and TEM images in Figure 4.2 shows well defined individually shaped particles that are suitable candidates for there is a slight size differences of each nanoparticle type.
Figure 4.2 Au nanoparticles imaged by SEM for a) NP\textsubscript{cube}, b) NP\textsubscript{octa} and c) NP\textsubscript{rd} and imaged by TEM for d) NP\textsubscript{cube}, e) NP\textsubscript{octa} and f) NP\textsubscript{rd}.

Figure 4.3 shows the electrodeposited Au honeycomb that was fabricated using DHBT. Figure 4.3 a) shows the stacked honeycomb morphology that is described to occur by DHBT in Section 1.5 due to the simultaneous co-reduction of Au\textsuperscript{3+} and H\textsuperscript{+}. Figure 4.3 b and c) show the fine surface morphology, exhibiting a surface that is composed of dendrites. These dendrites each grow in size up to ca 20 µm, with a number of smaller nanoscale features, which have previously been shown to be active for catalysis.[1, 30, 31] Well defined stacked honeycombs occur for Au electrodeposited by the DHBT method due to the faster metal deposition kinetics (Table 1.2) compared to Ru, thus deposition occurs under a diffusion limited regime and does not have compact growth observed when Ru is deposited by DHBT.
4.3.1.2. Pb Upd Crystal Facet Determination.

Pb upd and stripping is a sensitive technique that can be used to identify the different exposed Au low index planes. It is an ideal method to give an estimation of dominant crystal facets exposed on each of the materials.[3, 27-29, 32]. The Pb upd stripping is potential sensitive, and on the prepared Au structures, Pb upd stripping occurs at potentials of ca. -0.28, -0.24 and -0.18 V for the (111), (100) and (110) low index facets, respectively. These potentials are slightly different to those observed by other authors,[27] however it has been described previously that the size of the Au particle (nanoparticles) and the type of structure (nanoparticles vs. solid electrodes) affect the potentials of upd.[32] The final CV cycle (of 25 cycles) is shown in Figure 4.4 for Pb upd performed on the Au NPs that were prepared.
Figure 4.4 Pb upd response for the different Au nanoparticles to probe surface exposed low index facets. a) NP\textsubscript{cube} b) NP\textsubscript{octa} and c) NP\textsubscript{rd}.

The orientation of facets that predominant at the metal solution interface, as a consequence of their shape and face centred cubic crystalline structure should be NP\textsubscript{cube} (100), NP\textsubscript{octa} (111) and NP\textsubscript{rd} (110). Imperfections such as edge and corner truncation
(observable in SEM/TEM images in Figure 4.2) means that there are actually a mix of low index planes, but one plane does predominate for each nanoparticle shape. Table 4.1 shows the estimated amount of each facet corresponding to the low index planes for these studies.

Table 4.1 Peak Areas from the Pb upd on the Au nanoparticles to determine low index facet percentages

<table>
<thead>
<tr>
<th></th>
<th>Au (111)</th>
<th>Au (100)</th>
<th>Au (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP_{cube}</td>
<td>21.7</td>
<td>44.0</td>
<td>34.3</td>
</tr>
<tr>
<td>NP_{oct}</td>
<td>72.3</td>
<td>-</td>
<td>27.7</td>
</tr>
<tr>
<td>NP_{rd}</td>
<td>8.2</td>
<td>-</td>
<td>91.8</td>
</tr>
</tbody>
</table>

The same Pb upd analysis was performed on the Au honeycomb and the final CV response is shown in Figure 4.5. Compared to the nanoparticles in Figure 4.4, the Pb upd stripping peaks have a larger intensity due to the higher surface area of the Au honeycomb. The low index facets (111), (100) and (110) are evident, however there are other responses present. The main Pb upd stripping peak occurs at a potential in the region between those designated for (111) and (100). The Au honeycomb is expected to have a larger proportion of defects and edge sites due to the dendritic morphology (Figure 4.3).[1] In previous studies it has been shown that polycrystalline surface, whilst exhibiting the Pb upd stripping peaks for the three low index facets at (111),(100) and (110), have additional small peaks, which are associated to Pd upd stripping off the steps and kinks on a polycrystalline surface.[28, 29, 32] The nanoparticles mostly consist of predominantly one crystal plane, e.g. (100),(111) or (110), thus giving each their defined cubic, octahedral or rhombic dodecahedral shape, whereas the honeycombs have multiple orientations responsible for their morphology. The honeycomb’s dendritic morphology has a large number of kinks and terraces, leading to a
more complicated surface chemistry compared to the low index nanoparticles, and a shift in the potential for the Pb upd response. Pb upd is sensitive to each of these orientations and thus the CV shows peaks corresponding to these sites.[28, 29]

Figure 4.5 Pb upd response for the Au Honeycomb.

4.3.2. SO₂ Oxidation

Initially it was necessary to establish a comparison baseline, to investigate the effect of preconditioning at different E<sub>low</sub> potentials on the SO₂ oxidation on 2-D polycrystalline surfaces without surface modification. Previously, the reaction has been investigated on both Pt and Au electrodes, with the majority of works focussing on Pt. Therefore both Pt and Au are compared in Section 4.3.2.1.
4.3.2.1. The Effect of \( E_{\text{low}} \) on \( \text{SO}_2 \) for 2-D Polycrystalline Electrodes.

The effect of the \( E_{\text{low}} \) preconditioning was studied on Pt and Au 2-D polycrystalline disk electrodes. Figure 4.6 compares a) Pt and b) Au 2-D polycrystalline electrodes, demonstrating the effect that \( E_{\text{low}} \) has on the resulting \( \text{SO}_2 \) oxidation. There is a significant effect on \( \text{SO}_2 \) oxidation with a Pt electrode at differing \( E_{\text{low}} \) potentials (Figure 4.6 a). An \( E_{\text{low}} \) of 0.1 V on Pt gives a peak in region II as described by scenario 3. An \( E_{\text{low}} \) of 0.2 V gives the most favourable result with an enhanced catalytic peak in region I (scenario 2). An \( E_{\text{low}} \) of 0.3 V results in the peak shifting to a higher overpotential whilst maintaining a favourable current density.

For the Au electrode (Figure 4.6 b) the effect of \( E_{\text{low}} \) potential is not as significant. An \( E_{\text{low}} \) of 0.1 V produces a response at a more favourable (lower) overpotential, but with a lower current density. \( E_{\text{low}} \) potentials of 0.2-0.4 V slightly increase the peak potential from that of the \( E_{\text{low}} \) 0.1 V response, however increasing from 0.2 V does not result in any changes to the peak properties. This is significantly different from Pt, where the \( E_{\text{low}} \) preconditioning potential has a great impact on the resulting \( \text{SO}_2 \) oxidation scenario obtained.

![Figure 4.6](image-url)  
*Figure 4.6 The 5th CV cycle after preconditioning at \( E_{\text{low}} \) for 2 mins in 100 mM \( \text{SO}_2 \) 1 M \( \text{H}_2\text{SO}_4 \) and sweeping to 1.6 V at a scan rate of 15 mV/s for a) Pt and b) Au 2-D polycrystalline electrodes.*
From the literature it is known that there is an ideal $E_{\text{low}}$ that will yield a peak in the catalytic oxidation region for $\text{SO}_2$ (scenario 2).\cite{13, 22, 23} $\text{SO}_2$ oxidation on Pt is highly dependent on the adsorption of sulfur species to achieve a peak under scenario 2 conditions. This is expected due to reduced binding or poisoning of $\text{SO}_2$ on the Pt surface resulting in an enhanced response. On Au electrodes, the pathway can also proceed through adsorbed intermediates, however $\text{SO}_2$ does not bind to the Au surface. O’Brien, Hinkley and Donne preconditioned Pt and Au electrodes by holding at a designated potential for 2 mins. On Pt it was shown that the lower potential limit has a significant effect of the resulting $\text{SO}_2$ oxidation peak. For Au it was shown that the oxidation peak only appears in the catalytic region and shifts only a little bit as a consequence of sulfur surface coverage induced by the different $E_{\text{low}}$ potentials.\cite{23}

The observation in Figure 4.6 b) can be explained by the previous studies by Quijada et al. who looked to control sulfur species layer formation. They however did not precondition at an $E_{\text{low}}$, rather setting different potentials as the lower limit for the scans.\cite{20, 24} It was explained that the increase in sulfur species coverage from 0 to 0.5 causes the shift in peak to lower, more favourable potentials, with little effect on the peak current density. Increasing the coverage from 0.5 causes the peak potential to increase. At a coverage of 0.75, the peak current decreases, and upon further increasing of the coverage, it reaches a point where the oxidation peak is completely suppressed.\cite{24} The coverage would increase in relation to reduction in the lower potential limit according to Equation 4.1. It is therefore expected that there would be a limit where the adlayer coverage on the surface of the Au would reach the limiting coverage of 0.75, resulting in a reduction in the response for $\text{SO}_2$.\cite{23}
oxidation. This is observed to occur when the $E_{\text{low}}$ of 0.1 V was used, which while yielding a more favourable oxidation potential resulted in a limited peak current in Figure 4.6 b).

4.3.2.2. The Effect of Sweep Cycles on a 2-D Au Polycrystalline Disk

It was observed in Section 4.3.2.1 that the sulfur species formed on a Pt electrode has a greater impact on the SO$_2$ oxidation than on an Au electrode. It has been described that sulfur species adsorbed in the initial preconditioning procedure require five scans past 1.4 V to be completely removed off a Pt surface, where only a single scan is required for Au.

It was observed that there are limited differences between the initial scan response Figure 4.7 a) and the 5$^{th}$ scan response. Only on the lowest preconditioning potential of 0.1 V was a significant difference observed.[24]

Figure 4.7 a) shows the first sweep, and at the $E_{\text{low}}$ of 0.1 V it is seen that the peak is not in the catalytic region. This is believed to be due to the formation of excess sulfur species which inhibits the reaction. This excess layer formed in preconditioning can only be removed by scanning up past potentials of ca. 1.4 V, caused by the formation of Au surface oxides that the effectively strips off any remaining sulfur species from the surface. The 5$^{th}$ scan (Figure 4.7b) shows that the peak has shifted to a significantly lower potential than that of the 1$^{st}$ scan, into the catalytic region for the $E_{\text{low}}$ of 0.1 V. However the lower 0.1 V potential limit is still affected by an excess coverage of sulfur species on the surface, inhibiting the reaction, resulting in a peak current density lower than the other $E_{\text{low}}$ potentials investigated. The $E_{\text{low}}$ potentials of 0.2-0.4 V show very little difference between the 1$^{st}$ and 5$^{th}$ sweep. However there is a slight increase in the peak potential shifting upwards by ca. 0.02 V on the 5$^{th}$ sweep.
Figure 4.7 CV response for Au disk after preconditioning at $E_{\text{low}}$ in 100 mM SO$_2$ 1 M H$_2$SO$_4$, and scanning from $E_{\text{low}}$ to 1.6 V vs. SHE at 15 mV/s. a) 1$^{st}$ sweep and b) 5$^{th}$ sweep.

As the effect of $E_{\text{low}}$ preconditioning is nullified after the first sweep, the future investigations in this chapter will focus on the 1$^{st}$ CV response after preconditioning. Therefore as determined from the response in Figure 4.7 a) the best preconditioning potential for subsequent studies is the $E_{\text{low}}$ of 0.2 V.

4.3.2.3. The Effect of Scan Rate on a 2-D Au Polycrystalline Disk

The effect rate of scan rate on the SO$_2$ oxidation reaction was investigated (Figure 4.8). It is observed that an increase in the scan rate was responsible for an increase in the current density of the SO$_2$ oxidation peak. However, upon the increase in scan rate there is a slight increase in peak potential. The scan rate of 20 mV/s yields the highest current density (16.3 mA cm$^{-2}$ at 0.74 V), but at 50 mV/s the current drops (13.6 mA cm$^{-2}$ at 0.727 V). A scan rate of 15 mV/s results in a peak potential of 0.727 V, with a current density of 14.5 mA cm$^{-2}$, which while it doesn’t have the highest current density, has the lowest peak potential.
The conclusion of the study by O’Brien, Hinkley and Donne stated that a more significant electrode modification was required for improvements in the overpotential for SO₂ oxidation to be observed.[23] Therefore the influence of morphology and surface crystallography of Au on SO₂ oxidation was investigated.

4.3.2.4. The Effect of Morphology on SO₂ Oxidation.

Revisiting the Pb upd analysis of the surfaces, the distinct differences in the exposed crystal facets for each of the different Au surface morphologies can be investigated. Figure 4.9 shows the comparative Pb upd responses. The 2-D Au polycrystalline disk (Au Disk) (Figure 4.9 a) shows an as expected polycrystalline response with the upd stripping peaks in the three dominant (111), (100) and (110) facet regions. Figure 4.9 b) is the collection of the responses for the NPs in Figure 4.4 and Figure 4.9 c) is the same response as Figure 4.5. Both
the Au Disk and the Au Honeycomb are polycrystalline surfaces. One of the main difference between Au Disk and the Au Honeycomb surface is the shift in the Pb upd stripping peak in the (111) and (100) region, to a slightly more anodic potential. Hamelin and Lipkowski showed how the Pb upd response changed in relation to the presence of different terraces, kinks and ledges.[29] Whilst the same (100), (111) and (110) low index facets are present, as with the nanoparticles, for both the Disk and Honeycomb, there are other high index sites also exposed on the surface. Even though both the Disk and Honeycomb are polycrystalline surfaces, they have significantly different morphologies that cause the exposure of different ratios of different terraces, kinks and ledges, to which Pd upd is sensitive to, resulting in the changed observations in the CV response in Figure 4.9.
Figure 4.9 Pb upd response for the different Au structures to probe surface exposed low index facets. A) Au Disk b) Au NPs and c) Au Honeycomb
The activity towards the $\text{SO}_2$ oxidation reaction is shown comparing the three morphological types in Figure 4.10.

**Figure 4.10.** Voltammograms (0.2 to 1.6 V vs. SHE), 100 mM $\text{SO}_2$, 1 M $\text{H}_2\text{SO}_4$, at 15 mV/s after preconditioning at 0.2 V for 120s. a) Au Disk b) Au NPs and c) Au Honeycomb.
The voltammograms for SO$_2$ oxidation are shown in Figure 4.10, with relevant data about onset potentials ($E_{\text{onset}}$) and peak potentials ($E_{\text{peak}}$) given in Table 4.2. It is seen that for the nanoparticles the $E_{\text{onset}}$ (0.636-0.646 V) and $E_{\text{peak}}$ (0.833-0.864 V) are shifted to the more anodic potentials compared to Au Disk (0.613 and 0.743 V for $E_{\text{onset}}$ and $E_{\text{peak}}$, respectively). The current densities ($j_{\text{peak}}$) were very high for the nanoparticles compared to Au Disk, with 100 mA cm$^{-2}$ on the NP$_\text{cube}$ up to 388 mA cm$^{-2}$ on the NP$_\text{oct}$ compared to 9.4 mA cm$^{-2}$ for Au Disk. The $E_{\text{onset}}$ for the nanoparticles does not vary considerably, though it can be said that Au (100) $\approx$ (111) $>$ (110). However for $j$, the peak current density, is in the order of Au (111) $>$ (110) $>$ (100).

The Au Disk had much stronger Pb upd stripping peaks between that of (100) and (111) (Figure 4.9 a), which may explain the reduction in the peak potential towards SO$_2$ oxidation compared to the nanoparticles. This indicates that the polycrystalline surface is more beneficial compared to the specifically orientated crystal nature of the Au nanoparticles. The SO$_2$ oxidation peak shifts to an even lower potential on the Au honeycomb, with a significantly reduced $E_{\text{onset}}$ of 0.516 V and a peak potential of 0.619 V. This is an improvement of ca. 0.124 V over the 2-D polycrystalline surface. The honeycomb has a number of unresolved Pb upd peaks that have been associated with the exposure of the higher index facets of Au due to the dendritic nature of the morphology.[1] The presence of these facets due to the terraces and edges making up the dendrites, of which the Au honeycomb is composed, result in the significant shift of the onset potential.
Table 4.2 SO$_2$ oxidation peak property comparison.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{onset}}$ (V)</th>
<th>$E_{\text{peak}}$ (V)</th>
<th>$j_{\text{peak}}$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au Disk</td>
<td>0.613</td>
<td>0.743</td>
<td>9.390</td>
</tr>
<tr>
<td>NP$_\text{cube}$</td>
<td>0.636</td>
<td>0.833</td>
<td>100.3</td>
</tr>
<tr>
<td>NP$_\text{octa}$</td>
<td>0.658</td>
<td>0.836</td>
<td>388.5</td>
</tr>
<tr>
<td>NP$_\text{rd}$</td>
<td>0.646</td>
<td>0.864</td>
<td>154.0</td>
</tr>
<tr>
<td>Au Honeycomb</td>
<td>0.516</td>
<td>0.619</td>
<td>0.448</td>
</tr>
</tbody>
</table>

Table 4.2 shows there is a significant difference arising in the current densities between the three different structures. While there is an improvement in the oxidation potential on the polycrystalline Au Disk and Au Honeycomb surfaces, there is a drop in $j$ to 9.39 and 0.448 mA cm$^{-2}$ for the Disk and Honeycomb, respectively. This shows that there is still much to be understood regarding the oxidation of SO$_2$.

Usually in electrocatalytic processes, it is observed that high index surface defects and imperfections such as edges and kinks are active,[30] and in this study the dendritic morphology of the Au Honeycomb, shows a significant shift to lower, more favourable, onset and peak potential for the SO$_2$ oxidation when compared to the Au polycrystalline disk, with the low index nanoparticles having the highest potentials.

4.4. Conclusion

This chapter investigates the effect of morphology of Au structures on the SO$_2$ oxidation reaction. 2-D polycrystalline, nanoparticles and an Au honeycomb were prepared and characterised using microscopy and electrochemical methods.
The nanoparticles designated NP\textsubscript{cube}, NP\textsubscript{oct} and NP\textsubscript{rd} consisted of Au in predominately one crystal orientation, (100), (111) and (110), respectively, determined by Pb Upd. Pb Upd was also used to evaluate the crystal orientation of the Au honeycomb surface that was made up of dendritic structures. The Au honeycomb had the same three dominant crystal orientations but were accompanied by Pd upd stripping peaks associated to higher index facets due to terraces and kinks present due to the dendritic structures making up the overall honeycomb morphology.

The activity of the different Au morphologies was investigated using the SO\textsubscript{2} oxidation reaction. The nanoparticles showed that the reaction proceeded with a significant overpotential, however allowed the reaction to proceed with a higher current density than the Au Disk. The Au Disk served as a baseline for comparison, where the SO\textsubscript{2} oxidation proceeded at lower overpotential than the nanoparticles due to its polycrystalline nature.

The 3-D Au Honeycomb had the most favourable onset potential, which can be linked to the presence of the high index sites of the dendrites that make up the underlying structure. The reaction proceeds at a significantly lower overpotential of 0.619 V, which was 0.124 V less than the peak potential of the 2-D polycrystalline Disk.

Thus in this chapter the effects of morphology on the SO\textsubscript{2} oxidation reaction were compared, showing how Au honeycombs can show significant improvements over nanoparticles when the reaction potential is considered, which are typically used to model reactions. It is out of this scope of this research that the issues surrounding the SO\textsubscript{2} oxidation would be resolved. This case study using the Au of different morphologies shows that there are improvements to be made in relation to the electrode structure that may benefit the reaction. Further studies would be required to study the reaction mechanism.
and kinetics, allowing for the results here to be further explained, especially in regard to the lower current density on the honeycomb surface.

4.5. References


Chapter 5

Incorporation of Noble Metals into a Copper Nanostructured Framework:
Gold and Palladium.
5.1. DHBT Templated Trimetallic Catalysts.

This chapter seeks to investigate the application of the Dynamic Hydrogen Bubble Templating (DHBT) method to synthesise porous materials with varying combinations of precious metals, to increase our understanding of how the surface chemistry and morphology can be controlled in mixed electrolytes. When heterogeneous catalysis or electrocatalysis is the desired end-use, the control of both the morphology and specific surface area are key factors in material design. This is particularly the case when noble metals are used, primarily due their expense, and also due to the fact that Pt, Pd and Au are not easily replaced in many catalytic reactions, as cheaper alternatives still do not provide acceptable activity. Surface chemistry plays an important role in determining the activity of catalysts towards reactions, including those related to energy production. In particular, electrocatalysts are a key area of research in fuel cell technologies in order to maximise the energy output and lifetime of devices and therefore require continued attention. Catalytic activity is sensitive to surface and morphological properties such as shape, size and composition. It has been shown that materials fabricated by DHBT are suitable for applications including catalysis,[1] electrocatalysis[2] and sensing.[3] The use of model reactions such as the hydrogen evolution reaction (HER) (see Section 1.6.2) and ferricyanide reduction (FCN) by sodium thiosulphate (STS) (see Section 1.6.1) allows for the changes in surface properties to be related to catalytic activity, and for comparisons to the literature to be made.

Since the structural and chemical stability of catalysts is of crucial importance for long-term applications, the use of porous frameworks presents a promising alternative to supported nanoparticle catalysts due to their superior structural and chemical stability.[4-6] However,
in order to fabricate such materials, reliable methods to control the morphology and surface chemistry need to be further developed and understood, so that the specific activity can be improved to rival that of supported nanoparticles. The control of size, shape and morphology is crucial in preparing catalysts that meet the demands for the reactions involving the extraction of energy of new fuel sources.[7] Therefore, by establishing control over the electrodeposition of films, specific properties can be tailored, making the most efficient use of expensive metals. This includes maximising specific surface areas and active sites, with the aim of thus increasing the current density and reducing overpotentials for electrocatalytic processes. Interest into active film fabrication lies in a number of current and future applications including catalysis,[8] electrocatalysis[9, 10] and capacitors.[11] Most importantly, bulk self-supported porous framework materials have shown improvements in current density and electron mobility, over their non-porous counterparts,[12-14] and increased stability over supported nanoparticle catalysts. This chapter explores the DHBT technique, which takes advantage of the in-situ mixing and subsequent co-deposition to create multi-metallic films with porous frameworks.

5.1.1. Electrodeposition and DHBT of Multimetallic Films

Established methods to create porous metallic films include templating with polymers or inorganic materials, or de-alloying (see Section 1.4.2). A major disadvantage of these techniques is that although the specific surface areas can be high, the morphological features that lead to higher catalytic activity are not easily introduced and difficulties can arise with the removal of the templating material. Electrodeposition has been shown to allow direct growth of catalytically active morphologies such as dendrites, foams and high
facet nanostructures in a one-step procedure. Electrodeposition can be used to fabricate a range of different structures, with a variety of morphologies. Such an example is the CuPd system, where alterations in the electrodeposition bath yields nanostructures with varying morphologies.[15] Electrodeposition of porous materials can minimise the use of precious metals and thus address the issues of cost, whilst simultaneously optimising the activity and surface area.

Pure porous copper (Cu) honeycombs with dendritic surface structures are obtained readily through the deposition under DHBT conditions.[16-24] These films are highly repeatable with average pore sizes of ca. 52 µm (Figure 5.1). It has also been shown by Nadjovski et al. that incorporation of one or two noble metals into a Cu framework can increase the catalytic activity through synergism due to third-body and electronic effects, obtained by multi-metal incorporation (see Section 1.3.3).[10, 25, 26] However, further research into the synthesis, as well as the catalytic and electrocatalytic behaviour, of films formed by the DHBT method is required to optimise these materials for a range of important applications.

5.1.2. Research Aims

Given the importance of multimetallic materials in the fields of catalysis and electrocatalysis, the aim of this chapter is to choose two common catalytically active noble metals, Au and Pd, and incorporate them simultaneously into a Cu framework.

The main research aim of this chapter is to study the effect of adding relatively small concentrations of the noble metals Au and/or Pd (10 to 20 mM) into a predominately Cu electrolyte (0.4 M). Even such small amounts of Au and Pd may profoundly affect the morphology and catalytic activity of the surfaces. Cu has been well studied by the DHBT
Technique and is known to reliably create uniform porous honeycomb networks that are self-supported and easily made in quickly in a single step. Nadjovski et al. took this concept and applied it to the problem surrounding catalytic reactions, which called for reduced noble metal loadings with well dispersed and stable surface active sites.[10, 25-27] This led to the fabrication of three different bimetallic systems utilising Cu, a less noble and cheaper material, as the bulk metal. This chapter will follow a similar trend, however with the aim to extent the method to the fabrication of trimetallic materials. The effects of each noble metal, the deposition time and the effect of increasing the noble metal concentrations on the properties of the films will be studied. However in this work a current density of -2 A cm\(^{-2}\) is applied, unlike in Najdovski’s studies which implemented a current density of -3 A cm\(^{-2}\). Analysis of the catalytic properties of the surface can then be undertaken with two model reactions, for electrocatalysis (HER) and heterogeneous catalysis (FCN).

5.2. Experimental

5.2.1. Electrodeposition of Copper with Gold and/or Palladium.

The fabrication of the films was performed cathodically under galvanostatic conditions in a conventional three-electrode cell. The deposition occurred at a Cu foil substrate masked to an area of 0.28 cm\(^2\) using Kapton tape which acted as the working electrode with a graphite electrode as the counter electrode. The reference electrode was an Ag/AgCl (3 M NaCl, + 0.210 V vs. SHE), with all voltammetry in this chapter corrected to the SHE. A current of -0.565 A was applied to achieve an apparent applied current density of -2 A cm\(^{-2}\) to the original geometric surface area. The common electrolyte used for every electrodeposition consisted of 0.4 M CuSO\(_4\) in 1.5 M H\(_2\)SO\(_4\). To this common electrolyte, noble metal salts
were added with concentrations of either 10 or 20 mM (specified in each section), using the metal salts KAuBr$_4$ and Pd(NO$_3$)$_2$.xH$_2$O where $x$ was assumed to be equal to 2. All electrolytes were sonicated for 10 mins and purged with N$_2$ for 10 mins before the first deposition to ensure electrolyte consistency. Depositions were performed in sets of 3, with a 10 min purge before the first run, with a purge of at least 2 mins in between each deposition in a set. In Section 5.3.1 it was identified that the Cu honeycomb was susceptible to surface oxidation under ambient storage conditions. Therefore in all future work from Section 5.3.2 onwards, the films were all stored films in a vacuum desiccator, to minimise the contact with the oxygen from air in the ambient environment causing unwanted surface oxidation.

5.3. Results and Discussion

There are a range of factors that affect the morphology and surface chemistry of the films that were fabricated. Three main factors are the composition of the deposition electrolyte, the deposition time, and the concentration of each of the metal ion species present in the electrolyte. Initially the fabrication of two previously studied bimetallic systems copper/gold (CuAu) and copper/palladium (CuPd) with a precious metal addition of 10 mM was investigated. These two bimetallic systems were then directly compared with trimetallic copper/gold/palladium (CuAuPd) films.

The second area of research in this chapter looks at the effect of deposition time, while still using a current density of -2 A cm$^{-2}$, on the trimetallic films prepared. Deposition times at different intervals between 5 and 30 seconds were examined. And finally, the effect of
increasing the noble metal concentrations was examined, by studying the effects of either one or both of the noble metal concentrations being increased up to 20 mM.

5.3.1. Electrodeposition of Cu with Au and/or Pd.

In this section, Au and/or Pd metal ions were added to a Cu electrolyte (0.4 M) at a concentration of 10 mM. Initially only one additional metal was electrodeposited along with Cu to examine the influence of single metal addition. Subsequently the effect of having both Au and Pd present for electrodeposition alongside Cu was studied.

5.3.1.1. Morphology of Bimetallic and Trimetallic Cu Based Au and/or Pd Films.

The electrodeposition of porous Cu at a current density of -3 A cm\(^{-2}\) has been shown to form well-structured Cu networks in earlier studies.[10, 17, 25, 26] The aim of this work is to see if Cu could produce the same type of ordered networks at -2 A cm\(^{-2}\), which from experience in lead experiments by our research group, provides a favourable balance between H\(_2\) evolution and metal deposition. This may allow for different amounts of noble metals to be incorporated at a lower potential in a less vigorous environment for deposition than the current density of -3 A cm\(^{-2}\). Figure 5.1 shows the resulting SEM images for a pure Cu film deposited at -2 A cm\(^{-2}\) for 15 s, in which it can be seen that well defined honeycombs are still produced at the lower current density. The Cu honeycomb produced in Figure 5.1 are similar to the Au honeycombs electrodeposited in Figure 4.3 and are unlike the Ru deposits fabricated in Chapter 3. This is due to the difference in deposition regime, which is dependent on the metal deposition kinetics. The Cu deposits kinetically faster meaning that deposition by the DHBT method occurs via the diffusion limited regime.
The effect on morphology due to the co-deposition of Au and Pd was then studied, with the SEM images of these materials shown in Figure 5.2. Three levels of magnification are compared to reveal the macroscopic (level 1), microscopic (level 2) and nanoscopic (level 3) features of the surfaces. Looking first at the macroscopic level, uniformity and pore size information can be evaluated. The addition of either noble metal has the effect of drastically reducing the surface pore size from that of the pure Cu honeycomb. Figure 5.2 A1 shows the CuAu film, which is shown to have smaller pores (of ca. 12 µm) than P1, which is the CuPd film (pores of ca. 13µm). The CuPd film also shows the largest pore size distribution, indicating a less uniform surface. When all three metals are combined, the pore size reduces further and the uniformity is improved significantly (Figure 5.2 A3). In comparison to monometallic Cu (Figure 5.1), the multimetallic films have smaller pore sizes and less evidence of dendritic fine structure formation. The SEM images at level 2 show that the individual main particle sizes of about 4 µm are all similar but consist of slightly different structures. For example, Au (Figure 5.2 A2) induces structural formations of intersecting platelets in the CuAu framework, which is significantly different to the dendrites observed for pure Cu. The addition of Pd (Figure 5.2 P2) results in the loss of the dendrite structures seen for pure Cu. Where the pure Cu had pointed tips on the dendrites, the CuPd bimetallic film has nano-cubic structures (Figure 5.2 P3). This is possibly due to the increased charge
density at these tips sites due to the morphological surface affects during deposition that may cause the formation of differently shaped deposits. At the level 3 magnification, the SEM images reveal the significant effect that the noble metals have on the morphology. Figure 5.2 A3 shows triangular ‘jaw like’ structures and P3 the defined nano-cubic structures with an underlying dendritic base structure still being observed. The trimetallic film, CuAuPd (Figure 5.2 AP2), has influences from both the Au and Pd. There is a reduction in the number of platelets than observed for CuAu, and overall the framework is comprised of up of more densely packed particles. Figure 5.2 AP3 is of great interest, as both triangular Au influenced particles, observed for CuAu, and the smaller square Pd influenced particles, observed for CuPd, have combined and co-electrodeposited to form the resulting film. Figure 5.2 clearly shows the significantly large differences that occur as the result from the addition of one or more noble metals.

![Figure 5.2 SEM Images of multi-metallic deposits A) CuAu, P) CuPd, AP) CuAuPd at 1) 2,000x, 2) 50,000x and 3) 200,000x magnification.](image)
The factors that can be considered to explain the morphology are the bubble break off diameter, which is related to the rate of H\textsubscript{2} evolution (see Section 1.5), the influence of bubble evolution on the hydrodynamic conditions and the kinetics of metal growth during electrodeposition.[28] Fundamental studies on bubble behaviour show a direct relationship between the exchange current density, \(j_0\), for H\textsubscript{2} evolution and the bubble break off diameter, which is responsible for the average pore size on the surface as the metal grows around evolving bubbles. Faster rates of H\textsubscript{2} generation leads to smaller bubbles due to shorter residence times of the bubbles on the substrate surface before detachment occurs.[28] The bubble break-off diameter and H\textsubscript{2} evolution rate are determined by the surface energy, which is governed by the morphology, surface composition and applied overpotential.[29] The higher the HER exchange current density, that is the rate of H\textsubscript{2} evolution per unit surface area, the more rapid the H\textsubscript{2} evolution rate off the surface occurs.[30] The \(j_0\) between different metals and hydrogen are often published in the form of volcano plots (See Figure 1.4) which directly compare the hydrogen chemisorption energy or M-H bond strength,[30] or the work function[31] against different metals. The, \(j_0\) for H\textsubscript{2} evolution differs for each of the constituent metals, and have been determined for Au (10\textsuperscript{-5.4} A cm\textsuperscript{-2}), Cu (10\textsuperscript{-5.37} A cm\textsuperscript{-2}) and Pd (10\textsuperscript{-3} A cm\textsuperscript{-2}),[30, 31] indicating a significantly faster H\textsubscript{2} evolution rate off the electrodepositing Pd compared to either the Cu or Au. It describes that the addition of Pd would lead to a faster H\textsubscript{2} evolution rate compared to Cu or Au, which explains the observations in Figures 5.1 and 5.2. A faster rate means shorter residence times of bubbles on the surface, reducing the amount of time available for coalescence to occur. This in turn results in the formation of smaller bubbles and therefore reduced pore sizes, as the bubbles act as a template for the growth of the porous surfaces.
Bubbles are of an insulative nature and therefore their presence on the surface blocks the electrodeposition at particular surface sites. [32, 33] This results in an increase in the actual current density to more than the -2 A cm\(^{-2}\) applied at the bubble free sites across the surface. The effective current density is actually higher than the calculated current density. The current density directly influences the rate of hydrogen and metal deposition, which is reflected by changes to the morphology and composition of the depositing Cu, Au and/or Pd metals. The characteristics of H\(_2\) formation and bubble break-off diameter is constantly varying throughout the electrodeposition process and depends on the surface state with time, and the addition of each fresh deposit of metal. Therefore, the effects on the conditions surrounding deposition will continually change. Cu has a lower \(j_0\) compared to Pd,[30, 31] therefore slower hydrogen evolution rate, which leads to longer residence times, allowing bubbles to reach a larger average size before breaking off. For pure Cu a less turbulent process is ideal for metal deposition to occur over hydrogen reduction, allowing for metal deposition to build-up around the bubble to a greater extent before it breaks off. However, H\(_2\) evolution is still a turbulent process that disrupts Cu deposition, which leads to the formation of dendritic structures due to an underlying diffusion limited growth regime.[34] As the deposition process continues, more metal surface sites are formed, which then allows for increased numbers of H\(_2\) nanobubbles that can then coalesce into larger bubbles responsible for the large open pores seen in Figure 5.1.

The addition of noble metals increases the H\(_2\) evolution rate, which in turn affects the hydrodynamic conditions near the substrate surface. The intense H\(_2\) bubbling at the surface has a stirring effect that compresses the diffusion layer. This alters the availability of metal ions adjacent to the surface of the electrode and can lead to dendrite formation. As such,
both Cu and Au, when deposited as mono-metallic films, have been shown to exhibit
dendritic growth at high current densities in the presence of H₂ bubbling.[35, 36] Similarly,
porous foams of Pd have previously been deposited using a NH₄Cl electrolyte, preferring to
deposit as a foam rather than dendritic growth, unless very particular conditions were used,
owing to Pd’s slow growth kinetics.[37] CuPd has previously been shown to have large pore
size distributions and an uneven distribution of Pd across the surface of the material.[26] It
has also been shown that CuAu bimetallic porous nanostructures can be formed that have a
uniform distribution, which was linked to the isoelectronic pairing they share.[10] In the
case of CuPd no such pair exists, explaining the larger pore size distribution on this film.

Comparing the hydrogen evolution $j_0$ for the three metals, it would be more likely that the
increased evolution rate off Pd would result in a greater compression of the diffusion layer.
This in turn would increase the availability of Pd$^{2+}$ ions near the electrode and thus result in
a greater rate of metal deposition to occur. This results in a more ‘built-up’ surface with
larger pores when compared to the Au (Figure 5.2 A1 and P1), according to the ‘stack-up’
nature of DHBT. If the depositions were halted at a similar thickness, it is postulated that the
CuPd film would have smaller pores compared with CuAu. Au has the lowest hydrogen
evolution rate, which therefore means longer bubble residence times, coalescence of larger
bubble would result in larger pores. For the trimetallic film, CuAuPd, the pore sizes are the
smallest due to the synergistic increase in the hydrogen evolution rate that prevents the
long residence times responsible for larger bubbles.

The DHBT method relies on a balance between metal deposition and hydrogen evolution.
The small addition of noble metal changes alters this balance, resulting in the significant
changes to the Cu honeycombs morphology, causing formation of triangular plates (CuAu)
and small cubes (CuPd) observed in Figure 5.2. It is interesting to note the impact on the morphology that the relatively low concentrations of Au and/or Pd (0.01 M) can have relative to Cu (0.4 M).

Table 5.1 presents surface and textural properties of the films for direct comparison. Porous materials are important for catalysis and electrocatalysis (Section 1.4.2), therefore the surface area, pore size and accessibility to surface sites are important parameters to be examined. To study this, electrochemically active surface areas (ECSAs) were estimated using the double layer capacitance method as described in Section 2.2.1.4, and the mass of the electrodeposited materials was determined from elemental analysis by ICP-MS of the dissolved films as described in Section 2.2.5. The specific surface area (SSA) of a material can be determined by dividing ECSA by the overall mass of the deposit (m²/g).

The ECSA directly gives an indication of the roughness of the surface, and will be greatly increased if some porosity is present, or dendritic growth is observed. The pores created by DHBT on the surface, along with the nanoscale features, such as dendritic or branched growth will thus increase the overall surface area. A key aim in developing the DHBT method is to allow cheaper fabrication of metals, ensuring that the minimum amount of material is used. It is important to minimise the mass of the deposit, whilst increasing the ECSA. This is where the SSA is a useful parameter as it is able to compare the efficiencies of metal utilisation.

CuAu showed a surface with a large number of protruding shapes and surface structures that give it the highest SSA of 3.4 m²/g, indicating the best material utilisation. The trimetallic film CuAuPd has the smallest pore size, the smallest standard deviation, the largest pore density and a less built-up surface (i.e. thinner walls), which gives it a greater
SSA than CuPd (2.6 vs. 1.6, respectively) despite having the lowest surface area. The smallest exterior pore sizes (i.e. at the surface) and thin walls causes this material to have the highest pore density. These results complement the observations seen in Figure 5.2, in particular that the CuPd film had the largest and most random pores due to the rapid and less uniform deposition process. This gave the larger average pore size, as well as the greater size distribution of pores, whilst having the lowest number of pores.

Table 5.1 Surface Properties of CuAu, CuPd and CuAuPd films.

<table>
<thead>
<tr>
<th></th>
<th>Mass (g)</th>
<th>ECSA (m²)</th>
<th>SSA (m²/g)</th>
<th>Roughness Factor (RF)</th>
<th>Average Surface Pore Size (µm)</th>
<th>Pore Density (Pores cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu</td>
<td>8.08 x 10⁻⁴</td>
<td>2.73 x 10⁻³</td>
<td>3.4</td>
<td>98</td>
<td>11.8 ± 3.3</td>
<td>2.9 x 10⁵</td>
</tr>
<tr>
<td>CuPd</td>
<td>1.44 x 10⁻³</td>
<td>2.27 x 10⁻³</td>
<td>1.6</td>
<td>81</td>
<td>12.8 ± 7.2</td>
<td>1.8 x 10⁵</td>
</tr>
<tr>
<td>CuAuPd</td>
<td>7.51 x 10⁻⁴</td>
<td>1.95 x 10⁻³</td>
<td>2.6</td>
<td>69</td>
<td>6.29 ± 1.7</td>
<td>9.0 x 10⁵</td>
</tr>
</tbody>
</table>

The pores on the surface of the films confirm that templating around bubbles is occurring, with pore sizes indicating approximate break off diameters, but the deep, honeycomb-like 3-D structures typical of the DHBT stack-up model seen for the pure Cu were not as prominent, which coincided with a reduction in film thickness. This may be ascribed to the morphology produced by the growth mechanism on the nanoscale, which is not dendritic, and is thus less effective at templating around the bubbles to form a deep, stacked 3-D structure. This confirms the importance of the composition of the electrolyte, and demonstrates how only a small and seemingly insignificant addition of noble metals can result in dramatic changes in the overall film morphology. The nanostructures, which were directly affected by the changes induced by the co-deposition of Au and Pd with Cu, affected
the overall growth morphology and mechanism, leading to quite different macroscale morphology, and changes to porosity.

5.3.1.2. Film Composition Studies

In order to understand the electrodeposition process deeper, it was necessary to investigate how much of each metal was present in the films, both in the bulk of the material and at the surface. Shown in Table 5.2 are the atomic percentages (At %) of the elements present in the bulk (ICP-MS) and on the surface (XPS) of the films. Here it can be readily observed that the surface composition can be significantly different from that of the bulk. The concentration of Cu present in the bulk was much higher (95.4-97.6 %) than Au and/or Pd (2.4-4.6 %), which was expected due to the high relative concentration of Cu in the electrolyte (0.4 M for Cu compared to 0.01 M for Au and Pd). At the surface the Cu concentration still remains much larger than that of the noble metals. However, in the case of CuAu there is a 5.5 fold increase in the amount of Au at the surface compared to bulk, and for CuPd there is a 6.7 fold increase in the Pd at the surface compared to the bulk. This surface enrichment was not as pronounced in the trimetallic CuAuPd, with the Pd concentration for bulk and surface having a similar composition. However, Au has an enrichment factor of 2.6.

Table 5.2 Atomic Percentage (At %) estimation for the bulk (ICP-MS) and surface (XPS)

<table>
<thead>
<tr>
<th></th>
<th>Bulk At %</th>
<th>Surface At %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>CuAu</td>
<td>97.6</td>
<td>2.4</td>
</tr>
<tr>
<td>CuPd</td>
<td>97.5</td>
<td>-</td>
</tr>
<tr>
<td>CuAuPd</td>
<td>95.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>
There are a number of factors that may contribute to surface segregation and lead to surface enrichment in the films. These factors include strength of the bonds, surface energies, relative atomic sizes and charge transfer interactions.[38] Another factor to be considered is the surface redox chemistry, which relates the different reducing strengths of the deposited metals to metal ions near the substrate surface, which can involve galvanic replacement of the film surface, or spontaneous deposition on the surface.[39] Specific to the films prepared, the enrichment can be explained to occur with regard to the surface energies, relative atomic sizes, charge transfer (electronegativity) and differences in relative redox potentials when using up to three different metals.[38-40] From the XRD patterns obtained (see Section 5.3.1.3), it can be concluded that the noble metals are dissolved in the Cu, which acts as a solid solution through replacement of Cu atoms with noble metals atoms in the Cu lattice. There is a difference in surface energies between the Cu host and the Au and Pd solutes, causes them to diffuse to the surface of the Cu host, segregating them at the surface.[41, 42] Another factor is that segregation can occur by smaller atoms tending toward the bulk interior structure, with the larger atoms preferring the surface. The surface enrichment of Au has also been attributed to the surface strain,[43] caused by the difference in atomic radii of more than 10 % (145 pm and 174 pm for Cu and Au, respectively).[44] Pd has an atomic radii of 169 pm, which would also cause it to tend toward the surface.

The possibility of spontaneous deposition should also be considered. The reduction potential of \( \text{Au}^{3+}/\text{Au} \) (AuBr\(_4\)) compared to \( \text{Cu}^{2+}/\text{Cu} \) is 0.854 V vs. 0.34 V,[45] respectively, which causes Cu to be oxidised in the presence of \( \text{Au}^{3+} \) resulting in a higher concentration of Au at the surface.[39, 40] The same applies for Pd, with the difference between the
reduction potentials for Pd$^{2+}$/Pd (PtCl$_4^-$) and Cu$^{2+}$/Cu of 0.915 V vs. 0.34 V, respectively, therefore also potentially causing enrichment to occur,[45] and therefore the same reasoning for preferential Au enrichment can be applied to the CuPd bimetallic. However, it is difficult to determine the extent to which this may occur, as ion concentrations near to the growing deposits are low due to the high overpotential employed, which also dictates that electrodeposition should have faster kinetics than spontaneous deposition.

Charge transfer can occur with electrons transferring from less electronegative atoms to more electronegative atoms, and as Au and Pd have a higher electronegativity to Cu (2.6 and 2.2 vs. 1.9 for Au, Pd and Cu, respectively) they induce segregation of the noble metals at the surface.[38] The use of Cu also brings an instability due to its sensitivity to form an oxide layer that also drives the Au and Pd to the surface in an attempt to stabilise the film.[46]

For the trimetallic system, the noble metal surface concentrations more closely resemble their bulk values (i.e. there is less enrichment observed). Au showed surface enrichment, whereas Pd did not, as it was described due to Au$^{3+}$ having the largest reduction potential causing it to concentrate via spontaneous deposition at the surface, it also has the largest atomic radii all three of the metals, which would cause it to diffuse to the surface of the film. Pd is not likely to surface enrich when Au is present, and it may instead catalyse the electroless deposition of Cu, which further reduces any dominance it may have on the surface.[47, 48]

5.3.1.3. Structural and Surface Analysis by XRD and XPS

This section aims to study the structure and surface chemistry of the films by XRD and XPS. Important information such as bulk structure and the nature of surface segregation can also
be further probed using these techniques. Figure 5.3 shows the XRD patterns, at the most relevant 20 values for the multimetallic films, compared to the pure Cu honeycomb.

![XRD patterns for Cu, CuAu, CuPd, and CuAuPd.](image)

The XRD patterns predominately correspond to the metallic copper phase PDF # 040836. There are five strong peaks present in the XRD pattern. They occur at 20 values of ca. 36.6, 42.5, 43.5, 50.6 and 74.2 (not shown), and can be attributed to the Cu2O (111), Cu2O (200), Cu (111), (200) and (220) planes, respectively. Significantly, there are no characteristic patterns corresponding to the presence of metallic Au and Pd in any of the electrodeposited films. In particular the strongest (111) peaks of Au and Pd that occur at 20 values of 38.2 and 40.4 for Au and Pd, respectively, were absent. A blank pattern was obtained and accounted for, for the Cu foil used as a substrate. The pure Cu honeycomb showed that
Cu$_2$O (111) was present, which is not unexpected due to the susceptibility of Cu to oxidise readily in air.[46] However, the addition of either Au or Pd reduces this peak, thus indicating the susceptibility of Cu to oxidise to Cu$_2$O is reduced with the presence of these noble metals.

Analysing the peaks further can give the location (2θ angle), peak width (FWHM) and peak area that can yield information regarding the d-spacing and crystallite sizing, by using Bragg and Scherrer equations (Equation 2.8 and 2.9, respectively). Table 5.3 summarises this information regarding the d-spacing and crystallite size in relation to the pure Cu honeycomb. The addition of Au shifts the Cu (111) peak to a higher 2θ value, whereas addition of Pd has the opposite effect reducing the 2θ value for the Cu (111) peak. However the Cu (111) shifts to a higher 2θ in the case of the trimetallic, suggesting that both the Au and Pd influences combine to distort the copper honeycomb lattice. The changes in the d-spacing, calculated from the 2θ values, are quite modest, due to the relatively small amount of noble metal in the bulk film. Another indication is the influence on the crystallite size, with the size of Cu (111) decreasing with increasing Au and Pd content. The last column of Table 5.3 compares the relative ratios of the Cu (111):(200) peak areas, which the addition of the second or third metal affects the relative intensity ratio of both peaks. It shows that the preferential growth orientation is affected by the increased noble metal interaction. For these films it is shown that increasing noble metal content increases the (111):(200) ratio.
Table 5.3 XRD data including calculated d-spacings and crystallite size

<table>
<thead>
<tr>
<th></th>
<th>Peak Centre (2θ)</th>
<th>Crystallite Size (nm)</th>
<th>d-spacing</th>
<th>Peak Centre (2θ)</th>
<th>Crystallite Size (nm)</th>
<th>d-spacing</th>
<th>Area ratio (111):(200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>43.50</td>
<td>28.9</td>
<td>2.078</td>
<td>50.61</td>
<td>23.9</td>
<td>1.802</td>
<td>1.15</td>
</tr>
<tr>
<td>CuAu</td>
<td>43.58</td>
<td>27.2</td>
<td>2.074</td>
<td>50.69</td>
<td>24.5</td>
<td>1.799</td>
<td>1.17</td>
</tr>
<tr>
<td>CuPd</td>
<td>43.42</td>
<td>26.3</td>
<td>2.081</td>
<td>50.65</td>
<td>23.1</td>
<td>1.802</td>
<td>1.29</td>
</tr>
<tr>
<td>CuAuPd</td>
<td>43.68</td>
<td>23.6</td>
<td>2.070</td>
<td>50.79</td>
<td>23.6</td>
<td>1.796</td>
<td>1.43</td>
</tr>
</tbody>
</table>

The films were absent of any XRD peaks for the noble metals or alloys, though both Pd and Au were shown to be present by ICP-MS and XPS analysis. The crystal pattern was entirely composed of the Cu, which showed that its lattice (i.e. the (111) and (200)) planes were affected, by slight changes to d-spacings, when the noble metals were added. This is indicative of solid-solution formation, where the noble metals are interchanged or effectively dissolved in the Cu lattice, which is typical for electrodeposited materials.[49-51]

The XPS analysis of the surface that was previously used to determine the surface At % of the metals present (Section 5.3.1.2), can also yield further important information regarding the surface chemistry. Core-level scans were performed to investigate the surface energy and the electronic environment. Information about the electronic environments surrounding each element and the extent of oxidation or alloying can be evaluated (Figure 5.4).

The binding energy of the Cu 2p<sub>3/2</sub> core-level in all the films was found to be centred at ca. 932.6 eV, corresponding to the binding energy of metallic copper (Cu<sup>0</sup>), with an additional contribution at ca. 932.9 eV which can be attributed to Cu<sub>2</sub>O (Cu<sup>+</sup>).[52] The presence of small satellite peaks that appear at 945 eV rule out the formation of CuO but can indicate
Cu₂O formation.[53] This complements the observations seen in the XRD patterns in Figure 5.3. The Cu 2p₃/₂ binding energy shifted with the addition of Au to 932.4 eV, and increased slightly with the addition of Pd to 932.7 eV. For the trimetallic film with a combination of both Au and Pd, the binding energy increased up to 932.8 eV. This indicates a stronger interaction due to the combination of both Au and Pd, thus resulting in a binding energy that is dependent on the total noble metal content. Figure 5.4 c and d) display the Au 4f₇/₂ and Pd 5/₂ regions, and it is shown that both metals only have a single energy environment. The published metallic binding energy values for Au 4f₇/₂ and Pd 5/₂ are 84.0 and 335.0 eV, respectively.[52, 54] For the bimetallic films, the peak binding energies of each of the noble metals are shifted to increased binding energies of ca. 84.4 and 335.5 eV for the bimetallic CuAu and CuPd, respectively. Both these value are much higher than the published metallic values. For CuAu, the increase in peak binding energy is not a result of the formation of Au(I) species, which would have a binding energy of 85.0 eV, but suggests that the film surfaces have an electronic environment that may be tending towards Au(I).[10, 55] The increase in the binding energy for CuPd materials has been explained previously due to changes in the electronic environment caused by the loss of valence electrons to Cu.[56, 57]. For CuAuPd there is a further increase in the binding energy of Au 4f₇/₂ and Pd 3d₅/₂, which increase to 84.5 and 335.6 eV, respectively. This indicates a slight change in the electron environment induced from the interaction of all three metals. The Pd 3d₅/₂ peak has a slight overlap with Au 4d₅/₂ peak, which has a slightly lower binding energy of 335 eV, which is present in the case of CuAuPd film. The presence of this peak and the inactive native oxide of Pd at 336.7 eV which results in the broadening of the 3d₅/₂ peak.[58]
Through peak deconvolution, it was found that there were two chemically different oxygen environments that had peak energies of 530.7 and 532.3 eV (Figure 5.4 b). The lower binding energy of 530.7 eV is related to oxides on Cu, due to the susceptibility of Cu to oxidise.[59] The O 1s species observed at 532.5 eV is due to surface hydroxides and water.[60] Pd addition is shown to enhance the formation of hydroxides rather than oxides on the Cu surface (Figure 5.4d).

Surface oxide species play a critical role in the controlling the catalytic behaviour of metals. It has previously shown that Pd affects the kinetics and stability of Cu surface oxidation, and that only small amounts of Pd were able to have this affect.[61] Au is resistant to oxygen and this is observed through the lower intensity of the O 1s envelope in Figure 5.4b. The increase in binding energy for the CuAuPd trimetallic may be a result of another factor involving the decrease in noble metal content at the surface causing a greater interaction with the oxides forming on the surface of the Cu.
5.3.1.4. Model Catalysis Reactions: HER and FCN Reduction

After the morphology and composition of the electrodeposited films were determined, they were then studied for their catalytic ability through the use of the hydrogen evolution reaction (HER) and ferricyanide reduction (FCN) by sodium thiosulphate. These are both utilised as model reactions and can be used to directly compare the surface properties and activities of the films.

The HER is an ideal reaction to study electrocatalytic properties, as it is a well-studied inner-sphere reaction that is highly sensitive to the surface chemistry of a metallic catalyst. Therefore the differences that have been observed between the films such as morphology,
composition and electronic state of the surface can be compared. The two factors that allow comparison of HER activity are the onset potential (reduction in overpotential for HER to take place) and the current density of the electrochemical reaction at a designated potential. One of the key parameters that affects catalysis of the HER is the strength of metal-hydrogen (M-H) interaction. In order to effectively catalyse this reaction the adsorption energy of hydrogen to the surface of the film has to be optimal, so that it is not too strong, leading to slow kinetics in the rate determining desorption step, and not too weak such, that M-H interaction is insufficient to drive the inner sphere heterogeneous reaction (i.e. adsorption time isn’t long enough). Pd has a great affinity for hydrogen atoms which can limit desorption and therefore affect the rate of evolution.[62] In order to circumvent this problem the addition of more than one metal may allow for the interactions and surface properties to change, which can lead to improved overpotential and kinetics.[26] The reaction represents the most versatile way to probe the activity of a surface, with implications for a wide range of other catalytic reactions. The order of activity according to the volcano plot for the metals studied here is Pd>Cu>Au.[30] Palladium is unique for HER, as it has a strong affinity for hydrogen adsorption,[62] and shown to sit at the peak of volcano curves, close to platinum, giving it one of the fastest and most active rates for HER.[30, 63] However, for Pd the M-H interaction can be very strong, causing second order kinetics that are controlled by the desorption of adsorbed H on the surface before H₂ (g) can be evolved.[62] Pt nanoparticles loaded on carbon (Pt/C) are a benchmark in regard to comparing catalytic activity toward the HE. Pt/C has an activity of 105 mA cm⁻² at 0.4 V at a scan rate of 0.005 V/s in 0.5 M H₂SO₄.[64] As the materials examined consist of mostly Cu, it is expected that activity towards HER would be lower than that of pure Pt particles that are highly active in regard to their exchange current density. Figure 5.5 shows
the linear sweep responses for the films for HER, which are all normalised to the estimated ECSA (as measured in Section 5.3.1.2.) allowing presentation as current density, $j$. Pure Cu honeycomb has a low current density throughout the linear scan as is expected from the published volcano curve data. According to volcano curves and the surface At % (from Table 5.2), 16.7 % of Pd at the surface for CuPd should have had a greater activity towards the evolution of hydrogen, as Pd has a greater exchange current density than Au. It is observed that the CuPd has a greater current density than CuAu as the scan progresses more cathodic than -0.38 V. This can be explained by examination of the onset potential in Table 5.4, which shows that the CuPd performs the worst. What is interesting is that the combination of all three metals in CuAuPd yields the greatest current density of all the four films, even though its surface At % of noble metals is lower than that of the bimetallics. There are a few explanations as to why that this enhancement in the ability to evolve H$_2$ occurs. Changes to surface morphology and accessibility (porosity) and the changes observed in the electronic environment (shift in peak binding energies) may serve as one explanation. The synergism of combining the two noble metals has been observed in the morphology (Figure 5.2 AP3), which may also contribute to the improved surface activity. An important point also is that the volcano curves usually are measured with regards to specific crystallographic orientations e.g. Au (111) alone. By changing the morphology and thus crystal orientation of the surface, the surface activity may change independent of published volcano plots.
As mentioned previously, Pd has a very strong M-H interaction, which allows it to attract hydrogen ions to its surface, but this may be too strong. The addition of Au may act to change the electronic environment,[65] such that there is increased release rate. E.g. The Pd-H interaction is still strong, however Au incorporation reduces it such that H\textsubscript{2} is efficiently evolved. By combining both Au and Pd, a synergy is thus directly observed in this example. The catalysed deposition of Cu on Pd can also be used to explain the lower HER rate. If Pd sites become covered in Cu due to surface rearrangement a HER rate reflecting that of Cu may instead be obtained. It was observed over multiple experiments that the same responses for the surfaces were obtained, which suggests that the films are stable under the conditions that HER activity was examined.
Table 5.4 Data from the HER from Figure 5.5.

<table>
<thead>
<tr>
<th>Film</th>
<th>( j ) at -0.6 V (mA cm(^{-2}))</th>
<th>Onset (V) at 3% of ( j ) at -0.6 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-2.08</td>
<td>-0.182</td>
</tr>
<tr>
<td>CuAu</td>
<td>-2.42</td>
<td>-0.186</td>
</tr>
<tr>
<td>CuPd</td>
<td>-2.72</td>
<td>-0.212</td>
</tr>
<tr>
<td>CuAuPd</td>
<td>-4.60</td>
<td>-0.128</td>
</tr>
</tbody>
</table>

The reduction of ferricyanide (FCN) by sodium thiosulphate (STS) is a model reaction that can be used to probe the surface activity of the films, as a useful predictor of heterogeneous catalysis in aqueous solution at open circuit potential (OCP). It is a surface controlled, electron-transfer reaction; therefore the surface composition, accessibility and surface area are important factors in determining the reaction kinetics. Typically this reaction has been limited to coinage metals, and usually in the form of homogenous catalysis, however there is a distinct advantage for the use of heterogeneous catalysts as the separation of catalyst and solution step is avoided. The FCN reaction is a simple electron transfer reaction (see Section 1.2.1) whereby the catalyst surface acts as a mediator/proxy to transfer electrons between FCN and thiosulphate. The process (i.e. the rate) can be easily monitored by UV-Visible Spectroscopy. This is possible due to the colour change observed as the FCN is reduced. An absorbance peak is observed at ca. 420 nm in the visible spectrum, and as the reaction takes place the intensity of this peak decreases (Figure 5.6). As the reaction rate is dependent on surface state of the catalyst we could expect the different films have a
different rates. These rates, normalised to the measured ECSAs, are compared in Figure 5.7 and Table 5.5.

It can be seen that the surface composition does have an effect on the reaction rate. To start with is observed that pure Cu honeycomb has the ability to act as an effective catalyst with a rate of $-1.72 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}$.

![Figure 5.6 UV-Visible spectral monitoring of the reduction of the FCN peak at 420 nm due to reduction by STS on a sample CuAuPd film surface with time.](image)

Figure 5.6 allows determination of the reaction rate, through the comparison between the absorbance at a given time, $A_T$, compared to the initial absorbance, $A_0$. There is a difference in the shape of the curves. The pure Cu and bimetallic CuAu and CuPd films are more curved, with a slower rate that increases after an initiation period of around 420 s, which is not the case for the CuAuPd. This may be due to the absence of Cu$_2$O on the trimetallic sample, which may act as an insulator to the electron transfer reaction.
Figure 5.7 Kinetic comparisons of FCN reduction rates for the different multimetallic film catalysts.

Table 5.5 Reduction rates for the catalysed FCN reduction by STS on the film catalysts.

<table>
<thead>
<tr>
<th>Film</th>
<th>Rate (s(^{-1}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-1.72 x 10(^{-4})</td>
</tr>
<tr>
<td>CuAu</td>
<td>-1.51 x 10(^{-4})</td>
</tr>
<tr>
<td>CuPd</td>
<td>-2.31 x 10(^{-4})</td>
</tr>
<tr>
<td>CuAuPd</td>
<td>-1.60 x 10(^{-4})</td>
</tr>
</tbody>
</table>

The addition of Au was not seen to be beneficial, seen by the lowest rate obtained with this range of materials, being -1.51 x 10\(^{-4}\) cm\(^{-2}\) s\(^{-1}\) for CuAu. This may be a function of both the surface composition and morphology. The loss of dendrites upon the addition of Au to Cu, (see Figure 5.1 compared to CuAu Figure 5.2 A3) may lead to a decrease in the number of active sites for surface interactions to occur; and the relatively high concentration of Au at
the surface could also be unfavourable towards FCN reduction activity. For this FCN reduction reaction, the CuPd bimetallic film proves to be the most effective with the fastest rate of \(-2.31 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}\), which may be due to a compositional effect as a result of using Pd, leading to a different electronic environment, or due to the fine cubic structures obtained at the edges of the ‘dendrites’ (Figure 5.2 P3). It was seen in a previous study that Cu electrodeposited on Pd performed best in regards to HER and FCN, owing to the type of active sites present on the rough and porous surface.[17] The CuAuPd film performs in the middle with a reduction rate of \(-1.60 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}\) due to the combination of surface morphologies. However the Au-to-Pd ratio favours Au, resulting in a rate that closer reflects the CuAu film. It has been previously shown that the FCN rate on 2-D polycrystalline surface has activity in the order of Pd>Cu>Au.[17]

5.3.2. The Effect of Deposition Time

5.3.2.1. Effect on Morphology Depositing at Different Deposition Times.

The DHBT process is capable of following a ‘stack-up’ model, meaning the pores closer to the substrate are smaller than those further away. This is due to combination of the reduction in localised applied current density further away from the electrode and increased number of potential H\(_2\) evolution sites, therefore allowing the residence times and coalescence of bubbles to increase. The CuAuPd film was therefore studied to investigate the effect that the deposition time has on the resulting morphology and composition. The deposition was allowed to occur for 5, 10, 15, 20 and 30 s using the same electrolyte composition of 0.4 M CuSO\(_4\) in 1.5 M H\(_2\)SO\(_4\) with 10 mM of both the Au (KAuBr\(_4\)) and Pd
(Pd(NO$_3$)$_2$) at an applied current density of -2 A cm$^{-2}$. Figure 5.8 shows the SEM images of the CuAuPd films at various deposition times.

Figure 5.8 shows that at 5 and 10 s deposition times the porous structures are just starting to develop, and that at 15 s the porous structure has developed an even porous layer that is starting to increase in depth. Increasing the time above 15 s causes the surface structures to build-up or stack. Table 5.6 shows the pore size measurements from the SEM images in Figure 5.8.
Table 5.6 Pore size measurements from SEM images in Figure 5.8.

<table>
<thead>
<tr>
<th>Film</th>
<th>Average Surface Pore Size (µm)</th>
<th>Pore Density (Pores/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 s</td>
<td>11.5 ± 3.7</td>
<td>3.7 x 10⁵</td>
</tr>
<tr>
<td>10 s</td>
<td>10.7 ± 3.6</td>
<td>3.5 x 10⁵</td>
</tr>
<tr>
<td>15 s</td>
<td>7.07 ± 2.6</td>
<td>9.0 x 10⁵</td>
</tr>
<tr>
<td>20 s</td>
<td>10.1 ± 3.3</td>
<td>3.5 x 10⁵</td>
</tr>
<tr>
<td>30 s</td>
<td>12.9 ± 4.3</td>
<td>2.4 x 10⁵</td>
</tr>
</tbody>
</table>

The average pore size for the films fabricated at 5 and 10 s are larger than at 15 s as the porous structure has not started to build yet. Initially there is little uniformity to the deposition process, with somewhat chaotic and sporadic deposition of material in the initial stage of deposition, leading to ill-defined pores, and instead the formation of islands and preferential bubble nucleation and evolution sites. These sites, as described by Plowman et al., [28] have the ability to entrap a small pocket of gas that leads to further hydrogen evolution to occur off the same site. As the hydrogen evolution rate would surpass the rate of metal deposition, the metal does not have sufficient time to surround a single bubble before it is released. However, as the metal islands grow larger, they direct the coalescence of hydrogen to these sites, promoting the formation of pores across the surface. At 15 s sufficient metal has deposited to surround the hydrogen evolution sites, creating a completely interconnected surface. At this time, the pore size is the smallest at 7.07 µm, and the largest pore density (9.0 x 10⁵ pores per cm²), and the most uniform surface (standard deviation 2.6) is observed. Allowing the deposition to proceed to 20 and 30 s results in the increase in average pore size to 10.1 and 12.9 µm, respectively, in agreement with the stack-up model. As the bubble evolution rate decreases as the film thickness grows,
control is lost leading to reduced uniformity of the deposit decreases, i.e. more variance in pore sizing’s as bubble control is reduced.

This key advantage of DHBT is the control gained through the stack-up model, where the pore size at the surface of the film increases with increased distance from the substrate, allowing for a degree of control to be attained, with pore sizing accessible through the variation in deposition time. Pores can be tailored to be suit the analyte or reactant species under investigation by simply changing the time the deposition is allowed to proceed.

Looking at higher magnification SEM images (Figure 5.9), it is shown that the particles that make up the complete film structure have a consistent morphology regardless of the deposition time. They reflect the same surface structures that were prepared in the previous section (Section 5.3.1.1), showing a mixed surface with triangular and cubic features.

![Figure 5.9 SEM Images](image)

*Figure 5.9 SEM Images for deposition of CuAuPd at -2 A cm⁻², for a) 5, b) 10, c) 15, d) 20 and e) 30 s at 50,000x magnification.*
The surfaces were also investigated using the same characterisation techniques as in Section 5.3.1, with the ECSA measured by the $C_{dl}$ method, and the mass determined from dissolution of the sample and subsequent analysis by ICP-MS. As shown in Table 5.7, there is a key difference in the SSAs obtained in this section than those from Section 5.3.1, with the samples now stored under vacuum. The electrochemically active surface and surface area determination is sensitive to the oxidation of the Cu surface, which would have occurred in Section 5.3.1.1, leading to reduced surface areas. As the ECSA represent active sites, the normalisation in Section 5.3.1 would be still accurate for those samples.

<table>
<thead>
<tr>
<th>Film</th>
<th>Mass (g)</th>
<th>ECSA (m$^2$)</th>
<th>SSA (m$^2$/g)</th>
<th>Roughness Factor (RF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 s</td>
<td>$2.75 \times 10^{-4}$</td>
<td>$1.63 \times 10^{-3}$</td>
<td>5.91</td>
<td>58</td>
</tr>
<tr>
<td>10 s</td>
<td>$5.39 \times 10^{-4}$</td>
<td>$3.08 \times 10^{-3}$</td>
<td>5.03</td>
<td>96</td>
</tr>
<tr>
<td>15 s</td>
<td>$7.31 \times 10^{-4}$</td>
<td>$3.63 \times 10^{-3}$</td>
<td>4.97</td>
<td>129</td>
</tr>
<tr>
<td>20 s</td>
<td>$8.44 \times 10^{-4}$</td>
<td>$3.17 \times 10^{-3}$</td>
<td>3.78</td>
<td>112</td>
</tr>
<tr>
<td>30 s</td>
<td>$1.31 \times 10^{-3}$</td>
<td>$3.19 \times 10^{-3}$</td>
<td>2.43</td>
<td>113</td>
</tr>
</tbody>
</table>

As expected with increased deposition times, there is an increase in the mass of the deposit, however there is also a reduction in specific surface area (SSA) with increased metal deposition time. This can be explained by the ‘filling-in’ of the surface as the deposition proceeds. The metal islands turn into walls that develop and thicken at increased deposition times, therefore the metals at the interior of the structure do not contribute to the surface area, but act to support the honeycomb-like structure. Figure 5.10 shows a plot relating the deposition time to the mass obtained. It is observed that a steady deposition rate of metals of 39.8 µg s$^{-1}$ is maintained throughout the electrodeposition process.
Figure 5.11 relates the deposition time to the surface area properties. It is seen in a) that the surface area reaches a maximum at the 15 s deposition time, (which corresponds to the largest roughness factor) and even though overall the SSA reduces with time, it plateaus at the 15 s mark (Figure 5.11b) before continuing its pathway down.

![Figure 5.10 Scatter Plot of Deposition Time vs. Deposit Mass](image)

![Figure 5.11 Plot of a) Deposition Time vs. ECSA and b) Time vs. SSA](image)

Complementing the SEM images observations and the surface properties above, it can be established that the 15 s deposition is a critical point where the porous network is established, maximum ECSA and an acceptably high specific surface area is obtained.
5.3.2.2. **Film Composition Studies for Films Deposited for Increased Time.**

Similar characterisation was undertaken to that in Section 5.3.1.2, whereby the surface and bulk chemical compositions were determined, and the results are compared in Table 5.8 and shown in Figure 5.12. From the bulk At %, the only trend that is established is that longer deposition time results in an increase of Cu in the films, while Pd is simultaneously decreased. These happen to the same degree (±~1%). Au remains at a relatively constant concentration in the bulk. However, looking at the surface At %, there are very distinct differences occurring. The Au and Pd contents initially start off very high at 17.7 and 4.9 At %, respectively, however as the deposition proceeds these contents drop to 6.6 and 2.2 At %. The Cu concentration increases from 77.4 to 91.3 % on the surface. The explanation given in Section 5.3.1.2 takes into account the ability for Pd to catalyse Cu deposition, causing a reduction in Pd surface presence which is consistent with the observations in this present section. Figure 5.12b shows the time dependence of the deposition process. As the Pd sites cause Cu to deposit, the Au and Pd on the surface decreases. Enrichment of Au still occurs, as Au is the favoured metal to be at the surface, due to its reduction potential and size, but there is competition with the electroless deposition of Cu on the neighbouring Pd sites.[47, 48] At the 30 s mark a critical point is reached where the Pd concentration drops to its lowest bulk and surface At % value.
Table 5.8 Film composition, At % for various deposition times

<table>
<thead>
<tr>
<th>Deposition Time (s)</th>
<th>Bulk Cu At %</th>
<th>Bulk Au At %</th>
<th>Bulk Pd At %</th>
<th>Surface Cu At %</th>
<th>Surface Au At %</th>
<th>Surface Pd At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 s</td>
<td>94.8</td>
<td>2.0</td>
<td>3.3</td>
<td>77.4</td>
<td>17.7</td>
<td>4.9</td>
</tr>
<tr>
<td>10 s</td>
<td>95.0</td>
<td>2.0</td>
<td>3.0</td>
<td>85.8</td>
<td>9.8</td>
<td>4.4</td>
</tr>
<tr>
<td>15 s</td>
<td>94.9</td>
<td>2.0</td>
<td>3.1</td>
<td>89.0</td>
<td>8.0</td>
<td>3.0</td>
</tr>
<tr>
<td>20 s</td>
<td>95.5</td>
<td>2.1</td>
<td>2.4</td>
<td>91.5</td>
<td>5.8</td>
<td>2.7</td>
</tr>
<tr>
<td>30 s</td>
<td>95.7</td>
<td>2.1</td>
<td>2.2</td>
<td>91.3</td>
<td>6.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 5.12 a) Deposition time vs. Bulk At %, b) Deposition time vs. Surface At %.

5.3.2.3. Structural and Surface Analysis by XRD and XPS

Figure 5.13 shows the XRD patterns for the films obtained at the different deposition times. The XRD peaks are again dominated by metallic Cu, with only trace amounts of Cu$_2$O as expected, as it was previously shown that a combination of all three metals reduces surface oxidation. Again there are no peaks accounting for Au (111) and Pd (111) at 2θ values of 38.2 and 40.4, respectively. The three strongest peaks at ca. 43.5, 50.6 and 74.2 degrees and can be attributed to the Cu (111), (200) and (220) planes, respectively. There is a small peak that can be seen at 36.6 degrees, which is attributed to Cu$_2$O (111) and is significantly reduced compared to a pure Cu honeycomb film. This small contribution may be linked to

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pH changes due to the consumption of H⁺ in the vicinity of the electrode surface, causing Cu₂O formation instead of ex-situ surface oxide formation.

Figure 5.13 XRD patterns obtained for films fabricated at different deposition times.

Table 5.9 XRD pattern information, including the calculated d-spacing of Cu (111) planes using the Bragg equation and crystallite size using the Scherrer equation.

<table>
<thead>
<tr>
<th></th>
<th>Cu (111)</th>
<th></th>
<th>Cu (200)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Centre (2θ)</td>
<td>Crystallite Size (nm)</td>
<td>d-spacing</td>
</tr>
<tr>
<td>5 s</td>
<td>43.54</td>
<td>23.6</td>
<td>2.076</td>
</tr>
<tr>
<td>10 s</td>
<td>43.50</td>
<td>20.8</td>
<td>2.078</td>
</tr>
<tr>
<td>15 s</td>
<td>43.42</td>
<td>25.0</td>
<td>2.081</td>
</tr>
<tr>
<td>20 s</td>
<td>43.46</td>
<td>25.4</td>
<td>2.080</td>
</tr>
<tr>
<td>30 s</td>
<td>43.48</td>
<td>21.7</td>
<td>2.079</td>
</tr>
</tbody>
</table>
Table 5.9 yields the critical XRD pattern information, including d-spacing and crystallite size. It can be seen that both the (111) and (200) planes have peaks at lower 2θ values than the results from Section 5.3.1.3, possibly due to the involvement of the oxide species formed previously. Comparing the deposition at different times, the highest 2θ for Cu (111) was achieved at a deposition time of 5 s. This reflects the film with the highest Au and Pd content and lowest Cu concentration at the surface (Table 5.8). It is observed in Figure 5.13 that the peak intensities are the same for the Cu (111) and Cu (200) at the 5 s deposition time where the Au surface At % was the largest. This suggests that Au is incorporating, affecting the Cu (200) direction. From the 5 s deposition time there is a gradual reduction in the 2θ value until the 15 s deposition time and then it begins to increase at the 20 and 30 s deposition times. The 15 s deposition time is thus an important switching point, and it seems to complement the morphological changes (in Section 5.3.2.1.) where an interconnected porous surface was established. It is the point at which the (111):(200) ratio is at its highest indicating a strong interaction of Au and Pd on the Cu honeycomb. It is clear that there is an interaction that occurs due to Au and Pd incorporation affecting the crystallite size and ratios of the Cu lattice.

Surface analysis by XPS was also carried out to identify the Au and Pd interactions. Figure 5.14 shows the binding energy regions for Cu 2p$_{3/2}$, O 1s, Au 4f$_{7/2}$ and Pd 3d$_{5/2}$. The Cu 2p region is centred at ca. 932.7 eV and shows a volcano like effect where the binding energy for this peak increases up to 932.9 eV for the 15 s deposition time, but returns to 932.7 eV by the 30 s deposition time. A greater influence on the Cu 2p$_{3/2}$ peak for the 5 s film would be expected due to the relatively high noble metal concentration and therefore it would be more expected that the interactions in the electronic environment would be stronger for
this time. However it seems that the strongest interaction occurs with the 15 s film, which was shown to be the tipping point from where the porous interconnected network is first formed and the surface grows in a relatively uniform pattern. The formation of the close-packed porous network must involve a significant change to the surface, in which the energetic environment surrounding the metals is altered. This trend is followed for the Au 4f$_{7/2}$ and Pd 3d$_{5/2}$ in Figure 5.14 c and d. The 5 s deposition times had binding energies of 84.4 and 335.6 eV for the Au 4f$_{7/2}$ and Pd 3d$_{5/2}$, respectively. The maximum energy of 84.5 eV and 33.5.7 eV are observed for the 15 s deposition time, with binding energy peak shifting back to the lower 5 s values by the 30 s deposition time.

Figure 5.14 XPS spectra showing the a) Cu 2p$_{3/2}$, b) O 1s, c) Au 4f$_{7/2}$ and d) Pd 3d$_{3/2}$ regions for the films at various deposition times.
It was observed that there were three chemically different oxygen environments that had peak energies of 530.1, 530.7 and 532.2 eV (Figure 5.4 b). The lower binding energy of 530.1 and 530.7 eV is related to oxides on Cu and Pd. The O 1s species observed at 532.5 eV is due to surface hydroxides. The higher At % of Au and Pd enhances the formation of hydroxides rather than oxides on the Cu surface as observed with the 5 s deposition time having the largest peak for this binding energy.

5.3.2.4. Model Catalysis: HER and FCN Reduction and the Effect of Deposition Time

The HER and FCN reduction model catalytic reactions were applied to the films to study the effect of increasing the electrodeposition times on activity. Figure 5.15 and Table 5.10 display the data from the HER on these films. The most impressive response is from the 5 s film, as it has the highest current density in the potential window examined, with a value of -4.56 mA cm\(^{-2}\) at 0.6 V. This no doubt has to do with the largest noble metal ratio on the surface and SSA, which results in the largest current density for H\(_2\) evolution compared to Cu. However, looking closely at the comparison in Table 5.10, the 5 s sample does not have the optimal onset potential, meaning there is more to the effect of just a high surface At % of Au and Pd. The lowest onset potential (i.e. highest overpotentials) of -0.199 V was obtained for the two, not fully porous surfaces obtained at the deposition times of 5 and 10 s, respectively. The porous interconnected nature of the film plays a role in reducing the overpotential needed for the reaction to proceed, due to a more favourable film morphology. This is evident from the onset potential for the 15 s film in Table 5.8. By observing the SEM images, this is the first surface to establish a porous interconnected
network, which therefore reduces the onset potential to \(-0.176\) V. The closely-packed porous morphology provides a favourable surface for the electrocatalytic HER to proceed.

Figure 5.15 LSV for HER in 1 M H\(_2\)SO\(_4\) for films deposited for various deposition times at a scan rate of 0.01 V/s

Table 5.10 HER calculated data for films deposited for increasing times

<table>
<thead>
<tr>
<th>Film</th>
<th>(j) (mA cm(^{-2})) @ -0.6 V vs. SHE</th>
<th>Onset (V) 3% of (j) at -0.6 V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 s</td>
<td>-4.56</td>
<td>-0.199</td>
</tr>
<tr>
<td>10 s</td>
<td>-2.91</td>
<td>-0.199</td>
</tr>
<tr>
<td>15 s</td>
<td>-2.85</td>
<td>-0.176</td>
</tr>
<tr>
<td>20 s</td>
<td>-2.67</td>
<td>-0.190</td>
</tr>
<tr>
<td>30 s</td>
<td>-3.18</td>
<td>-0.174</td>
</tr>
</tbody>
</table>
The FCN (as explained in Section 5.3.1.4) is a useful model reaction for heterogeneous catalysis and was thus used to compare the surface activities at different deposition times. It is very interesting to observe (Figure 5.16) that the completely interconnected porous films (deposition times of 15, 20 and 30 s) all performed better for the reduction rate of FCN, compared to the films that did not have the interconnected surface i.e. the 5 and 10 s deposits. Fine surface morphology was similar between the films (Figure 5.9) even though the surface compositions varied significantly (Table 5.8). The higher activity of the 5 s deposit compared to the 10 s deposit can be attributed to the higher noble metal content on the surface. It was previously observed that the higher Pd At % in Section 5.3.1.4 was responsible for an increased FCN reduction rate, but that was not followed for these trimetallic samples. The 15 and 20 s deposits are identical in performance whereas the 30 s has the greatest activity, even though it doesn’t have the highest noble metal content at the surface or in the bulk. Keeping in mind that these are surface area normalised responses, the 30 s film had a stacked porous surface, which would allow excellent access to the taller wall structure and surface defect sites that are highly active, giving the largest reduction rate of $-1.29 \times 10^{-4}$ cm$^{-2}$ s$^{-1}$. Due to the negligible amounts of Cu$_2$O on the surface of all the films, the activity was mostly consistent (straight line curve) from the initial point of contact with the reaction solution, as the surface was better stored than for the trimetallic film in Section 5.3.1.
Table 5.11 Reduction Rates for the catalysed FCN reduction by STS on the film deposited at increasing times.

<table>
<thead>
<tr>
<th>Film</th>
<th>Rate (s^{-1} \text{cm}^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 s</td>
<td>-8.94 \times 10^{-5}</td>
</tr>
<tr>
<td>10 s</td>
<td>-6.20 \times 10^{-5}</td>
</tr>
<tr>
<td>15 s</td>
<td>-1.11 \times 10^{-4}</td>
</tr>
<tr>
<td>20 s</td>
<td>-1.15 \times 10^{-4}</td>
</tr>
<tr>
<td>30 s</td>
<td>-1.29 \times 10^{-4}</td>
</tr>
</tbody>
</table>

This section shows the benefits of the stack-up model which is inherent in the DHBT method, which produces films with interconnected surfaces as long as the deposition time is sufficient, and conditions are carefully controlled. For the conditions used in this section, there is a critical time of 15 s at which the interconnection of the porous film is established.
After such time the film continued to grow following a ‘stack-up’ model where the surface pores grew larger as the distance of growth from the substrate increased.

The 15 s deposition has the largest pore density. This causes significant changes to the Cu lattice, indicated by the greatest shift in peak centre for Cu (111) in the XRD pattern and electronic environment shown by the increase of the core-level binding energies for Cu 2p$_{3/2}$, Au 4f$_{7/2}$ and Pt 4f$_{7/2}$ levels in XPS. These above properties are linked to an optimal potential of -0.176 V for the HER reaction whilst achieving a high current density of -2.85 mA cm$^{-2}$. For the FCN reaction the 15 s film performed well, as did all the films that achieved uniform porous surfaces, but was exceeded by the 30 s film that allowed for better access to the array of surface morphological features established by using DHBT.

5.3.3. The Effect of the Increase in Noble Metal Concentration.

The third section in this chapter focusses on the effect of increased noble metal concentration, expanding on the previous section where the deposition time of 15 s was found to be the most optimal. It has been established in the previous sections that by using electrodeposition and the DHBT method, that control over porous films and their surface properties can be attained through the changing the deposition parameters. The addition of small concentrations of noble metal salts into the deposition solution has a significant effect on the morphology of the trimetallic films. In this section, four deposition solutions with varying noble metal concentrations were employed for the deposition of the films. Each has been labelled with regards to their respective electrolyte noble metal concentration with 10 and 20 representing 10 and 20 mM concentrations, respectively. The four films are CuAu10Pd10, CuAu20Pd10, CuAu10Pd20 and finally CuAu20Pd20.
5.3.3.1. Effect of Au and Pd on morphology

By variations in the electrolyte composition between 10 and 20 mM of both Au and Pd, the specific effects on the morphology can be observed. The relatively low concentrations of these noble metals in comparison to large concentration 0.4 M of Cu results in drastic changes in the overall surface morphologies of films, as is observed in Figure 5.17. The four trimetallic films all have uniformly covered surfaces. The films with the smallest pores sizes are those with the lowest concentration of Pd in the electrolyte: Figure 5.17 a) CuAu10Pd10 and Figure 5.17 b) CuAu20Pd10 that have measured sizes of 7.1 and 10.9 µm respectively, as is summarised in Table 5.12. The addition of noble metals (to a combined total of 30 mM or more) results in an increase in the pore size from that of the CuAu10Pd10 film. The pore size is highest for surfaces with highest concentration of Pd, 14.9 and 13.1 µm. There is deviation in pore size for the four different films, with the lower deviation values of 2.2 and 2.6 for low Pd films and 3.3 and 4.6 for the high Pd films. Figure 5.17 shows that the film with highest noble metal concentrations in the electrolyte, CuAu20Pd20, has relatively undefined pores and therefore the values obtained are of an indicative nature only.
Figure 5.17 SEM images for the trimetallic films deposited at -2 A cm$^{-2}$ for 15 s with the following electrolyte compositions: a) CuAu10Pd10, b) CuAu20Pd10, c) CuAu10Pd20 and d) CuAu20Pd20.

The film thickness of the Cu films is affected when Au and Pd are added at different concentrations (Figure 5.18). Cu fabricated by DHBT typically results in multi-layered honeycomb structures with small pores close to the electrode, and larger pores with increased distance away from the electrode surface, often described by the ‘stack up’ model (see Figure 5.8), as observed in the previous section of this chapter. It is known that an increase in acid or H$_2$ evolution tends to decrease the diffusion layer thickness, affecting the growth mechanism and subsequent morphology of the metal. In these multimetallic films, the change to the amounts of noble metals added, results in alterations to occur in regard to the hydrodynamic conditions affecting the metal growth mechanism. Stacking of the surface occurs to some degree, but is not as developed as pure Cu or those established
using lower concentrations, and at shorter deposition times, resulting in thinner overall films. The noble metal concentration affects the film thickness as seen by 85° tilted SEM images in Figure 5.18. The low noble content CuAu10Pd10 has a maximum film thickness of 55.4 µm, which drastically reduces to 29.7 µm when the Au content is increased to 20 mM. CuAu10Pd20 has a relatively large film thickness of 83.3 µm and CuAu20Pd20 is slightly increased, but also has thicker wall structure of 59.3 µm. From these observations it can be seen that a larger Pd concentration of 20 mM has the effect of increasing the overall film thickness. As Pd has the largest exchange current density of \( 10^{-3} \) A cm\(^{-2}\) for H\(_2\) evolution,[30] the increase to 20 mM of Pd would increase the H\(_2\) evolution rate, causing a more, turbulent deposition environment. The turbulent environment has shown to compress the diffusion layer, allowing for the ‘stack-up’ model to apply, with pores sizes increasing with deposit thickness. Therefore this explains the CuAu10Pd20 film, which has the largest film thickness and large surface pore sizes; due to a favourable H\(_2\) evolution rate for effective templating as described by the DHBT method. It is seen that the mass of the CuAu10Pd20 is almost the largest (with CuAu10Pd10 having the largest mass) compared to the other films (Table 5.12), which complements this interpretation. However, for the CuAu20Pd20 film, the interconnected porous surface was not formed. This surface is similar to the 10 s deposition time in Section 5.3.2.1 where the interconnected surface had not completed due to insufficient deposition time, causing large undeveloped pores. Therefore, for the CuAu20Pd20, the H\(_2\) evolution rate in this case, may prevent the effective bubble templating, resulting in the underdeveloped porous morphology.
Looking closely at Figure 5.18, the CuAu10Pd10 (Figure 5.18 a) surface consists of a much finer dendrite-like structure which can more easily template around the evolving H\textsubscript{2}. This relates to the surface with the smallest average pores size, as dendritic growth is more capable of templating around H\textsubscript{2} bubbles in a stack up approach. When the noble metal concentration is increased to 20 mM, in particular, when Pd concentration is increased to 20 mM, there is a loss of the dendritic fine surface structure. This reflects surfaces with larger pore sizes as the structures can no longer as effectively template around the bubbles.
A closer inspection of the surface by higher magnification SEM images in Figure 5.19 compare the films deposited with different electrolyte compositions. It is found that there are very little differences between the structures formed under these deposition conditions at this magnification, however Figure 5.19 a) shows slightly finer (and taller) structures is observed tilted SEM images in Figure 5.18. Composition, leading to changes in fine structure formation governs the differences in the growth mechanism resulting in the film macroscale morphology (as observed in Figures 5.17 and 5.18).

Figure 5.19 SEM images for the trimetallic films deposited at -2 A cm\(^{-2}\) for 15 s with the following electrolyte compositions:  

\begin{itemize}
  \item a) CuAu10Pd10
  \item b) CuAu20Pd10
  \item c) CuAu10Pd20
  \item d) CuAu20Pd20
\end{itemize}

Figure 5.19 SEM images for the trimetallic films deposited at -2 A cm\(^{-2}\) for 15 s with the following electrolyte compositions: a) CuAu10Pd10, b) CuAu20Pd10, c) CuAu10Pd20 and d) CuAu20Pd20.
The surfaces were investigated similarly to those in Section 5.3.1.1 and 5.3.2.1, with the electrochemical surface area (ECSA) measured by the C\text{dl} method and the mass determined from samples mechanically removed from the substrate and analysed by ICP-MS. Table 5.12 shows the information obtained from the SEM images (in Figure 5.17) and the mass from ICP-MS.

Table 5.12 Surface properties for deposition with varying electrolyte composition.

<table>
<thead>
<tr>
<th>Film</th>
<th>Mass (g)</th>
<th>ECSA (m²)</th>
<th>SSA (m²/g)</th>
<th>RF</th>
<th>Average Pore Size (µm)</th>
<th>Pore Density (Pores/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu10Pd10</td>
<td>7.31 x 10^{-4}</td>
<td>3.63 x 10^{-3}</td>
<td>4.97</td>
<td>129</td>
<td>7.07 ± 2.6</td>
<td>9.0 x 10^5</td>
</tr>
<tr>
<td>CuAu20Pd10</td>
<td>4.99 x 10^{-4}</td>
<td>2.67 x 10^{-3}</td>
<td>5.37</td>
<td>95</td>
<td>10.9 ± 2.2</td>
<td>3.0 x 10^5</td>
</tr>
<tr>
<td>CuAu10Pd20</td>
<td>6.74 x 10^{-4}</td>
<td>3.07 x 10^{-3}</td>
<td>4.55</td>
<td>109</td>
<td>14.9 ± 4.6</td>
<td>1.9 x 10^5</td>
</tr>
<tr>
<td>CuAu20Pd20</td>
<td>5.28 x 10^{-4}</td>
<td>3.11 x 10^{-3}</td>
<td>5.89</td>
<td>110</td>
<td>13.1 ± 3.3</td>
<td>2.6 x 10^5</td>
</tr>
</tbody>
</table>

SSA has been highlighted as an important factor as it describes the metal loading requirements as well as surface accessibility to active sites. As the amount of expensive noble metal increases in the electrolyte the importance of this parameter is more prominent. Compared to CuAu10Pd10, the higher Au concentration films CuAu20Pd10 and CuAu20Pd20 both have larger SSAs of 5.37 and 5.89 m²/g, respectively. The CuAu20Pd20 surface had the least defined pores (Figure 5.17d), however it had the largest SSA of 5.9 m²/g, presumably due to lack of complete wall formation as compared to the other three films, which had lower SSAs due to decrease in the surface accessibility and therefore in the ECSA. The least surface and specific surface areas coincided with CuAu10Pd20 that had the largest pore size and densest, most filled-in growth. In combination with the largest pore size distribution, it is seen that the increased evolution of H₂ causes the least uniform
surface coverage and a relatively large mass to deposit on the surface. The films with 20 mM of Pd both have the largest pores when compared with the 10 mM films and have the largest deviations in pore size. The difference of almost two orders of magnitude in the exchange current densities between Pd and Au, results in differences to arise in the bubbles generated that cause the hydrodynamic condition surrounding metal grown. For the films noble metal concentration of Au and Pd of 20 mM, the deposition occurs where fine structures is partly lost, which prevent the templating of the metal around the bubbles, thus creating less uniformity in the overall structure.

5.3.3.2. Electrolyte Composition Dependent Film Composition Studies

ICP-MS and XPS were employed to quantify the bulk and surface At %, respectively. The compositions are given in Table 5.13. This investigation is to gain an understanding of the quantities of each metal present in the bulk and surface as a function of the varying electrolyte composition.

Table 5.13 Surface Atomic Composition Percentage (At %) for the Bulk and Surface.

<table>
<thead>
<tr>
<th></th>
<th>Bulk At %</th>
<th></th>
<th>Surface At %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Au</td>
<td>Pd</td>
<td>Cu</td>
</tr>
<tr>
<td>CuAu10Pd10</td>
<td>94.9</td>
<td>2.0</td>
<td>3.1</td>
<td>89.0</td>
</tr>
<tr>
<td>CuAu20Pd10</td>
<td>93.3</td>
<td>4.5</td>
<td>2.2</td>
<td>91.6</td>
</tr>
<tr>
<td>CuAu10Pd20</td>
<td>93.1</td>
<td>2.2</td>
<td>4.7</td>
<td>90.0</td>
</tr>
<tr>
<td>CuAu20Pd20</td>
<td>91.6</td>
<td>4.1</td>
<td>4.3</td>
<td>87.2</td>
</tr>
</tbody>
</table>

As expected, Cu again made up the majority contribution to the film in agreement with the composition of the deposition electrolyte. As the concentration of Au and Pd was increased
from 10 to 20 mM, their bulk concentrations were found to be increased by a factor of 2. The surface concentration of Au and Pd did not follow any linear increase with respect to the increase in the electrolyte concentration. However, like in the films produced in Sections 5.3.1 and 5.3.2, the surface concentrations of Au were found to be higher than their bulk concentrations, showing surface enrichment is again occurring. In the case of Pd, there is no enrichment occurring like in Section 5.3.2.2, due to the phenomena of electroless Cu deposition on freshly deposited Pd active sites, therefore reducing the XPS surface content of Pd.

5.3.3.3. **Structural and Surface Analysis by XRD and XPS**

To characterise the surface state and index the facets, XRD patterns were obtained as seen in Figure 5.20. The XRD patterns of the films only showed diffractions relative to the metallic polycrystalline Cu as before in the above sections. The peaks are centred at 2θ values of ca. 43.4, 50.6 corresponding to the Cu (111) and (200) planes, respectively. There is a trace peak at a 2θ value of 36.4 that can be attributed to the slight formation of the Cu₂O (111). The increase in Au and Pd concentration resulted in a decrease of this peak, which is different from what was seen previously for CuAu bimetallic films that showed Cu₂O (111) peak intensity increased with Au content.[10]

Table 5.14 affords the peak information data obtained from the patterns as well as calculations using the Bragg and Scherrer Equations (Equations 2.8 and 2.9, respectively). Increasing noble metal concentrations are responsible for the peak centre changes in the 2θ values. There are significant changes to the crystallite sizes with the largest crystallite sizes (30.8 and 27.4 nm) obtained when Au concentration is high (CuAu20Pd10 and CuAu20Pd20, respectively). The CuAu20Pd10 film that has the largest Cu (111) crystallite size also has the
largest (111:200) ratio which indicates that the Au is incorporating into the Cu lattice promoting preferential growth in the (111) direction. The smallest Cu (111) crystallite size of 21.1 nm is when CuAu10Pd20 indicating that the Pd suppresses the growth of the Cu (111) plane. It can be speculated that the addition of Au increases the crystallite size and relative ratio of the Cu (111) to (200) phase, due to incorporation that results in increased growth along the (111) direction. However it is observed that Pd has the opposite effect, where by the incorporation of Pd blocks the growth of the Cu (111) site. The significant reduction in the Cu (111) crystallite size upon the addition of Pd to Cu has been previously observed.[26] The CuAu20Pd20 film has relatively large crystallite sizes and a (111:200) ratio of 1.05 indicating that both the noble metals are exerting their relative blocking and promotional effects on the Cu (111) plane. There is a competitive process during the deposition process whereby the Cu (111) growth is directly affected by the small addition of the noble metals Au and Pd. From the d-spacing and crystallite sizes, it is clear that the size and relative ratio of Cu (111) vs. Cu (200) changes as a function of Au and Pd concentration reflecting the changes to the Cu lattice when the noble metals are added. [49-51]
Figure 5.20 XRD patterns of a) CuAu10Pd10, b) CuAu20Pd10, c) CuAu10Pd20 and d) CuAu20Pd20 showing intensities of Cu$_2$O (111), Cu (111) and Cu (200) facets from left to right.

Table 5.14 XRD pattern information for the varying electrolyte composition films, including the d-spacing of Cu (111) planes calculated using Bragg equation and crystallite size determined using the Scherrer equation for increased noble metal films.

<table>
<thead>
<tr>
<th></th>
<th>2θ (111) (degrees)</th>
<th>d-spacing (111) (Å)</th>
<th>Crystallite Size (111) (nm)</th>
<th>Crystallite Size (200) (nm)</th>
<th>Peak Area Ratio Cu (111) : (200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu10Pd10</td>
<td>43.42</td>
<td>2.081</td>
<td>26.2</td>
<td>25.4</td>
<td>1.96</td>
</tr>
<tr>
<td>CuAu20Pd10</td>
<td>43.46</td>
<td>2.080</td>
<td>30.8</td>
<td>23.3</td>
<td>3.63</td>
</tr>
<tr>
<td>CuAu10Pd20</td>
<td>43.48</td>
<td>2.079</td>
<td>21.1</td>
<td>24.0</td>
<td>2.04</td>
</tr>
<tr>
<td>CuAu20Pd20</td>
<td>43.58</td>
<td>2.074</td>
<td>27.4</td>
<td>28.7</td>
<td>1.05</td>
</tr>
</tbody>
</table>

XRD results did not show the presence of metallic Au or Pd, however, the more sensitive XPS technique clearly showed their presence (Figure 5.21). Given that Au and Pd are present at bulk and at the surface (from ICP-MS and XPS), it can be explained that these films are in the form of solid-solution type alloys, where Au and Pd are interlaced into the Cu network,
as seen in other films prepared in this chapter. This was previously ascertained from compositional studies and through the influence that the Au and Pd had on the shift in d-spacings and crystallite sizes (Table 5.14). XPS analysis of these films delved further to investigate the chemical state of these three metals in trimetallic films for the Cu 2p$_{3/2}$, O 1s, Au 4f$_{7/2}$ and Pd 3d$_{5/2}$ core level spectra given in Figure 5.21. The binding energy of the Cu 2p$_{3/2}$ core-level in all these materials were found to be centred at ca. 932.8 eV, which is shifted higher than the zero valent Cu binding energy, usually observed at 932.6 eV.[52] The presence of small satellite peaks at 945 eV rule out the formation of CuO, which has strong satellite peaks. It instead indicates the presence of Cu$_2$O, which is in agreement with the XRD patterns as before.[53] The Cu 2p$_{3/2}$ binding energy of the films with combined Au and Pd concentration greater than or equal to 30 mM (eg. CuAu$_{20}$Pd$_{10}$, CuAu$_{10}$Pd$_{20}$ and CuAu$_{20}$Pd$_{20}$) resulted in an increase of the binding energy to 932.9 eV, which relates to greater interactions due to the effect of increased noble metal incorporation. The peak binding energies of Au 4f$_{7/2}$ and Pd 3d$_{5/2}$ for the CuAu$_{10}$Pd$_{10}$ film are at 84.5 and 335.7 eV respectively, which indicates a strong electronic interaction due to the significant shift from the pure Au and Pd published values of 84 and 335 eV respectively.[52, 54]
Upon further increase in the total Au and Pd concentration to $\geq 30$ mM, the binding energy of Au $4f_{7/2}$ increases to 84.6 eV. This increase is similarly seen for and Pd $3d_{5/2}$ with an initial increase from 335 eV for metallic Pd to 335.7 eV in CuAu10Pd10, which further increases to 335.8 eV in the trimetallic systems with total Au and Pd concentrations $\geq 30$ mM. Asymmetry in the Pd peak shape has been observed for CuPd alloys where the palladium concentration is higher than that of the Cu. Upon increasing the Cu concentration the peak becomes symmetric.[57] As the films prepared in this work all have a high Cu to Pd ratio, asymmetry in the peaks is not observed. The Pd $3d_{5/2}$ peak is in close proximity with both the Au $4d_{5/2}$ peak which has a slightly lower binding energy of 335 eV and the native oxide of palladium at 336.7 eV which results in the broadening observed in the $3d_{5/2}$ peak.[58]
Surface oxide species play a critical role in the controlling the catalytic activity of metals. Therefore the O 1s core-level spectra analysis was carried out (Figure 5.21b). It was observed that there were three chemically different oxygen environments that had deconvoluted peak energies of 530.0, 530.6 and 532.3 eV. The lowest binding energy of 530.0 eV is the result of copper oxides,[59] which had a low atomic percentage of between 4.6 – 6 %. As explained from the Cu 2p spectra and XRD this is expected as it has been observed that Cu$_2$O was formed in minimal quantities. The second O 1s peak observed at 530.6 eV falls in the metal-oxide interaction region from the presence of adsorbed oxides on the film surface. The O 1s species observed at 532.5 eV is due to surface hydroxides on the trimetallic films.[60] The increase in Pd concentration causes the formation of increase surface hydroxides, as seen by the increase in the relative peak binding energy at 532.5 eV. For CuAu10Pd10 and CuAu20Pd10 the adsorbed hydroxides (i.e. the 532.5 eV peak magnitude) are low, but as the Pd concentration increases to 20 mM so too does the peak intensity relating to adsorbed hydroxides. It is therefore evident that the small concentrations of Au and Pd metals are responsible for the large changes in the electronic environments of each of the metals in the trimetallic films.

The results show how changes to the small amounts of Au and Pd added to a Cu electrolyte can have a significant effect on the morphology, including the pore sizing and surface area. XRD patterns show critical information with regards to the lack of alloy formation, however the Cu lattice is influenced with changes to the crystallite size and orientations due to the ability of either the Au or Pd to change the growth pattern of the Cu. XPS analysis was able to confirm the presence of metallic Au and Pd, and showed there were increases in the peak
binding energies of all three metals, relative to increases in Au and Pd concentrations. These influences caused by the small amounts of Au and Pd, that directly affect the morphologies and surface compositions of Cu films also lead to changes in the electronic structure of the film, suggesting catalytic activities of the films may also be altered.

5.3.3.4. Model Catalysis Reactions: HER and FCN Reduction

In order to investigate the effect of Au and Pd addition on the catalytic behaviour, HER activity was investigated. The voltammograms in H₂SO₄ under identical conditions, adjusted for surface area, are presented in Figure 5.22 with the onset potential (3 % of current density at -0.6 V vs. SHE) for each curve in Table 5.15. The slope of the curve in the region where faradaic processes take place is the same for all samples. The main difference is in the onset potential. A Cu honeycomb deposited under identical conditions without the addition of noble metals, has a reasonable activity towards hydrogen evolution with an onset potential of -0.258 V and current density of -1.92 mA cm⁻² at -0.6 V. The small additions of the noble metals shows a significant decrease in onset potential down to between -0.189 and -0.217 V. This decrease in onset potential of 70 mV for the optimal CuAu10Pd10 film in significant in showing how the minimal amount of Au and Pd addition can result in improved activity towards HER.

The surface with the lowest onset potential of -0.189 V, and therefore the best activity, is CuAu10Pd10, which reflects the film with the largest surface area due to the largest pore density. As the results are normalised, it is the access to the active sites that is most likely responsible for the lowest onset potential and acceptably high activity. The film with the lowest percentage of Pd on the surface, CuAu20Pd10, expectedly had the highest onset potential of -0.217 V. This shows how important it is to optimise the surface, and shows how
the significant effects of the small changes in noble metal content can be on the films fabricated.

![Graph](image)

**Figure 5.22** Hydrogen Evolution Reaction (HER) in 1 M \( \text{H}_2\text{SO}_4 \) for each of the films deposited with increasing noble metal concentrations at a scan rate of 0.01 V/s.

**Table 5.15** HER data for the films deposited with increasing noble metal concentrations.

<table>
<thead>
<tr>
<th>Film</th>
<th>( j ) (mA cm(^{-2})) @ -0.6 V vs. SHE</th>
<th>Onset (V) at 3% Current density at -0.6 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Honeycomb</td>
<td>-1.92</td>
<td>-0.258</td>
</tr>
<tr>
<td>CuAu10Pd10</td>
<td>-2.85</td>
<td>-0.189</td>
</tr>
<tr>
<td>CuAu20Pd10</td>
<td>-2.86</td>
<td>-0.217</td>
</tr>
<tr>
<td>CuAu10Pd20</td>
<td>-2.69</td>
<td>-0.210</td>
</tr>
<tr>
<td>CuAu20Pd20</td>
<td>-2.47</td>
<td>-0.211</td>
</tr>
</tbody>
</table>

It can be said there is not a significant difference for the most part in the achievable current density between the four CuAuPd films. CuAu20Pd20 showed there was no benefit in increasing noble metals for improvement to the onset potential and also resulting in a
decrease in the achievable current density. The loss of porosity and interconnectivity of the surface is likely to be the cause, indicating the importance of morphology on catalysis. This may be explained by the similarities in the surface structures observed in Figure 5.19. For HER, the results all show that there is very little benefit in increasing the Au and Pd concentrations past CuAu10Pd10 as it is this film that has the best onset potential of -0.189 V compared to the next best of -0.210 V and showed a current density of -2.85 mA cm$^{-2}$ which is comparable to the higher noble metal content films, avoiding the extra expense of increased noble metal concentration in the deposition electrolytes. As it was shown in Section 5.3.2.4, it was the stage at which the interconnection of the porous surface was initially obtained that yielded a film with the best activity.

The activity towards the FCN reduction is shown by the plot in Figure 5.23 that shows the differences in activities of the four films with increasing noble metal content.

Figure 5.23 Kinetic comparison of FCN reduction reaction monitored by UV-Vis with time for films deposited at increasing noble metal concentration.
Figure 5.23 shows the distinct differences in the rate of reduction of FCN for the four trimetallic surfaces, with rates normalised for surface area. The fastest reaction (see k in Table 5.16) occurs in the CuAu10Pd20 surface, which has the highest Pd concentration, and lowest Au percentage on the surface. Even though the CuAu20Pd10 has the lowest Pd surface percentage, its rate is not the lowest as it might be expected.

Table 5.16 Reduction Rates for the catalysed FCN reduction by STS on films deposited with increasing noble metal concentration.

<table>
<thead>
<tr>
<th>Film</th>
<th>Rate k (s(^{-1}) cm(^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu10Pd10</td>
<td>-8.08 x 10(^{-5})</td>
</tr>
<tr>
<td>CuAu20Pd10</td>
<td>-9.50 x 10(^{-5})</td>
</tr>
<tr>
<td>CuAu10Pd20</td>
<td>-10.8 x 10(^{-5})</td>
</tr>
<tr>
<td>CuAu20Pd20</td>
<td>-8.91 x 10(^{-5})</td>
</tr>
</tbody>
</table>

Comparing the two surface reactions, the CuAu10Pd10 which has the lowest onset for the HER, has the slowest reaction rate for FCN reduction, which shows there are opposing pathways for the different reactions and that it is not just specific surface sites that are responsible for reaction behaviour but overall composition. Despite the small concentrations of Pd and Au on the surface, all of the surfaces show reasonably high activity toward the model reactions and give indication that they can be altered to be possibly suitable to other electrocatalytic and electron transfer reactions.

5.4. Conclusions

It is shown that small concentrations of Au and Pd can be used to control the synthesis of porous Cu based trimetallic films using the DHBT method. The incorporation of the noble metals, Au and Pd, into the electrolyte used for bubble templating, can be utilised to tailor
design films with controlled surface area, and most importantly, with designated morphologies. This reflects the different concentrations of noble metals such as Au and Pd on the surface, which is where model catalytic reactions are controlled. We have shown that subtle differences in surface chemistry can lead to measurable variances in model reactions such as the hydrogen evolution reaction and ferricyanide reduction in the presence of sodium thiosulphate.

In regard to control and optimisation of the surface, the DHBT method for trimetallic materials is shown to follow a ‘stack-up’ model whereby the pore size at the surface of an electrodeposited film is increased as the overall structure grows away from the substrate.

Interestingly it was found that the addition of the noble metals, Au and Pd, lead to changes in the hydrodynamic conditions surrounding the deposition, which is revealed through significant changes to the overall surface morphology of the resulting film.

The deposition proceeds through incorporation of the Au and Pd into the Cu lattice, observed by the peak analysis of XRD data, whereby changes to the Cu (111) crystal orientation occurred. An increase to crystallite size was observed when Au was added, and a decrease in size occurred when Pd was added. There were no XRD peaks due to Au and Pd, however as there were changes to the host Cu lattice, suggesting solid-solution formation. It was found that 5 and 10 s was not a sufficient time for the interconnected porous film to form. The 15 s time was found to be optimal to form the porous structure, and changes to the electronic environment of the films leading to favourable surfaces, by improved onset potentials and pleasing rates for catalysing the HER and FCN model reactions, showing efficient use of the noble metals.
To further optimise the surfaces, the noble metal concentration in the electrolyte was increased which was reflected by changes in the morphology, crystal structure and electronic environment. The changes to the films with different electrolyte conditions resulted in different activities towards the model reactions. In regard to the HER reaction, it was found that whilst the CuAu20Pd10 had the highest rate, the CuAu10Pd10 showed a comparable rate with a much lower onset potential. In regard to the FCN reduction reaction, the increased noble metal content resulted in a marginally, but not significantly increased rate. Therefore, it was observed that an increased noble metal content was not required for optimisation of the film properties.

In this chapter it has been found that less than 5 % of noble metal, incorporated into a porous Cu scaffold is sufficient for these surfaces to exhibit optimised catalytic activity. It is found that Au concentrates towards the surface, facilitating its efficient use, but that Pd tends to have a lower surface concentration than bulk, possibly due to its higher surface activity for electroless deposition of Cu. As such, superior specific areas for other noble metals such as Pt may be ideal to prepare trimetallic porous templates, as they should also show good activity, but lead to higher surface concentrations of the noble metals.
5.5. References


Chapter 6

Incorporation of Gold and Platinum into a Nanostructured Copper Framework.
Application to the Electrooxidation of Sodium Borohydride.
6.1 Introduction

As discussed in Chapter 1, there is a continuing need for new, alternative energy generation technologies. Fuel cells, especially PEMFCs, are one of the areas that are being heavily explored as suitable energy sources due to their high efficiencies and low emissions. The fuel for PEMFCs is hydrogen, however there are a number of key issues in regards to the difficulty in its storage and handling of gaseous hydrogen. As an alternative, sustainable liquid fuel sources including methanol, ethanol and sodium borohydride are being investigated for use in Direct Fuel Cells (DFCs). The DHBT method has been shown in Chapter 5 to be a suitable method for incorporating small amounts the noble metals Au and Pd into a Cu framework in a controlled manner. Here in Chapter 6, the DHBT method is to be used again to identify the effects of morphology on activity, by incorporating Au and Pt into a Cu framework. The sodium borohydride reaction is an interesting reaction that requires further study. The films prepared in this chapter may provide favourable surfaces for the reaction to proceed, and are thus used as an application for borohydride oxidation.

As described in Section 1.2.2.3 an alternative fuel cell is the direct borohydride fuel cell (DBFC) that uses sodium borohydride (NaBH₄) directly. The DBFC has a high theoretical cell voltage of 1.64 V, which is significantly higher than the cell voltages of fuel cells utilising hydrogen (1.24 V) or methanol (1.19 V).[1, 2] The reaction does not involve carbon, therefore has no undesirable carbon based emissions. DBFCs are understudied due to difficulty in identifying reaction mechanisms, in favour of the simple hydrogen and methanol fuel cells.[3]
The DBFC uses sodium borohydride as a fuel source that is directly electrooxidised with a high anodic specific capacity of 5.7 A h g\(^{-1}\), associated with the eight electron process.[4] \(\text{NaBH}_4\) rapidly dissociates in contact with moisture to release hydrogen (hydrolysis), however it can be stabilised in alkaline solutions.

The anodic reaction can proceed via two pathways. The first, and most favourable, is the direct eight electron oxidation, and the second pathway is the four electron indirect electrooxidation of sodium borohydride, which involves hydrolysis and the evolution of hydrogen. The four electron pathway is undesired as it reduces the cell efficiency affecting the maximum cell voltage.

From the limited voltametric studies that have been performed on Au and Pt electrodes, for borohydride oxidation, mechanisms have been proposed to explain the oxidation peaks observed both in the anodic and cathodic direction for a CV. There are key differences on Pt and Au. At a slow scan rate of 0.025 V/s on Pt, complex processes occurs; initially involving the hydrolysis of \(\text{NaBH}_4\) and the evolution of hydrogen from -0.8 to ca. -0.4 V vs. SHE (Equation 6.1 and 6.2).

\[
\text{BH}_4^- + \text{H}_2\text{O} \leftrightarrow \text{BH}_3\text{OH}^- + \text{H}_2 \quad (6.1)
\]
\[
\frac{1}{2}\text{H}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^- \quad (6.2)
\]

The process then continues to oxidise the \(\text{BH}_3\text{OH}^-\) formed in Equation 6.1, to complete the overall four electron oxidation of \(\text{BH}_4^-\) according to Equation 6.3 in a wide potential window from -0.4 up to ca. -0.2 V.[3]

\[
\text{BH}_3\text{OH}^- + 3\text{OH}^- \rightarrow \text{BO}_2^- + \frac{3}{2}\text{H}_2 + 2\text{H}_2\text{O} + 3e^- \quad (6.3)
\]
The eight electron oxidation reaction (Equation 6.4) does occur to a minimal extent on Pt at a potential of 0.07 V but is dominated by hydrolysis processes.[3, 5]

\[
BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (6.4)
\]

On an Au electrode at a scan rate of 0.025 V/s there is a distinct difference; there is no peak corresponding to the four electron pathway. The first peak occurs at -0.2 V which is assigned to the process in Equation 6.4. A small wave then follows that has been described as a process involving the direct pathway reactive intermediate BH$_3$, which can be converted into BH$_3$OH.[3, 6]. Scan rate can affect the peak positions and the peak currents.

For both the Pt and Au electrode, a sharp peak is observed on the reverse sweep at -0.4 V due to the oxidation of BH$_3$OH$^{-}$ formed either during hydrolysis (Pt) or as a reaction intermediate for the eight electron pathway (Au) according to Equation 6.3.

The increase in the scan rate to 1 V/s resulted in the shift of the direct oxidation peak from 0.07 to 0.15 V vs. Ag/AgCl and from-0.2 V to -0.1 V vs. SHE for Pt and Au, respectively.[3]

The electrode material decides the oxidation pathway taken, however so too does the solution. Working in an alkaline environment improves the direct oxidation of NaBH$_4$ over hydrolysis, especially for Pt electrodes. It has been shown for the eight electron pathway to take precedence it is important to have a OH$^-$/BH$_4^-$ concentration ratio above 4.4.[7]

A further technique to improve the process has been to create bimetallic materials, which serve to both improve direct oxidation activity and also reduce Pt and Au metal loadings through improved activity. Pt combined with Cu has been shown to be able to form nano-PtCu surfaces that showed mixed four and eight electron pathway, but with a significantly enhancement in activity towards the direct eight electron activity compared to pure Pt.[2]
Au is established to be inactive for the four electron pathway whilst being selective for the eight electron pathway.[8] Gyenge, Atwan and Northwood investigated the synergistic effects of combining Pt with a secondary metal. In particular, PtAu bimetallic nanoparticles were fabricated with the aim to combine Pt’s high activity shown towards hydrolysis and Au’s direct eight electron process to drive the eight electron reaction at a faster rate with better kinetics and a high anodic specific capacity.[9] These studies showed that while Pt is highly active for the indirect oxidation pathway, the electrode surface properties can be altered or modifications to the reaction solution can be made to favour the direct pathway.

6.1.1 Research Aims of Chapter

As it has been described in Chapter 1 and demonstrated in Chapter 5, Cu bimetallic and trimetallic honeycombs are readily fabricated by the dynamic hydrogen bubble templating (DHBT) method. Bi- and trimetallic systems of PtAu, NiCu and Cu/Ni/AuNi have been investigated previously for NaBH₄ electrooxidation and shown to have improvements due to the compositional and morphological effects resulting in an improved charge transfer reaction.[9, 10] Cu is relatively cheap and can form stable frameworks that can significantly reduce the cost of catalysts. Until now there has been no bimetallic CuPt system fabricated by the DHBT method. Cherevko, Kulyk and Chung, fabricated CuPt by DHBT, yet it was further dealloyed to create high surface area mesoporous Pt-only films.[11] The aim of this chapter is to study the conditions that allow the preparation of trimetallic films CuAuPt by the DHBT method, and study the morphology and surface properties of the films deposited under a range of conditions. Their activity for catalysis will be investigated,
with particular emphasis on NaBH$_4$ electrooxidation, which has been identified as a process that could benefit from these materials. Bimetallic films of CuAu and CuPt will be prepared and compared to trimetallic CuAuPt films, focusing on two systems with a range of noble metal concentrations, especially 5 and 10 mM. The model hydrogen evolution reaction (HER) and FCN reduction reaction described previously, will also be used to assess the differences in surface activity between the different fabricated films as initial insight into surface activity that allows better comparison with other materials in the literature.

6.2 Experimental

6.2.1 Electrodeposition of Copper with Au and/or Pt

The fabrication of the films was performed cathodically under galvanostatic conditions using a conventional three-electrode cell. The deposition was performed on a Cu foil substrate, masked to an area of 0.28 cm$^2$ using Kapton tape, which acted as the working electrode with a graphite electrode as the counter electrode. A current of -0.565 A was applied to achieve a current density of -2 A cm$^{-2}$ in regard to the original geometric surface area. The common electrolyte used for every electrodeposition consisted of 0.4 M CuSO$_4$ in 1.5 M H$_2$SO$_4$. To this common electrolyte, noble metal salts were added with concentrations of either 5 or 10 mM (specified in each section), using the metal salts KAuBr$_4$ and K$_2$PtCl$_4$. All electrolytes were sonicated for 10 mins and purged with N$_2$ for 10 mins before deposition. Depositions were performed in sets of 3, with a 10 min purge before the first run, and 2 mins between each run in a set.
6.2.2 NaBH₄ Electrooxidation

The electrooxidation of NaBH₄ was performed in an alkaline environment using 0.5 M NaOH. Voltammograms to study catalysis were performed in a similar cell to above, however in a solution containing 0.05M NaBH₄ in 0.5M NaOH, consisting of sweeps between -0.8 and 0.2 V vs. SHE for 5 cycles at 0.05 V/s.

To measure the stability of the electrocatalysts films, a chronoamperometric step (CA) was performed from -0.8 to 0.0 V for 1800 s to determine the stability of the current for the direct electrooxidation of NaBH₄.

6.3 Results

6.3.1 Fabrication of CuAu, CuPt and CuAuPt Noble Metal Concentration Levels of 5 or 10 mM.

This section will investigate the effects on the morphology of the Cu honeycombs (including shape, size and crystal structure) caused by addition to the deposition electrolyte of 5 or 10 mM of Au and/or Pt. The prepared films will then be studied using the model catalysis reactions of HER (Section 2.2.2.1) and FCN reduction (Section 2.2.2.2). They will then be tested for the electrooxidation of NaBH₄. Bimetallic samples of CuAux and CuPtx will be compared with trimetallic films CuAuxPtx, where x is defined by the concentration of the noble metal in the electrolyte either being 5 or 10 mM of KAuBr₄ or K₂PtCl₄.

6.3.1.1 The Effect of Au and/or Pt on the Film Morphology at 5 or 10 mM.

Figure 6.1 shows the SEM images of the Cu films with variable amounts of Au and Pt added to the electrolyte. Figure 6.1 a-c) show the films obtained when 5 mM of Au and/or Pt is
added and Figure 6.1 d-f) compares films from the 10 mM additions of Au and/or Pt. These were compared to a pure Cu honeycomb, and as was previously observed in Chapter 5, there is a reduction in the surface pore size of the resulting deposits with the addition of noble metals. The pore sizes are tabulated in Table 6.1. The effect of adding 5 mM of noble metals will first be considered. Au addition results in a slight reduction in pore size from that of the pure Cu from 36.9 to 30.1 µm. The effect of Pt addition results in the significant reduction in pore size from 36.9 to 10.1 µm. The effects on morphology can be explained by the differences in the exchange current density for hydrogen (H₂) evolution off the three metals that are being deposited. The exchange current density for the three metals used in this chapter are Cu (10⁻⁵.37 A cm⁻²), Au (10⁻⁵.4 A cm⁻²) and Pt (10⁻³.1 A cm⁻²).[12, 13] This indicates that the rate of H₂ evolution would proceed in the order of Pt>Cu>Au.

The pore size is directly related to H₂ evolution off the surface, with more rapid evolution resulting in shorter residence times and smaller bubble sizes that act as a template, therefore resulting in smaller pores of the film deposited. Pt has a greater H₂ evolution rate than Au, therefore the 72.7 % reduction in pore size with Pt over the 18.4 % reduction with Au is expected. The CuAu5Pt5 film (Figure 6.1 c) shows a more significant reduction of pore size to 4.5 µm (87.8 % reduction) indicating a synergistic effect when both Pt and Au are added to the electrolyte.
Figure 6.1 SEM Images of multimetallic deposits for a) CuAu5, b) CuPt5 c) CuAu5Pt5, d) CuAu10, e) CuPt10 and f) CuAu10Pt10. Scale bar is 50 μm on all images.

Table 6.1 Effect of Au and/or Pt addition on Surface Pore Size of Cu based honeycombs.

<table>
<thead>
<tr>
<th></th>
<th>Average Surface Pore Size (μm)</th>
<th>Pore Density (pores/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>36.9 ± 13.5</td>
<td>3.70 x 10⁴</td>
</tr>
<tr>
<td>CuAu5</td>
<td>30.1 ± 7.7</td>
<td>5.89 x 10⁴</td>
</tr>
<tr>
<td>CuPt5</td>
<td>10.1 ± 3.5</td>
<td>4.70 x 10⁵</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>4.50 ± 1.5</td>
<td>1.84 x 10⁶</td>
</tr>
<tr>
<td>CuAu10</td>
<td>23.6 ± 6.2</td>
<td>1.01 x 10⁵</td>
</tr>
<tr>
<td>CuPt10</td>
<td>7.01 ± 2.1</td>
<td>9.61 x 10⁵</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>4.79 ± 1.9</td>
<td>1.37 x 10⁶</td>
</tr>
</tbody>
</table>

The increase in noble metal concentration to 10 mM in the electrolyte results in further reduction of the pores sizing in comparison to the 5 mM results. This may be explained by the availability of more Au and/or Pt on the growing surface, resulting in the reduction of
the bubble residence times and therefore smaller bubble break-off diameters. CuAu10 and CuPt10 resulted in pore sizes of 23.6 and 7.01 µm, respectively, which are 21.6 and 30.6 % smaller than their 5 mM counterparts. CuAu10Pt10 involved a slight increase to 4.79 µm (+ 6.4 %) in the pore size compared to CuAu5Pt5. This may be explained by the increased availability of Au and Pt ions, which with a faster deposition rate than Cu, causes differences to arise in the resulting hydrodynamic conditions surrounding the deposition.

Table 6.1 also shows the standard deviations of the pore sizes and pore density. As the increase in H\textsubscript{2} rate resulted in the reduction in pore size, the pore density increased across the films surface. The pore size standard deviation is shown to decrease with the addition of Au, Pt and AuPt to Cu. A decrease in the deviation is representative of the formation of a more uniform surface, indicating that H\textsubscript{2} evolution rate can be used to assist in the development of a more uniform deposition process.

Figure 6.2 shows the thickness of the films, obtained from 85° tilted SEM images. The film thickness reduces with an increasing H\textsubscript{2} evolution rate, with a pure Cu honeycomb having an average film thickness of 103.4 µm. The addition of 5 mM Au, Pt and Au + Pt results in average film thicknesses of 89.7, 20.0 and 16.7 µm, respectively (Figure 6.2 a-c). The increase in noble metal concentration to 10 mM for Pt and Au + Pt results in the reduction of film thickness to 16.2 and 11.9 µm, respectively (Figure 6.2 e and f). However in the case of Au, when the concentration is increased from 5 to 10 mM so too does the film thickness, up to 102.3 µm (Figure 6.2 d).

For the films that display a reduction in thickness, the explanation can be given that the rate of H\textsubscript{2} evolution results in the suppression of metal growth as the DHBT method is sensitive to the metal/hydrogen reduction relationship. The lower H\textsubscript{2} evolution exchange current
density associated with Cu and Au does not suppress the metal deposition rate as occurs when Pt is added, which results in a significant decrease in the films thickness as can be observed in Figure 6.2.

For the CuAu10 film, the increase in Au concentration increases the H₂ evolution rate, which leads to a smaller average pore size compared to CuAu5 (Figure 6.1 a and d), but also leads to a thicker deposit. This may be explained by the decrease in the diffusion layer thickness caused by the stirring action of the increased H₂ evolution, causing more Cu and Au ions to be in proximity to the surface of the electrode resulting in an increase in the metal deposition rate.

Figure 6.3 shows the fine surface morphology of the surface of the films. Pure Cu honeycombs exhibit dendrites that are around 5 µm long on the surface (Figure 5.1). Comparing the relative 5 and 10 mM examples of each of the CuAu, CuPt and CuAuPt films,
each pair show very similar fine surface morphology. The addition of Au reduces the size and the shape of the Cu dendrites, and instead the growth is directed to form a series of intersecting platelets (Figure 6.3 a and d). The addition of Pt causes the surface dendrites to effectively smooth out into dense, rough ‘torpedo-like’ structures (Figure 6.3 b and e). The combination of Au and Pt (Figure 6.3 c and f), shows a rather smooth nanostructure, with individual pores visible. This less developed fine structure may explain lack of stacked honeycomb development, resulting in a thinner film comparing to the bimetallic films (Figure 6.2).

![Figure 6.3 SEM Images of multi-metallic deposits for a) CuAu5, b) CuPt5 c) CuAu5Pt5, d) CuAu10, e) CuPt10 and f) CuAu10Pt10.](image)

The most important properties of the films were measured and tabulated in Table 6.2, including the electrochemical surface area (ECSA) and mass, which were used to determine the specific surface area (SSA). ECSA was measured by the double layer capacitance ($C_{dl}$) method described in Section 2.2.1.4, and the mass was determined by mechanically...
removing the deposits from the substrate then analysing the dissolved films by ICP-MS as described in Section 2.2.5.

Table 6.2 Textural Surface Properties for the prepared films

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass (g)</th>
<th>ECSA (m²)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.24 x 10⁻³</td>
<td>2.82 x 10⁻³</td>
<td>2.26</td>
</tr>
<tr>
<td>CuAu5</td>
<td>9.49 x 10⁻⁴</td>
<td>2.21 x 10⁻³</td>
<td>2.33</td>
</tr>
<tr>
<td>CuPt5</td>
<td>9.43 x 10⁻⁴</td>
<td>9.66 x 10⁻⁴</td>
<td>1.02</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>2.03 x 10⁻⁴</td>
<td>6.55 x 10⁻⁴</td>
<td>3.36</td>
</tr>
<tr>
<td>CuAu10</td>
<td>7.41 x 10⁻⁴</td>
<td>2.58 x 10⁻³</td>
<td>3.48</td>
</tr>
<tr>
<td>CuPt10</td>
<td>9.85 x 10⁻⁴</td>
<td>6.75 x 10⁻⁴</td>
<td>0.68</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>2.56 x 10⁻⁴</td>
<td>9.16 x 10⁻⁴</td>
<td>3.79</td>
</tr>
</tbody>
</table>

If the films prepared by 5 mM additions are compared to pure Cu, it is observed that the mass of the deposits decreases with an increase in noble metal content, with the heaviest multimetallic film being the CuAu5 and the lightest being the CuAu5Pt5. This can be thought to follow the trend with H₂ evolution, with the addition of the noble metal bringing larger exchange current densities favouring H⁺ reduction over Mⁿ⁺ reduction. The ECSAs also follow the same trend, with the surface area decreasing with H₂ evolution rate. Increasing the noble metal concentration to 10 mM results in a reduction in the mass for CuAu10 compared to pure Cu, but an increase compared to the 5 mM films for both CuPt10 and CuAu10Pt10. The ECSA increases for CuAu10 and CuAu10Pt10, but decreases for CuPt10. These results match the observations with regard to the fine surface morphology in Figure 6.3.

The properties in Table 6.2 can be explained by variations to the H₂ evolution during deposition. The addition of Au resulted in fine platelets across the surface, leading to more
open nanostructures that maximises the surface area. The increase in Au from CuAu5 to CuAu10 is expected to cause an increase in the rate of H₂ evolution, leading to a more compressed diffusion layer. With the compression occurring, there is an increased availability of metal resulting in a thicker film (102.2 vs. 89.7 µm). The increased H₂ rate leads to changes to the hydrodynamic conditions near the substrate surface causing the deposition of finer branched structures, which is more efficient for the formation of a more open stacked honeycomb film. The finer structures also correspond to a lower overall mass compared to CuAu5, showing how H₂ can be used to affect the amount of metal growth occurring. The fabrication of a more open and accessible film with a low deposit weight results in the increase of the SSA (2.33 and 3.48 for CuAu5 and CuAu10, respectively) and thus more efficient material use.

The addition of Pt results in a significant increase in the H₂ evolution rate, which greatly affects the morphology. The metal structures deposited are much smoother, leading to a reduction in film thickness when Pt is added. This is due to the structures of the metals being deposited not being able to effectively template around the evolving H₂ bubbles. The metal structures close in upon themselves, causing dense particles to form resulting in the reduction in surface area which corresponds to low SSAs (1.02 and 0.68 for CuPt5 and CuPt10, respectively). The trimetallic samples exhibit a low number of protrusions and fine structures, which have prevented the film’s thickness to build up similar to those observed for the CuPt_x bimetallic films. However, they exhibited much higher SSAs than those obtained with the bimetallic materials. This predominantly is due to the smaller mass (2.03 and 2.56 x 10⁻⁴ g) obtained rather than the significant increase in surface area. The addition of Au and Pt causes the deposition of an overall thinner film, however structures that had
sufficient surface areas yielded high SSAs. It was observed that the combination of all three metals results in the synergistic increase, in regard to the rate of H$_2$ evolution, which results in changes to the hydrodynamic conditions near the electrode to a point where there is a suppression of M$^{n+}$ reduction in favour of H$^+$ reduction.

6.3.1.2 Film Composition Studies for Addition Au and/or Pt at 5 or 10 mM.

It was necessary to investigate how much of each metal was present in the films, both in the bulk of the material and at the surface. It was found that the surface composition can be significantly different from that of the bulk, which is of critical importance for catalytic applications, as the surface chemistry will control the activity. Table 6.3 shows the atomic percentages (At %) of the elements present in the bulk (ICP-MS) and on the surface (XPS).

Table 6.3 Film composition for the bulk At% and Surface At%.

<table>
<thead>
<tr>
<th></th>
<th>Bulk At %</th>
<th>Surface At %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>CuAu5</td>
<td>99.1</td>
<td>0.9</td>
</tr>
<tr>
<td>CuPt5</td>
<td>99.1</td>
<td>-</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>98.9</td>
<td>0.4</td>
</tr>
<tr>
<td>CuAu10</td>
<td>97.5</td>
<td>2.4</td>
</tr>
<tr>
<td>CuPt10</td>
<td>98.3</td>
<td>-</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>98.8</td>
<td>0.4</td>
</tr>
</tbody>
</table>

As expected, and as was observed in Chapter 5, the composition both in the bulk and at the surface is predominately Cu, due to its high concentration in the electrolyte. It is found 5 mM noble metal addition to the electrolyte yields a 0.9 % of either Au or Pt in the bulk when just one noble metal is added. When Au and Pt are combined, the Pt content is
approximately twice that of Au. Doubling the concentration in the electrolyte results in a roughly doubling effect in the bulk, except for CuAu10Pt10 whose composition matches that of CuAu5Pt5.

At the surface there is a significant surface enrichment effect, whereby the noble metals are shown to enrich compared to their bulk values. This was previously observed for Au and Pd in Chapter 5. Au enriches to the larger extent, being 18 and 10 times greater at the surface than the corresponding bulk At % for additions at 5 and 10 mM, respectively. Pt surface At % for 5 and 10 mM films only contributes 4.0 and 4.4%, respectively, indicating that enrichment of Pt in the bimetallic surface is less pronounced than Au. However, in the trimetallic samples it is observed that Pt enriches to a greater extent than Au. The Au at the surface reduces significantly from that of the bimetallic from 24.6 down to 1.0 At% in the trimetallic film.

For these films, the enrichment can be explained with regard to the surface energies, relative atomic sizes, charge transfer (electronegativity) and differences in relative redox potentials when using up to three different metals, similarly to the trends observed in Chapter 5.[14] Au would diffuse to the surface as before, due to having a smaller surface energy than Cu, however Pt has a high surface energy which would not promote surface segregation.[15] There are another two factors that can be used to explain the enrichment of Pt. The relative atomic size difference (177 vs. 174 vs. 145 pm for Pt, Au and Cu, respectively) can induce surface strain that would cause the Cu diffuse to the interior of the structure leaving larger Pt and Au at the surface.[16] The other factor is the reduction potential, which accounts for each couples (e.g. Cu²⁺/Cu) redox properties. For Au deposition, the reduction potential of Au³+/Au (AuBr₄⁻) compared to Cu²⁺/Cu is 0.854 V vs.
0.34 V, respectively, which causes Cu to be oxidised in the presence of \( \text{Au}^{3+} \) (thus \( \text{Au}^{3+} \) reduces), causing enrichment of Au to occur at the surface.\[17, 18\] The same applies for Pt, with the difference between the reduction potentials for Pt\(^{2+}/\text{Pt} \) (PtCl\(_4\)) and Cu\(^{2+}/\text{Cu} \) of 0.758 V vs. 0.34 V, respectively, therefore also possibly a reason for enrichment to occur. The more significant Pt enrichment compared to Au is not expected, as it has a higher surface energy and lower reduction potential. The difference between atomic size is not sufficient for it to be the reason for segregation to occur. However, as is observed for our films, a Pt skin has previously been found to form on CuAu bimetallic nanoparticles through displacement of Cu atoms with Pt.\[19\] Therefore it may be proposed that the Pt is not enriching over Au, however it is enriching over Cu. There are also other studies showing that Pt segregation over Au is possible, due to Au’s ability to more easily reduce, placing it under Pt at the surface.\[14, 20\]

6.3.1.3 Structural and Surface Analysis by XRD and XPS

In this section the structure and surface chemistry of the films are studied by XRD and XPS. Figure 6.4 shows the diffraction patterns for each of the films. The main peaks observed at 43.5 and 50.6 correspond that of crystalline planes of (111) and (200) for metallic Cu, respectively (PDF # 040836). The small peak observed at 36.7 in the Cu honeycomb film results from Cu\(_2\)O (111). It is important to note the reduction or absence of this peak in the other films, indicating stabilisation of the Cu surface by the introduction of noble metal components. Significantly however, there are no characteristic peaks corresponding to the presence of metallic Au and Pt. In particular the strongest (111) peaks of Au and Pt at 20 values of 38.18 and 39.28 for Au and Pt, respectively, were absent. As compositional
analysis (ICP-MS and XPS) confirmed the presence of Au and Pt, this suggests that no surface segregation of pure Au or Pt phases, or significant alloying has occurred.

The main differences that can be observed are the shift in the 2θ values for the Cu (111) and Cu (200) peaks, with the broadening of peaks and the changes in the relative peak area ratios for the two crystallite patterns, that indicates that Au and Pt are incorporating into the copper lattice, suggesting the formation of a solid solution, common for electrodeposited materials.[21-23] Table 6.4 gives the diffraction pattern information for the Cu (111) and Cu (200) for the 5 and 10 mM concentration sets. For the 5 mM set, the peak centres for both Cu (111) and (200) increase slightly with Au and/or Pt addition, which goes in accordance with minor changes to the d-spacings, indicating that the noble metals are affecting the growth of the Cu lattice. For the 10 mM system, the change to peak centres and d-spacings is a bit different compared to the 5 mM, with Au addition at 10 mM decreasing the peak centre. Increase in Pt addition to 10 mM does not significantly affect the peak positioning.
The effects of Au and Pt incorporation into the Cu host are more clearly shown by changes to the Cu crystallite sizes. The Scherrer equation (Equation 2.9) was used to calculate the
crystallite sizes from the FWHM of the (111) and (200) diffraction peaks. The pure Cu has a Cu (111) crystallite size of 28.2 nm. The addition of Au has the effect whereby the Cu (111) crystallite size reduces to 26.5 and 21.4 nm upon the addition of 5 and 10 mM Au, respectively. The addition of Pt results in an increase of the Cu (111) crystallite size to 34.5 and 34.9 nm for 5 and 10mM Pt addition, respectively. When both Au and Pt are added the changes to the Cu (111) size seemingly cancel each other out, with crystallite sizes of 28.8 and 28.7 nm obtained for CuAu5Pt5 and CuAu10Pt10 respectively. Since there was no clear sign of Au or Pt in the diffraction pattern, it is important to study their effect on the Cu lattice through relative effects on the growth planes of Cu (111) and Cu (200). By observation of the peak area ratios of these two planes, it can be observed that the addition of Pt increases the (111):(200) ratio, whereas Au reduces this ratio (Table 6.4).

Table 6.4 Peak Information from the XRD patterns in Figure 6.4.

<table>
<thead>
<tr>
<th></th>
<th>Cu (111)</th>
<th></th>
<th></th>
<th>Cu (200)</th>
<th></th>
<th></th>
<th>Area ratio (111):(200)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Centre (2θ)</td>
<td>Crystallite Size (nm)</td>
<td>d-spacing (Å)</td>
<td>Peak Centre (2θ)</td>
<td>Crystallite Size (nm)</td>
<td>d-spacing (Å)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>43.54</td>
<td>28.2</td>
<td>2.076</td>
<td>50.64</td>
<td>23.8</td>
<td>1.800</td>
<td>1.17</td>
</tr>
<tr>
<td>CuAu5</td>
<td>43.64</td>
<td>26.5</td>
<td>2.072</td>
<td>50.76</td>
<td>23.8</td>
<td>1.796</td>
<td>1.04</td>
</tr>
<tr>
<td>CuPt5</td>
<td>43.60</td>
<td>34.5</td>
<td>2.074</td>
<td>50.71</td>
<td>27.0</td>
<td>1.798</td>
<td>1.25</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>43.58</td>
<td>28.8</td>
<td>2.074</td>
<td>50.66</td>
<td>22.9</td>
<td>1.800</td>
<td>1.22</td>
</tr>
<tr>
<td>CuAu10</td>
<td>43.50</td>
<td>21.4</td>
<td>2.078</td>
<td>50.64</td>
<td>20.5</td>
<td>1.801</td>
<td>0.78</td>
</tr>
<tr>
<td>CuPt10</td>
<td>43.60</td>
<td>34.9</td>
<td>2.074</td>
<td>50.69</td>
<td>26.4</td>
<td>1.799</td>
<td>1.47</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>43.55</td>
<td>28.7</td>
<td>2.076</td>
<td>50.69</td>
<td>24.4</td>
<td>1.799</td>
<td>1.72</td>
</tr>
</tbody>
</table>

XPS analysis was used to yield important information regarding the surface chemistry of all elements present. High resolution core-level scans specific to regions for elements of
interest were performed to obtain binding energy information of specific peaks. Figures 6.5 and 6.6 compare the core level spectra for the Cu 2p\textsubscript{3/2}, O 1s, Au 4f\textsubscript{7/2} and Pt 4f\textsubscript{7/2} peaks for the 5 and 10 mM systems, respectively.

For the Cu 2p\textsubscript{3/2} region there is a decrease in the binding energies upon the addition of Au and/or Pt. The pure Cu honeycomb had a 2p\textsubscript{3/2} binding energy of 932.5 eV. For the 5 mM films, the Au had the largest influence, shifting the Cu2p\textsubscript{3/2} peak to 932.3, with the addition of Pt causing a lesser shift to 932.4 eV. For the pure Cu and CuAu5, the peak was broadened with the slight emergence of an additional energy state at 933.8 eV due to Cu\textsubscript{2}O formation. The trimetallic binding energy for Cu2p\textsubscript{3/2} remained the same as the pure Cu at 932.5 eV. There were minimal satellite peaks around 945 eV, which indicated that there is only a small amount of Cu\textsubscript{2}O formation.[24] As the XRD did not show that there was any significant Cu\textsubscript{2}O present, this may be formed as a result of surface oxidation of Cu. For the 10 mM films (Figure 6.6), the higher noble metal content in the bimetallic CuAu10 and CuPt10 resulted in shift of the Cu 2p\textsubscript{3/2} binding energy to 932.3 eV.

For metallic Au the binding energy of the Au 4f\textsubscript{7/2} peak sits at 84.0 eV. In CuAu5 it is shifted to a higher binding energy of 84.3 eV, and higher again for CuAu5Pt5 to 84.5 eV. This may be due to a change in the electron environment around the Au, moving it closer to the +1 oxidation state due to the proximity of Au to the oxide that formed on Cu under ambient conditions.[25] For metallic Pt the binding energy for Pt 4f\textsubscript{7/2} is 71.0 eV. For CuPt5 the binding energy of the Pt 4f\textsubscript{7/2} peak is 71.1 eV, which shifts higher to 71.2 eV when Au is added, indicating that there is an interaction of an electronic nature occurring. The oxygen region deconvoluted into three peaks, 529.4, 530.6 and 531.8 eV that correspond to three chemically distinct oxygen environments, reflecting oxidised Cu, adsorbed oxides and
adsorbed hydroxides, respectively. 529.4 eV has a very minimal contribution, with the majority of the peak coming from the 530.6 eV energy for the pure Cu honeycomb. The addition of Au has the biggest influence on the oxygen environment. The peak at 530.6 eV is reduced in comparison to the peak at 531.8 eV, which suggests that oxide adsorption/formation is reduced in the presence of Au, with hydroxide formation being favoured.

Figure 6.5 XPS overlays for a) Cu 2p\_3/2, b) O 1s, c) Au 4f\_7/2 and d) Pt 4f\_7/2 for the 5 mM films. The Au binding energy is the same for the CuAu10 and CuAu10Pt10 at 84.4 eV, which is higher and lower than the 5 mM system, respectively. In CuAu10, the Au surface At % is higher than the CuAu5 film, as a result of more Au interacting with Cu, resulting in a larger shift. For CuAu10Pt10 the peak shifts to a lower binding energy as a result of an overall
lower Au surface At %. For the Pt the same 71.1 and 71.2 eV peak binding energies were observed for CuPt10 and CuAu10Pt10, respectively, with similarities in the surface At % between the 5 and 10 mM films. And finally for the O 1s spectrum there was no significant change spectral overlays from the 5 mM films.

The CuAu5 and CuAu10 responses in Figure 6.5 and 6.6 show the most significant change with regard to the Cu 2p$_{3/2}$ and O 1s peak. Figure 6.5 b) and 6.6 b) show the lowest intensity for the O 1s envelope, which demonstrates Au’s stability towards oxidation. Cu is very sensitive to oxygen,[25] but the addition of Au is able to disrupt oxide formation on the film, leading to a reduction in the oxide layer thickness. With a thinner oxide layer, the incoming
photoelectron is able to afford clearer information with regard to the binding energy of the elements under the oxide layer. The Au addition has the effect of reducing the binding energy of the Cu2p\(_{3/2}\) peak. In the trimetallic films the three metals interact, and changes to the oxygen environment occur, which are reflected by the shifting of the binding energies of the metals present at the film surface. As Au and Pt have a greater electronegativity than Cu (2.4 and 2.2 vs. 1.9, for Au, Pt and Cu, respectively)[4] the addition of the noble metals would be expected to affect the electronic environment of the film surfaces. These changes are reflected in the increase in the peak binding energies.

6.3.1.4 Model Catalysis: HER and FCN Reduction

The hydrogen evolution reaction (HER) was studied for the films by determining the current density and onset potential for the electrocatalytic reaction (as described in Section 2.2.2.1). Visually, as observed in Figure 6.7, the films have significant differences for their current densities across the surfaces prepared.

Table 6.5 shows the current density, \(j\), at -0.6 V vs. SHE. The onset potential for the reaction was taken at the voltage where the current reaches 3% of the current density at -0.6 V. Pure Cu is shown to be the least active with a \(j\) of -2.61 mA cm\(^{-2}\), which is expected from the reported trends in exchange current densities.[12] As the exchange current density for Au is similar to Cu, it is expected that the combination of CuAu would not yield a significant improvement in the current densities either. It was found to have \(j\) = -3.20 and -2.89 mA cm\(^{-2}\) for CuAu5 and CuAu10, respectively. Pt is the most active metal for HER in this series, and this is confirmed by the higher activities of CuPt5 and CuPt10 with \(j\) = -8.91 and -14.0 mA cm\(^{-2}\), respectively. For the trimetallic CuAu5Pt5, Au addition is shown to increase \(j\) to -11.2 mA cm\(^{-2}\) compared to CuPt5. However as seen in Figure 6.7 b the same increase is not
achieved for CuAu10Pt10, with the $j$ dropping to -10.2 compared to 14.0 mA cm$^{-2}$ attained for CuPt10.

Figure 6.7 LSV for HER in 1M H$_2$SO$_4$ for a) 5 and b) 10 mM films.
Table 6.5 HER current density and overpotential.

<table>
<thead>
<tr>
<th></th>
<th>$j$ (mA cm$^{-2}$) @ -0.6 V vs. SHE</th>
<th>Onset (V) 3% of $j$ at -0.6V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-2.61</td>
<td>-0.151</td>
</tr>
<tr>
<td>CuAu5</td>
<td>-3.20</td>
<td>-0.169</td>
</tr>
<tr>
<td>CuPt5</td>
<td>-8.91</td>
<td>-0.110</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>-11.2</td>
<td>-0.109</td>
</tr>
<tr>
<td>CuAu10</td>
<td>-2.89</td>
<td>-0.161</td>
</tr>
<tr>
<td>CuPt10</td>
<td>-14.0</td>
<td>-0.102</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>-10.2</td>
<td>-0.099</td>
</tr>
</tbody>
</table>

In regard to the onset potential, addition of Au (CuAu5) increases the overpotential compared to the pure Cu honeycomb, -0.169 vs. -0.151 V. Pt decreases the overpotential to -0.110 V (CuPt5) as a result of improved reaction kinetics. There is a marginal reduction to -0.109 V when Au and Pt are combined. The increase to 10 mM for Au and/or Pt resulted in reduction of the overpotentials in all of the film combinations by approximately 0.01 V, due to the changes induced by increased bulk and surface concentrations of the noble metals.

The second model reaction investigated was the ferricyanide (FCN) reduction by STS. Section 2.2.2.2 described the reaction as being dependent on a number of factors including the specific shapes and crystal facets.[26] The reaction therefore allows for the morphological differences of the films to be directly compared for their activity and stability towards the electron transfer reaction. The reaction was monitored by UV-Visible spectroscopy, with the change in the absorbance ($A_T/A_0$) over time shown by the plot in Figure 6.7. Table 6.6 shows the calculated rates, which have been corrected for surface area.

On the Cu honeycomb surface the reaction proceeds at a rate of $1.83 \times 10^{-4}$ s$^{-1}$ cm$^{-2}$, which
reduces for both CuAu5 and CuPt5 to \(-1.27\) and \(-1.21 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-2}\), respectively. The CuAu5Pt5 showed a rate similar to that of pure Cu of \(-1.78 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-2}\). Overall the 5 mM films perform relatively the same, however for the 10 mM films (Figure 6.6b) the differences are more defined. The increase in Au shows the lowest activity with the slowest rate of \(-9.22 \times 10^{-5} \text{ s}^{-1} \text{ cm}^{-2}\). The CuPt10 had the best rate of \(-2.17 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-2}\) but this rate was reduced when Au was added, to \(-2.00 \times 10^{-4} \text{ s}^{-1} \text{ cm}^{-2}\). Although CuAu10Pt10 was better than pure Cu it was less active than CuPt10.

![Graph](image1.png)

*Figure 6.8 Uv-Visible determined FCN reduction rates for the prepared a) 5 and b) 10 mM films.*
Table 6.6 FCN reduction rates

<table>
<thead>
<tr>
<th></th>
<th>Rate ($s^{-1} , cm^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>$-1.83 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuAu5</td>
<td>$-1.27 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuPt5</td>
<td>$-1.21 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>$-1.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuAu10</td>
<td>$-9.22 \times 10^{-5}$</td>
</tr>
<tr>
<td>CuPt10</td>
<td>$-2.17 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>$-2.00 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The results reflect the changes to the films that are occurring through the addition of Au and/or Pt and the effect of increasing the concentration. It has been previously shown that the surface composition,[27] and the shape and size of catalyst surfaces can be shown by changes to the rate of reduction of FCN.[26, 28] Au has been shown to be inherently less active to this reaction than Cu and Pd,[27] therefore in terms of composition, the addition of Au would not be beneficial towards the reaction. Pt nanoparticles have been shown to be active towards this reaction,[29] but in CuPt5 they show the lowest activity. When the three metals were combined in CuAu5Pt5 there was an increase in the reaction rate, showing a surface that was more effectively able to catalyse the reaction. This may be due to a higher Pt surface At % and a larger SSA, which reflects a more morphological accessible film surface. When the Au and Pt concentrations were increased, the CuAu10 rate further decreased (due increased Au content). The CuAu10Pt10 film resulted in an increased rate as well, however the doubling of Pt concentration in CuPt10 exhibited in a rate twice as fast as CuPt5.
6.3.1.5 NaBH₄ Electrooxidation

Figure 6.9 shows the voltametric responses for the electro-oxidation of NaBH₄ in an alkaline solution. Previous studies have described direct oxidation peaks in voltametric studies on Au and Pt electrodes at ca. -0.2 and 0.07 V vs. SHE, respectively, at a scan rate of 0.025 V/s.[3, 5] In this work, a scan rate of 0.05 V/s was used, therefore it is expected that the peak potentials will slightly increase from these values.

Figure 6.9 a and b) shows the CVs for the first cycle, in a solution containing 0.05 M NaBH₄ in 0.5 M NaOH. Cu has a small peak at -0.021 V with a \( j \) of 0.263 mA cm\(^{-2}\). The CuAu5 and CuAu10 have small peaks with \( j \) values of 0.187 and 0.262 mA cm\(^{-2}\), due to the direct oxidation pathway (Equation 6.4) at -0.145 and -0.172 V, respectively. There is an absence of responses for hydrolysis between ca. -0.8 and -0.4 V (Equation 6.1 and 6.2). On Pt containing films however, the response is complicated by both the four electron hydrolysis and the direct eight electron pathway. For both of the bimetallic Pt containing films, CuPt5 and CuPt10, the direct eight electron oxidation, following Equation 6.4, occurred with a broad peak centred at 0.051V, with peak currents of \( j = 1.82 \) and 2.96 mA cm\(^{-2}\), respectively. This shows that the increase in Pt content directly increases the current density. A synergistic effect is seen when Au and Pt are combined, with the main, direct oxidation peaks shifting to more favourable potentials of 0.011 and -0.012 V for CuAu5Pt5 and CuAu10Pt10, respectively. There is a smaller unresolved peak that occurs before the main peak, which occurs at ca. -0.165 V for both CuAu5Pt5 and CuAu10Pt10. This possibly relates to the direct oxidation taking place on the Au portion of the surface. The relative peak responses towards NaBH₄ electrooxidation, following the model HER electrocatalytic predictions, predict activity in the order of Pt>Au>Cu. For the 5 mM system, the
combination of Au and Pt showed an increase in the peak current density over CuPt5 and in the 10 mM system, it is shown that the Au addition to Pt dampens the peak compared to CuPt10.

A sharp peak is observed on the reverse sweep due to the oxidation of BH$_3$OH$^-$ that can be formed either during hydrolysis (on Pt) or as a reaction intermediate for the eight electron pathway (on Au) according to Equation 6.3.

![Voltammetry for the electrooxidation of 0.05 M NaBH4 in 0.5 M NaOH. 1st CV cycle for a) 5 and b) 10 mM systems and chronoamperometric step for c) 5 and d) 10 mM.](image)

*Figure 6.9 Voltammetry for the electrooxidation of 0.05 M NaBH4 in 0.5 M NaOH. 1st CV cycle for a) 5 and b) 10 mM systems and chronoamperometric step for c) 5 and d) 10 mM.*
Table 6.7 NaBH$_4$ electrooxidation CV and CA response information

<table>
<thead>
<tr>
<th></th>
<th>1$^{\text{st}}$ CV Cycle</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Potential (V)</td>
<td>$j$ (mA cm$^{-2}$) at 1800 s % of $j$ after 1800 s compared to 5 s</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.021</td>
<td>0.263</td>
</tr>
<tr>
<td>CuAu5</td>
<td>-0.145</td>
<td>0.178</td>
</tr>
<tr>
<td>CuPt5</td>
<td>0.051</td>
<td>1.82</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>0.11</td>
<td>2.26</td>
</tr>
<tr>
<td>CuAu10</td>
<td>-0.172</td>
<td>0.262</td>
</tr>
<tr>
<td>CuPt10</td>
<td>0.051</td>
<td>2.96</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>-0.012</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Overall the reaction occurs with similarities to both previous works containing Cu; the Pt(Cu)/Ti system [2] and PdCu/C nanoparticles.[30] Behmenyar and Akm proposed a mechanism explaining the processes occurring at the peaks that are similar to those observed in the voltammograms in Figure 6.9 a and b. Initially, in the scan from the initial potential at -1.0 V up to -0.4 V vs. SHE, hydrolysis of BH$_4$ occurs and release of hydrogen, H$_2$ according to Equation 6.1, which is then followed by the eight electron oxidation according to Equation 6.4 at ca. -0.4 V. The eight electron process has been shown to have a peak centred ca. 0.0 V vs. SHE (on Pt) [3, 6] whereas the four electron process occurs at the lower potential of -0.4 V. The direct oxidation peak drops off at ca. 0.1 V with the peaks following due to the formation of surface oxides at > 0.25 V.

Figure 6.9 c and d show the chronoamperometric response, to enable an estimation of the long term stability of the electrooxidation, with a potential step from -0.8 to 0.0 V over 1800 s (30 min). Table 6.7 shows current density at 1800 s and also the current density after
1800 s, as a percentage of initial current density (i.e. after 5 s). A low current response of 0.263, 0.178 and 0.262 were obtained for Cu, CuAu5 and CuAu10 films, respectively. For the 5 mM films containing Pt, a current density of 1.82 and 2.62 mA cm$^{-2}$ was maintained after 1800 s for the CuPt5 and CuAu5Pt5 films, respectively, which is 67.1 and 86.6 % of the current density at 5 s. It shows that the addition of Au to Pt, at this concentration level, was able to produce a more active and more stable film for the electrooxidation of NaBH$_4$. For the 10 mM system, CuPt10 and CuAu10Pt10 have current densities of 2.96 and 1.49 mA cm$^{-2}$, respectively, showing that the addition of Au was not beneficial at the higher concentration level. However, the retained current density was improved with Au addition with CuAu10Pt10 retaining 74.6 % of initial current compared to 66.6 % retained for CuPt10.

It is shown in this section that bimetallic CuPt and CuAuPt can be fabricated by electrodeposition using DHBT. The morphological effects on a Cu honeycomb can be altered significantly depending on the noble metal and the quantity of noble metal added. Differences occur in the composition between the surface and the bulk with enrichment of the noble metals occurring providing favourable surfaces for (electro-) catalytic reactions to take place. At the low concentration level (5 mM) it was found that the CuAuPt combination provided the most favourable surface for the HER. When the noble metal concentration was increased to 10 mM there was a change in the most active surface now being the bimetallic CuPt, due to Pt’s more inherent activity towards HER. It was shown that the HER reaction was effective in giving an insight into activity toward the NaBH$_4$ electrooxidation reaction.

For NaBH$_4$ electrooxidation, it was shown that films with Pt were active towards both the indirect (hydrolysis) and direct oxidation pathways, whereas CuAu$_x$ films were inactive for hydrolysis. The addition of Au to CuPt (CuAuPt films) was able to reduce the overpotential
for the direct oxidation pathway and improve the long term activity and stability of the electrocatalyst surface.

6.3.2 Effect of Independently Increasing Au and Pt Concentrations

The effect on increasing one noble metal over the other is investigated in this section. As the surface composition and morphology plays a significant role in determining activity, the optimisation of the surface by changes to the deposition electrolyte were investigated.

6.3.2.1 The Effect of Au and/or Pt on Film Morphology.

The effect of the increasing the concentration of Au or Pt in the electrolyte was independently performed to identify specific effects on the resulting films in this section, to study the relationship between the \( \text{H}_2 \) evolution and metal deposition growth kinetics that are influenced by electrolyte composition.

As shown in the previous section, the relatively low concentrations (5 and 10 mM) of the noble metals in comparison to the large concentration 0.4 M of Cu can lead to drastic changes on the morphology of the deposits. Four electrolyte concentrations were investigated; two repeated from Section 6.3.1 (CuAu5Pt5 and CuAu10Pt10) and two additional with the Au or Pt concentration increased independently of the other CuAu10Pt5 and CuAu5Pt10. As observed in Figure 6.10, the four trimetallic films all have uniformly covered surfaces, which is expected when using the DHBT for the fabrication of Cu based films.
The pore sizes remain relatively the same size across the trimetallic species (Table 6.10), with a slight increase in the pore sizes for the repeated films from Section 6.3.1. Even though precautions were taken to ensure repeatability, some differences still occurred between batches. The two smallest pore sizes were achieved when the Au and Pt concentrations were equal (CuAu5Pt5 and CuAu10Pt10). When the two noble metals were present in different concentrations the pore sizes were slightly larger, being 5.9 and 6.2 µm for CuAu10Pt5 and CuAu5Pt10, respectively.

The pore size deviation increased slightly with a larger (10 mM) Pt metal concentration. This indicates a reduction in film uniformity caused by increased H₂ evolution rate associated
with increased Pt concentration, affecting the hydrodynamic conditions of the deposition process.

Table 6.8 Film surface pore information

<table>
<thead>
<tr>
<th></th>
<th>Average Surface Pore Size (µm)</th>
<th>Pore Density (pores x 10^6/ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu5Pt5</td>
<td>4.7 ± 1.6</td>
<td>1.86</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>5.9 ± 1.6</td>
<td>1.27</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>6.2 ± 2.0</td>
<td>1.22</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>5.4 ± 2.2</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Figure 6.11 shows the fine surface morphology of the deposits with the increased noble metal concentrations. Figure 6.11 a and d) complemented those images in Figure 6.1 c and f) for the CuAu5Pt5 and CuAu10Pt10. Figure 6.11 b) shows a more densely occupied surface, with slightly more rounded/spherical particles. Figure 6.11 c) show a very interesting fine morphology. The particle overall shape consists of underlying dense ‘torpedo’ like structures, as observed with the CuPt x bimetals in Section 6.3.1, however, the surface exhibits drastically finer structures. This is possibly due to a change in the growth caused by the effect on the hydrodynamic conditions with increased Pt concentration over Au.
Textural surface properties were measured and tabulated in Table 6.9, including the electrochemical surface area (ECSA) and mass, to determine the specific surface area (SSA). ECSA was measured by the double layer capacitance ($C_{dl}$) method described in Section 2.2.1.4, and the mass was determined by mechanically removing the deposits from the substrate then analysing by ICP-MS as described in Section 2.2.5.
Table 6.9 Textural Surface Properties

<table>
<thead>
<tr>
<th></th>
<th>Mass (g)</th>
<th>ECSA (m²)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu5Pt5</td>
<td>3.88 x 10⁻⁴</td>
<td>7.34 x 10⁻⁴</td>
<td>2.06</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>7.88 x 10⁻⁴</td>
<td>1.58 x 10⁻³</td>
<td>1.94</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>3.92 x 10⁻⁴</td>
<td>6.02 x 10⁻⁴</td>
<td>1.55</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>2.70 x 10⁻⁴</td>
<td>8.65 x 10⁻⁴</td>
<td>3.57</td>
</tr>
</tbody>
</table>

It is observed that smaller pores sizes obtained with the CuAu5Pt5 and CuAu10Pt10 yielded more favourable specific surface areas of 2.06 and 3.57, respectively. The increased Au concentration in CuAu10Pt5 yielded the largest ECSA, but also the largest mass, giving a SSA of 1.94. For CuAu5Pt10 the fine surface morphology was not significant enough to boost the ECSA compared to the underlying dense particles below giving the deposit a low SSA of 1.55.

6.3.2.2 Film Composition Studies

The films compositions were measured; in Table 6.10 the atomic percentages (At %) of the elements present in the bulk (ICP-MS) and on the surface (XPS) are presented.

Table 6.10 Film composition for the Bulk At % and Surface At%.

<table>
<thead>
<tr>
<th></th>
<th>Bulk At %</th>
<th>Surface At %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>98.9</td>
<td>0.4</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>97.6</td>
<td>1.7</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>98.7</td>
<td>0.3</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>98.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>
There is a slight difference in the relative concentrations in the bulk of the films. Previously in Section 6.3.1.2, it was found that Au had a bulk At % half that of Pt for the CuAu5Pt5 and CuAu10Pt10 films, where as in for this set there is much smaller difference observed. For CuAu10Pt5 a significant increase in the amount of Au in the bulk increasing from 0.4 to 1.7 At %. For CuAu5Pt10, the Au bulk content remains constant and the Pt At % doubles.

At the surface in all cases the Pt enriches to a greater extent than Au. In the CuAu10Pt5 film, the Au At % at the surface is higher than Pt, but it should be noted that Au has a significantly higher bulk value in this film, as to be expected due to its higher concentration in the electrolyte. Pt has been shown to cause displacement of Cu from a CuAu intermetallic substrate,[19] and also has been shown to segregate over Au,[14, 20] even though it should not according to surface energy, electronegativity and redox parameters. Therefore it may be the interchangeability of Pt with Cu occurring at the surface and or the effect that Au more easily reduces placing it under Pt in relation to the surface. [14, 19]

6.3.2.3 Structural and Surface Analysis by XRD and XPS

Figure 6.12 shows the diffraction patterns for each of the films. The main peaks observed at 43.5 and 50.6 correspond that of metallic Cu in the crystalline planes of (111) and (200), respectively (PDF # 040836). There is complete absence of the Cu$_2$O (111) crystallite peak that was observed in the pure Cu and bimetallic systems seen in Figure 6.4 at 36.7 degrees, confirming that noble metal addition can stabilise the Cu surface to prevent oxidation. The absence of crystalline peaks characteristic for Au or Pt again, but changes to the Cu host metal lattice suggests the formation of a solid solution, common for electrodeposited materials.[21-23] Table 6.11 gives the diffraction pattern information for the Cu (111) and Cu (200) peaks.
There is a gradual increase in the peak centre $2\theta$ values to 43.57 and 50.69 for the Cu (111) and Cu (200) peaks, respectively, with increased noble metal concentration. The effects of Au and Pt incorporation on the Cu host are more clearly shown by changes to the crystallite size. Using the CuAu5Pt5 as a baseline for comparison, the effect of increasing the Au concentration from 5 to 10 mM in CuAu10Pt5 is shown to decrease the Cu (111) crystallite size to 26.3 nm. The Pt concentration in CuAu5Pt10 is able to maintain a relatively large Cu (111) crystallite size of 31.6 nm. This follows the trend in Section 6.3.1.3 where Au inhibits growth in the <111> direction and Pt enhances it.

![XRD Patterns for the four trimetallic films.](image)

The peak area ratios show the smallest ratio of (111):(200) of 1.39 is obtained for CuAu5Pt5, where the noble metal concentration is the lowest. CuAu10Pt10 has an increased peak area ratio of 1.50. When the noble metal concentration is not equal, the largest differences in the peak areas ratios are obtained. This reflects the more significant changes to the Cu crystal lattice when the Au or Pt are in higher concentration, exerting their individual effects.
Table 6.11 Peak Information from the XRD patterns in Figure 6.12

<table>
<thead>
<tr>
<th></th>
<th>Cu (111)</th>
<th>Cu (200)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Centre</td>
<td>Crystallite</td>
</tr>
<tr>
<td></td>
<td>(2θ)</td>
<td>Size (nm)</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>43.52</td>
<td>2.077</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>43.54</td>
<td>2.076</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>43.57</td>
<td>2.075</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>43.57</td>
<td>2.075</td>
</tr>
</tbody>
</table>

The XPS analysis can be used to yield important information regarding the elements on the surface. Figures 6.13 compares the core level spectra for the Cu 2p\textsubscript{3/2}, O 1s, Au 4f\textsubscript{7/2} and Pt 4f\textsubscript{7/2} peaks for the four prepared trimetallic films.

The Cu 2p region was measured for Cu, and there is a decrease in the shift for the binding energies upon the addition of Au and/or Pt. The pure Cu honeycomb had a Cu 2p\textsubscript{3/2} binding energy of 932.5 eV. The trimetallic samples all had a stable Cu 2p\textsubscript{3/2} peak binding energy of 932.4 eV with the same relative intensity for all (Figure 6.13 a).

For metallic Au the binding energy of the Au 4f\textsubscript{7/2} peak sits at 84.0 eV. The CuAu5Pt5 film is shifted to a higher binding energy of 84.5 eV. When the Au concentration is increased to 10 mM, the binding energy is shifted lower to 84.4 eV. The relative intensities are markedly different, with the largest peak intensity when Au is in greater concentration in CuAu10Pt5 and expectedly lowest in CuAu5Pt10 (Figure 6.13 b).
For metallic Pt the binding energy for Pt 4f\textsubscript{7/2} is 71.0 eV. For both CuAu\textsubscript{5}Pt\textsubscript{5} and CuAu\textsubscript{10}Pt\textsubscript{10} the Pt 4f\textsubscript{7/2} binding energy is 71.2 eV. It is slightly lower at 71.1 eV for CuAu\textsubscript{5}Pt\textsubscript{10} and shifted again to 71.0 eV for CuAu\textsubscript{10}Pt\textsubscript{5} (Figure 6.13 c). As explained in Section 6.3.2.2, Pt enriches towards the surface, therefore the drop in peak intensity is not observed like it was for Au. The O 1s oxide region deconvoluted into three peaks, 529.4, 530.8 and 531.8 eV (Figure 6.13 d). The profile of the oxygen overlay was similar with the same intensities that indicated that the oxygen environment on the films is the same.

6.3.2.4 Model Catalysis: HER and FCN Reduction

Figure 6.14 shows that the four films have quite different current densities for HER. Table 6.12 shows the current density, \( j \), at -0.6 V vs. SHE. The onset potential is taken at the
voltage where 3 % of the current density at -0.6 V is reached. The curves are more significantly disrupted for HER on these films due to the formation and evolution of \( \text{H}_2 \text{(g)} \) off the electrode surface. This indicates that these surfaces are more active compared to the others presented in this thesis so far.

The exchange current densities are in the order of slowest to fastest: \( \text{Au} \approx \text{Cu} < \text{Pt} \). Pure Cu was previously found to be the least active with a \( j \) of -2.61 mA cm\(^{-2}\), which is expected from the reported exchange current densities.[12] As the exchange current density for Au is low, it follows that a lowest current density of -8.09 mA cm\(^{-2}\) is obtained with CuAu10Pt5 when Au has the highest atomic composition in the film. Pt is the most active and therefore the remaining order of activity is governed by the surface At % of Pt relative to Au surface At %. CuAu5Pt10 and CuAu5Pt5 have a \( j \) of -13.8 and -13.5 mA cm\(^{-2}\), respectively. CuAu10Pt10 has a low surface At % of Pt giving it a lower current density of -11.1 mA cm\(^{-2}\).

![Figure 6.14 LSV for HER in 1M H\(_2\)SO\(_4\) for the four trimetallic films.](image)
It can be observed from Table 6.12 that the Pt:Au ratio has an effect on the resulting reaction activity with the highest rate of -13.8 mA cm$^{-2}$ obtained with the CuAu5Pt10, which has the largest Pt:Au ratio of 7.6. However, it is not a linear response as the CuAu10Pt5 film that has the lowest ratio of 0.8, which is almost ten times lower than that of CuAu5Pt10, does not result in a current density that is ten times lower. Even though the Au is not the most ideal metal for HER in terms of achievable current density, it is shown to improve the kinetics by the lowering of the onset overpotential. The onset potential was the best when Au addition was 10 mM, with the onset potential of -0.112 V, which is 0.1 V better than CuAu5Pt5 and 0.2 V better than CuAu5Pt10.

Table 6.12 HER current density and overpotential.

<table>
<thead>
<tr>
<th>Pt:Au Ratio</th>
<th>$j$ (mA) @ -0.6 V vs. SHE</th>
<th>Onset (V) 3% of $j$ at -0.6V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu5Pt5</td>
<td>5.3</td>
<td>-13.5</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>0.8</td>
<td>-8.09</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>7.6</td>
<td>-13.8</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>3.7</td>
<td>-11.1</td>
</tr>
</tbody>
</table>

The second model reaction investigated was the FCN reduction by STS (Section 2.2.2). The reaction was monitored by UV, with the change in the absorbance over time shown by the plot in Figure 6.15. Table 6.13 exhibits the measured reduction rates. The CuAu5Pt5 showed a rate of -1.23 x 10$^{-4}$ s$^{-1}$ cm$^{-2}$. The increased concentration of Au gave the slowest rate of -8.75 x 10$^{-5}$ s$^{-1}$ cm$^{-2}$, which was the same trend observed previously. The CuAu10Pt10 performed the next best with a rate of -1.34 x 10$^{-4}$ s$^{-1}$ cm$^{-2}$. The CuAu10Pt10 had the best rate of -1.52 x 10$^{-4}$ s$^{-1}$ cm$^{-2}$ but did not have the highest surface Pt At %.
reaction there was not such a significant difference in the activity of the films. The difference may lie in the reactions dependence on the surface structures. As it was seen in Figure 6.11 c) the CuAu5Pt10 had unique surface structure, and it is these to which the FCN reaction is sensitive to along with maintaining a relative high surface Pt At %.\[26, 28, 29\]

![Figure 6.15 FCN reduction rates for the for trimetallic films.](image)

**Table 6.13 FCN reduction rates**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate (s(^{-1}) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAu5Pt5</td>
<td>-1.23 \times 10^{-4}</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>-8.75 \times 10^{-5}</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>-1.52 \times 10^{-4}</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>-1.34 \times 10^{-4}</td>
</tr>
</tbody>
</table>

The HER and FCN model reactions are able to reveal the changes observed in the surface properties of the films fabricated. Even though the morphologies of the films did not
significantly differ (except for the interesting structure on top if the film for CuAu5Pt10) the change in the composition, leading to changes of the crystal structure and electronic environment resulted in significant differences in the catalytic properties of the films. It is shown that the CuAu5Pt10 film has the best activity for both the HER and FCN reaction. This reflects the surface with the largest Pt:Au concentration.

6.3.2.5 NaBH₄ Electrooxidation

In this section, the aim is to look at effect of individually increasing the Au or Pt concentration over the other, using the CuAu5Pt5 and CuAu10Pt10 as baselines for comparison. Figure 6.16 shows the voltametric responses for the electro-oxidation of NaBH₄ under identical reaction conditions as in Section 6.3.1.5 with, Table 6.15 exhibiting the most relevant information. Figure 6.16 a) shows the CV responses on the four trimetallic films. The direct oxidation, following Equation 6.4, occurs via the response at two different peaks, the main peak at ca. -0.03 to -0.05 V and a smaller less resolved peak at ca. -0.176 V. As these trimetallic samples contain both Au and Pt it is expected that the direct oxidation may take place at the lower peak potential due to the presence of Au, with the main peak occurring as a result of the direct oxidation on Pt at potentials greater than -0.05 V. In this batch the peak potentials are slightly improved with potentials of -0.037 and -0.023 V for the CuAu5Pt5 and CuAu10Pt10 films, respectively. The peak currents obtained were $j = 1.81$ and $1.32 \text{ mA cm}^{-2}$, respectively, a similar trend to that observed in Section 6.3.1.5, with a decrease in peak current with the doubling of Au and Pt concentration. When either the Au or Pt was increased in concentration independently changes to the peak response occurred. An increase in Au (CuAu10Pt5) decreases the direct oxidation peak potential to -0.021 V with a lower peak current density of 1.0 mA cm². The peak at -0.176 V is better defined, as
expected, with the increased contribution of Au (red line Figure 6.16 b). For an increased Pt content (CuAu5Pt10), the peak potential is higher at -0.045 V due to the eight electron oxidation being favoured on the Pt. The increased Pt concentration results in the most active surface with a current density of 1.98 mA cm$^{-2}$.

Figure 6.16 Voltammetry for the electrooxidation of 0.05 M NaBH4 in 0.5 M NaOH. a) 1st CV cycle b) chronoamperometric step for the four trimetallic films.
A sharp peak is observed on the reverse sweep due to the oxidation of BH$_3$OH$^-$ that can be formed either during hydrolysis (on Pt) or as a reaction intermediate for the eight electron pathway (on Au) according to Equation 6.3. On CuAu5Pt5 there is a ‘double’ sharp peak, indicating the oxidation of BH$_3$OH$^-$ formed during hydrolysis or as a step involving through a pathway that forms BH$_3$. The increase in noble metals results in the removal of the peak at 0.3 V but an increase in the -0.18 V with higher surface Pt At%. CuAu10Pt5 does not exhibit this reverse oxidation peak, indicating it is due to BH$_3$OH$^-$ formed due to hydrolysis rather than the direct oxidation on an Au surface.[3]

Figure 6.16 b) shows the chronoamperometric response to probe the longer term stability for the electrooxidation with a step from -0.8 to 0.0 V for 1800 s (30 min). The relevant information is presented in Table 6.14, showing the final current density at 1800 s and the final current density compared with the current density taken at 5 s as a percentage. Similar current densities of 0.724, 0.762 and 0.823 mA cm$^{-2}$ are obtained for CuAu10Pt5, CuAu10Pt10 and CuAu5Pt5, respectively. CuAu5Pt10 shows a relatively high current density of 1.61 mA cm$^{-2}$, which is almost double that of the next best film (Cu5Pt5). This reflects a surface with a reasonable Pt At % at the surface, but not the largest; however this was the film with the significantly different surface morphology compared to the other three films in this section.
Table 6.14 CV Peak Information for NaBH₄ electrooxidation and long term stability chronoamperomtric information.

<table>
<thead>
<tr>
<th></th>
<th>1st CV Cycle</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Potential (V)</td>
<td>j (mA cm⁻²)</td>
</tr>
<tr>
<td>CuAu5Pt5</td>
<td>-0.234</td>
<td>1.81</td>
</tr>
<tr>
<td>CuAu10Pt5</td>
<td>-0.218</td>
<td>1.00</td>
</tr>
<tr>
<td>CuAu5Pt10</td>
<td>-0.242</td>
<td>1.98</td>
</tr>
<tr>
<td>CuAu10Pt10</td>
<td>-0.220</td>
<td>1.32</td>
</tr>
</tbody>
</table>

As for the stability, it was determined by comparing the final current density at 1800 s, using 5 s as a reference point, the CuAu5Pt5 and the CuAu10Pt10 had the lowest maintained current density of 64.4 and 80.9 %, respectively. However in CuAu10Pt5 and CuAu5Pt10 the current density improved to 106.2 and 105.4 %, respectively. When the Au and Pt concentration was equal it seems that a more uniform environment is created that stabilises over a longer period of time. When the Au or Pt concentration is not equal an imbalance occurs, which results in more favourable and active surface reaction conditions towards NaBH₄ electrooxidation.

6.4 Conclusion

It is shown that small concentrations of Au and Pt can be used to control the synthesis of porous trimetallic films using the DHBT method. The incorporation of the noble metals, Au and Pt, into the electrolyte used for bubble templating, can be used to design films with controlled surface area and morphology. It was shown how the model catalytic reactions of
HER and FCN reduction can be used to probe the surface activity of the films. We have shown that subtle differences in surface chemistry can lead to measurable variances in these model reactions. Less than 5% of noble metal incorporated into a porous Cu scaffold is sufficient for these surfaces to exhibit acceptable catalytic activity. It was found that the films were deposited as a solid solution, where the Au and Pt metals concentrate towards the surface for the bimetallic films fabricated. When all three metals are combined to fabricate porous trimetallic films, it was found that Pt preferentially enriches on the surface over Au. The enrichment is important in facilitating higher surface activity materials.

It was shown how the properties can be tailored for the important electroooxidation of NaBH₄ for the production of clean energy. Pt is highly active for both the desired eight electron pathway and the side reaction involving the four electron oxidation involving hydrolysis and the release of hydrogen. The CuPtx bimetallics showed significantly more active surfaces towards the reaction, with the higher obtained current densities of 1.82 and 2.96 mA cm⁻² for CuPt5 and CuPt10, respectively; which are significantly higher than the 0.178 and 0.262 mA cm⁻² obtained for CuAu5 and CuAu10. However, as it has been previously established that the direct oxidation pathway occurs at a lower overpotential on Au as compared to Pt surfaces. Hence, it was observed that through the addition of Au, the oxidation potential improved on CuAu5Pt5 and CuAu10Pt10 by 0.04 and 0.06 V respectively. The CuAuxPtx combination also resulted in increased stability, measured by maintained current density after 1800 s.

It was established that the properties of the trimetallic films could be further controlled to yield more favourable films surfaces. The overpotential for the direct oxidation pathway was further reduced to -0.255 V with an acceptably high current density of
1.98 mA cm\(^{-2}\) with the CuAu5Pt10 surface, which showed excellent stability, with improvements in the current density obtained of 105.4 % over 1800 s.

These surfaces again exhibit the advantages of using electrodeposition and the DHBT method to fabricate electroactive materials. The main advantage of these materials is their chemical and structural stability, as well as tunable activity, making them excellent candidates for applications in solution or gas phase where catalysts based on supported nanoparticles have suffer from long term stability problems. Further work on the effects of electrodeposition conditions on the morphology and activity of the resulting surfaces will lead to a broad range of materials with many potential real-world applications.

6.5 References


Chapter 7

Conclusion and Future Work
7.1 Conclusions

This thesis explored the DHBT method for the fabrication of nanostructured metal films. The advantages of using electrodeposition and the DHBT method over other deposition methods were shown to include the ease of access to a range of nanostructures of varying morphologies, control of the deposition process and the fabrication of materials with large specific surface areas. These advantages led to the fabrication of effective nanomaterials for use in catalytic and electrocatalytic applications in this thesis that has increased our understanding of the technique. Alternative methods for the preparation of porous or nanostructured materials require a broad range of parameters to be controlled to prepare either nanoparticles or similar nanostructured materials. Such parameters include the use of high purity reagents, including stabilising agents, shape directing molecules, as well as the use of high temperature and pressure in some cases. Each of the parameters brings a degree of complexity, leading to difficulties in controlling the morphology and structures of the materials obtained.

In this work, electrodeposition via the DHBT method was used to access a range of metal nanostructured films, which are easily controlled by changes to the electrolyte composition, whilst being performed at mild deposition conditions (i.e. 25 °C and 1 atm pressure) from aqueous metal salt solutions. The solutions used cheaper lower purity metal salt than required for other methods, however electrodeposition was able to produce high purity nanostructured materials. The DHBT method differs from traditional electrodeposition by using significantly large deposition overpotentials where metal deposition was accompanied by H₂ evolution. The relationship between the H⁺ and Mⁿ⁺ reduction is the key to controlling the metal nanostructures formed. The bubbles serve as templates to control and direct the
morphology of the metal deposits, but are cleanly removed from the surface without leaving behind any impurities on the surface. It was shown that the different exchange current densities for H$_2$ evolution off the different depositing metals affected the hydrodynamic conditions surrounding deposition, which caused significant differences in the morphology and surface properties of the films produced.

The high overpotential used for the DHBT method, and the hydrodynamic conditions imposed by H$_2$ evolution at the cathode has produced Ru dendrites for the first time. The high overpotential served to shift the deposition regime for Ru from kinetically limited to diffusion limited. There are two key reasons for this, the first being the large potential applied that causes the rate of deposition to be limited by diffusion. The second is the rapid evolution of H$_2$ bubbles that induce mixing of the solution, which compresses the thickness of the diffusion layer near the substrate. This compression serves to drive the diffusion limited deposition regime further causing the deposition of dendrites close to the surface of the substrate. However, this effect has its limitations, only occurring close to the substrate for Ru deposition, with the growth becoming compacted further away from the substrate due to change to the hydrodynamic conditions as the H$_2$ evolution rate is lower, and therefore less turbulent.

DHBT has thus been shown to allow access to new morphologies for Ru, which has been shown to be difficult to control in previous electrodeposition studies. It suggests that other metals which also have slow deposition kinetics, or have been shown to be difficult to control morphologically, could benefit from the DHBT technique to access morphologies not attainable under traditional electrodeposition conditions.
The kinetics of the metal being electrodeposited determines the regime in which the deposition via the DHBT method occurs, either under a diffusion limited or kinetic limited regime. Both of the regimes were present in regards to the electrodeposition of Ru, which was shown to have dendrites close to the surface and compact growth further out from the substrate as the kinetically limited regime takes over. It is the fine structure that is determined to influence how well the stack-up model can apply and is the reason why Au and Cu can effectively template the hydrogen bubbles being produced at the surface of the electrode, allowing for large, open and thick honeycomb films to be formed, at shorter deposition times.

The DHBT allowed for the fabrication of multimetallic films, which showed specifically how the composition of the deposition electrolyte and deposition time can result in significant changes to the morphology and surface properties. This thesis significantly enhanced our understanding of how the electrolyte composition affects the final morphology of an electrodeposited film. Copper was effectively used as a host, in which the noble metals gold and palladium (Chapter 5) and gold and platinum (Chapter 6) were dissolved. XRD was able to afford the information supporting the formation of a solid-solution, as the noble metals were not segregated into their own phase or new discrete alloy, but instead inflicted changes to the host Cu lattice. The addition of noble metals results in changes to H\textsubscript{2} evolution because of the larger exchange current density of H\textsuperscript{+} reduction rates associated with Au, Pd and Pt. Due to the increased H\textsubscript{2} evolution rate when the noble metals were added, diffusion layer thickness was reduced due to a stirring effect, and the size of the H\textsubscript{2} bubbles was reduced. Kinetic limitations were thus overcome when depositing more than
one metal as all metals deposit under one diffusion limited regime. The hydrodynamic condition affected the metal growth for the multimetallic films, which could be observed compared to a pure Cu honeycomb with the shapes of structures being altered significantly when Au, Pd or Pt were added. As the H₂ acts as a template, pore sizes in films were generally reduced by the addition of noble metals. The addition of Au caused the deposition on triangular platelet structures, Pd, nanocubes and Pt resulted in the formation of torpedo like structures for the bimetallic films. When trimetallic films of CuAuPd or CuAuPt were deposited, the morphologies reflected combined factors from those observed in the bimetallic films. The incorporation of noble metals affected the growth mechanism of the predominately copper films. In particular, the CuAuPd film exhibited both the triangular and cubic features. The fine structures were found to also affect the overall film morphology, with the addition of Au, Pd or Pt limiting the ability for H₂ bubble templating to occur affecting the pore sizes and thickness of the film.

Control of metal nanostructured films can be obtained by changes to the deposition conditions, which include the applied potential, the deposition electrolyte (including acid and metal salt concentration) and deposition time. In particular Chapters 3, 5 and 6 were able to explore these changes. Chapter 3, involving the deposition of Ru, studied the effects of applied potential, H⁺ concentration and Ru³⁺ concentration on the morphology of the films deposited. It was shown how control of the deposited film could be obtained by changing the potential, acid or metal salt concentration, which directly affects H₂ evolution leading to films with different morphologies.
The effect of deposition time was explored on the trimetallic CuAuPd films. The ‘stack-up’ feature of the DHBT method was exhibited with control over the morphology with time. It was observed that insufficient time led to an incomplete porous film formation. At the critical time of 15 s (for this Cu based film), the interconnected porous network was formed. At longer deposition times, as the ‘stack-up’ model describes, the pore size increases in relation to distance of the deposit from the substrate. This was a direct demonstration of how the overall pores size could be controlled using deposition time.

It was shown in Chapter 5 and 6 how the alterations to the electrolyte composition could be used to control the properties of the deposited films. The changes to the electrolyte directly affected the subsequent H₂ evolution and metal salt deposition rate, effecting the final film morphology and composition. Adding a secondary metal (Au, Pd or Pt) with a larger exchange current density for H₂ evolution resulted in the drastic reduction in the Cu honeycomb pore size. A faster rate meant shorter residence times of H₂ bubbles on the surface, resulting in the smaller bubbles and therefore reduced pore sizes in the resulting deposit. It was that doubling the noble metal content in the electrolyte resulted in the doubling of the noble metal concentration in the bulk of the films deposited, thus giving the ability to control noble metal content.

These films were prepared to showcase the DHBT method in the ability to create a range of useful nanostructured material films. Chapter 3 showed how Ru dendrites were fabricated with high specific surface areas, and with controllable oxidation states. Noble metals are expensive and therefore it is important to reduce the quantity of noble metal. DHBT allows
for prepare materials with high specific surface areas ensuring excellent material utilisation and thus reduction in cost.

Previous to this work, Au honeycombs deposited under similar conditions were fabricated for electrocatalytic purposes.[1] In Chapter 4, DHBT was employed to access an Au honeycomb nanostructured material consisting of spiked, dendrite structures. This nanostructured film was found to improve the SO$_2$ oxidation reaction compared to a 2-D polycrystalline disk and Au nanoparticles of well-defined shapes. The shape of the dendrites were compared and evaluated alongside specifically shaped cubed, octahedral and rhombic docahedral Au nanoparticles. Whilst nanoparticle shapes consisted of predominately one crystal orientation, the Au honeycomb, due to its underlying dendritic morphology, had a polycrystalline orientation and offered access to high index Au facets. These facets are believed to be responsible for a significant reduction in the overpotential for SO$_2$ reduction, thus showing how DHBT can be used to access favourable morphologies for electrocatalysis applications.

The multimetallic films fabricated by DHBT were shown to be a solid solution, with surfaces enriched with the noble metals. This is desirable for catalytic applications as it allows for small amounts of the expensive noble metals to be effectively used. The films were evaluated with the model catalytic HER and FCN reactions. It was shown that the noble metal present affected the HER and FCN rate, which could be linked to the morphology and surface chemistry, which are both controlled by the conditions used to fabricate the films.
In Chapter 6, the Cu, Au and/or Pt films had their activity towards the NaBH$_4$ electrooxidation reaction investigated as a test case of the potential use of these films to be active towards an underdeveloped electrocatalytic reaction for the direct borohydride fuel cell. DHBT was shown to create multimetallic films that are active and relatively stable when used as an anode for borohydride oxidation.

The work has shown that DHBT can be used to access a wide variety of different metallic nanostructures, in a simple and controlled manner using H$_2$ bubbles produced at high overpotential. The conditions of the electrodeposition process have been studied. It was shown how deposition parameters could be used to fabricate high surface area structures with an array of different morphologies. It was shown how the changes in deposition parameters affect the morphology, composition and crystal planes of the films prepared, especially in the case of the multimetallics where noble metals affected the Cu host metal. The surface properties of the films prepared could be analysed and compared via the use of catalytic and electrocatalytic reactions.

The key findings surrounding the use of the DHBT are listed below.

- Rapid H$_2$ evolution caused deposition under a diffusion limited regime allowing for Ru films to deposited in the form dendrites with high specific surface areas. Films could then have their oxidation state controlled electrochemically
- Fabrication of an Au honeycomb showing a significant improvement to SO$_2$ oxidation reaction onset and peak potential compared to specifically orientated model Au nanoparticles.
• DHBT used to override kinetic limitations associated with the deposition of more than one metal, producing multimetallic film catalysts with access to a range of morphologies.

• Control of multimetallic films obtained by changes to the deposition conditions, with film property changes evaluated with model catalytic reactions.

• The application of multimetallic film catalysts deposits using DHBT towards a practical application. Noble metal enriched surfaces able to show excellent catalytic activity and stability towards the NaBH₄ electrooxidation.

7.2 Future Work

There are seemingly unlimited possibilities with regard to using the versatility of electrodeposition and the DHBT method for the fabrication of an array of different active film structures. In this thesis the scope of possibilities has been touched on, exhibiting how the method can be used to force metals with slow deposition kinetics to deposit under diffusion limited regimes with access to structures not readily obtained by other methods. Thus other metals that suffer slow deposition kinetics or are difficult to deposit with close control on morphology, such as palladium or other low melting point metals may benefit in the production of well-defined nanostructured materials using this method.

There seems to be never enough time to investigate every pathway possible for research, and never underestimate the value of hindsight. There are many pathways that could be
further explored for the films produced in this thesis. The Ru dendrites may be a suitable for electrocatalysis applications, including hydrogen and oxygen evolution reaction. Ru dendrites have been made for the first time, but applications of these dendrites were not exploited as this was not the main purpose of this thesis.

The study of the SO$_2$ oxidation is an area that requires significant investigation, which would require a thesis dedicated solely to its study. It was found in this thesis that the morphology plays a significant role in reducing the overpotential, opening up the pathway for further fundamental studies that may reveal the ideal morphology to most effectively catalyse the reaction allowing it to proceed closer to its $E^0$ value of 0.157 V. However, overpotential is but one part, the current response must also be improved to allow this reaction to become practical for the industrial production of hydrogen.

The CuAuPt showed excellent activity to the NaBH$_4$ reaction, but still could benefit from further investigation in film surface properties, in particular the Au:Pt ratio that may prove to be successful in producing a suitable material to catalyse the direct oxidation reaction. The parameters for the deposition under DHBT templating could be further optimised to enhance the segregation of the noble metals in the multimetallic films, placing them where they can most effectively affect reactions. The use of synchrotron beamtime could be also be applied for, to look at higher resolution XRD (or XPS) of the multimetallic films that are somewhat difficult for us to accurately analyse due to the lower concentration of noble metals. A greater understanding of the specific effects of the noble metals and their specific location in the film could be developed, to gain a greater understanding of the effects on the practical catalytic reactions where they find application.
The activity of the multimetallic catalysts prepared by DHBT could be tested towards other catalytic reactions, such as SO$_2$ oxidation or CO$_2$ conversion. However, the use of Cu based film catalysts on other oxidation reactions would not be favourable, due to Cu dissolution, and therefore other cheap/base metals would be required to be evaluated. This opens up the opportunities to study other combinations of multimetallic films, allowing for further understanding of the conditions for H$_2$ evolution and its effect on film properties such as morphology, composition, crystallography and chemical state with base metals such as Zn and Ni.

In regard to future multimetallic films that may be investigated, the possibilities for which film fabrication by DHBT can be used are numerous. As the method uses high overpotentials for the formation of the hydrogen bubbles, it allows for the kinetic limitations that may affect alloy content when more than one metal is present to be overcome. The practical simplicity of the method also allows for the deposition parameters to be studied in an efficient manner, to find the most ideal conditions required to obtain materials with specific properties for new applications. The increased understanding developed in this thesis, where metal deposition and H$_2$ evolution are in a delicate, but controllable balance, ensures that further classes of new, useful materials will be able to be created by this technique for practical applications in catalysis and sensing.

7.3 References