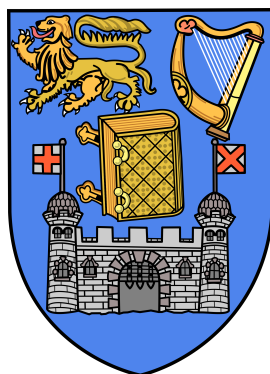


Nanostructured Electrodes as Catalysts for the Water Splitting Reaction

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A thesis submitted for the degree of Doctor of Philosophy in Physics

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To Mum, Dad and Phoebe

Decleration

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Abstract

The production of hydrogen through the electrochemical water splitting reaction is an attractive energy storage solution for intermittent natural resources. This comprises of the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. However, these reactions are kinetically sluggish and require efficient electrocatalysts. Thus, identifying cheap, yet effective catalyst materials is critical to the advancement of water splitting.

Inorganic layered compounds such as transitional metal dichalcogenides (TMDs) and layered double hydroxides (LDHs) have properties that are ideal for applications as high performance HER and OER electrocatalysts respectively. Exfoliating these materials into nanoscale dimensions can serve to further enhance the activity through increasing the density of catalytically active sites. However, the low electrical conductivities of these material can severely hinder performance, particularly for high mass loading electrodes.

In this thesis we use liquid exfoliation methods to produce large quantities of high quality two dimensional (2D) nanosheets of molybdenum disulphide (MoS_2) and cobalt hydroxide ($\text{Co}(\text{OH})_2$). Nanosheet films are fabricated from porous, interconnected nanosheet networks and used as model catalytic systems to develop simple procedures for producing high performance electrodes. These procedures are general, and should be applicable to any solution-processable, nano-particulate HER or OER catalyst to maximise its activity.

Initially, we demonstrate that the performance of HER catalytic films fabricated from nanosheets of MoS_2 can be optimised by maximising electrode thickness. We find the current, and so the H_2 generation rate, at a given potential to increase linearly with electrode thickness to up $\sim 5\text{ }\mu\text{m}$ after which saturation occurs. This linear increase is consistent with a simple model which allows a figure of merit to be extracted. Based on the knowledge that the catalytically active sites of MoS_2 reside on the crystal edges, this figure of merit can be used to characterize the activity of these active sites via their site density along the nanosheet edge. The magnitude of this figure of merit implies that approximately two thirds of the possible catalytically active edge sites in the liquid exfoliated MoS_2 are inactive. Saturation

at high electrode thickness, partially due to poor electrical properties limits further improvement.

Using this model developed for HER catalysts, we take a similar approach to maximizing the activity of OER catalysts using $\text{Co}(\text{OH})_2$ nanosheets. In comparison to MoS_2 , active sites of LDH materials such as $\text{Co}(\text{OH})_2$ remain ambiguous. Thus we begin by confirming the nanosheet edges as the active areas by analyzing the catalytic activity as a function of nanosheet size and electrode thickness. This allowed us to select the smallest nanosheets produced (mean length 50 nm) as the best performing catalysts. While the number of active sites per unit area can be increased via the electrode thickness, we found this to be impossible beyond $\sim 8 \mu\text{m}$ (due to mechanical instabilities). At this point a critical cracking thickness was reached, where by further increase in material loading results in cracking and mechanical instabilities.

Limitations in producing thick electrode films hinders further catalytic improvement. For our thick MoS_2 electrodes we propose that the saturation in current at high electrode thickness is partly due to limitations associated with transporting charge through the resistive electrode to active sites. Our $\text{Co}(\text{OH})_2$ films on the other hand, are limited by the poor mechanical properties of nanosheet networked films. We show these issues can be mitigated by fabricating composite electrodes of 2D nanosheets mixed with 1D single walled carbon nanotubes (SWNTs). SWNTs can be prepared using the same solution processing methods as nanosheets, facilitating the production of hybrid devices through simple dispersion mixing, coupled with vacuum filtration. This method also allows for the nanotube content to be tuneable.

For MoS_2/SWNT composite films we find both the electrode conductivity and the catalytic current at a given potential increase with nanotube content as described by percolation theory. Likewise, adding nanotubes to $\text{Co}(\text{OH})_2$ films increased the toughness, conductivity and catalytic activity by $\times 100$, $\times 10^8$ and $\times 4.5$ respectively, in a manner consistent with percolation theory.

These enhancements meant that composite electrodes consisting of small $\text{Co}(\text{OH})_2$ nanosheets loaded with 10wt% nanotubes could be made into free standing films with

thickness of up to 120 μm with no apparent mechanical or electrical limitations. The presence of diffusion limitations resulted in an optimum electrode thickness of 70 μm . Through further optimisations to electrolyte concentration and temperature a current density of 50 mA cm^{-2} at an overpotential of 235 mV can be obtained, close to the state of the art in the field.

It is hoped that the work presented in this thesis can be used as a roadmap for future catalyst optimisation. In particular, applying these procedures to a high performance catalyst such as NiFeOx should significantly surpass the state of the art.

List of Publications

- 1) McAteer D, Gholamvand Z, McEvoy N, Harvey A, O'Malley E, Duesberg GS, Coleman JN. Thickness Dependence and Percolation Scaling of Hydrogen Production Rate in MoS₂ Nanosheet and Nanosheet–Carbon Nanotube Composite Catalytic Electrodes. *ACS nano*. 2015 Dec 16;10(1):672-83.
- 2) McAteer D, Godwin IJ, Ling Z, Harvey A, He L, Boland C, Vega-Mayoral V, Szydłowska B, Rovetta A, Backes C, Boland JB, Chen X, Lyons MEG, Coleman JN. Liquid Exfoliated Co(OH)₂ Nanosheets as Low-Cost, Yet High-Performance, Catalysts for the Oxygen Evolution Reaction. *Advanced Energy Materials*. 2018:1702965
- 3) Higgins TM, McAteer D, Coelho JC, Sanchez BM, Gholamvand Z, Moriarty G, McEvoy N, Berner NC, Duesberg GS, Nicolosi V, Coleman JN. Effect of Percolation on the Capacitance of Supercapacitor Electrodes Prepared from Composites of Manganese Dioxide Nanoplatelets and Carbon Nanotubes. *ACS Nano*. 2014 Sep 11;8(9):9567-79.
- 4) Gholamvand Z, McAteer D, Backes C, McEvoy N, Harvey A, Berner NC, Hanlon D, Bradley C, Godwin I, Rovetta A, Lyons ME, Duesberg GS, Coleman JN. Comparison of liquid exfoliated transition metal dichalcogenides reveals MoSe₂ to be the most effective hydrogen evolution catalyst. *Nanoscale*. 2016;8(10):5737-49.
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Coleman JN. Production of $\text{Ni}(\text{OH})_2$ nanosheets by liquid phase exfoliation: From optical properties to electrochemical applications. *Journal of Materials Chemistry A*. 2016;4(28):11046-59.1.

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Chapter 1

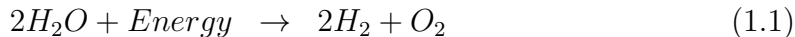
Introduction

Motivation

Modern society is growing at a rapid pace. In just over one hundred years we have gone from living without electricity to relying on portable computers, internet communications, chemical production and a plethora of other technologies that depend on a constant supply on electrical power. Currently, global energy consumption is at 13 TW per year and this is projected to more than triple by the end of the century.¹ Energy production must be increased, and with the impending threat of climate change this must be done without the use of fossil fuels. Renewable energy supplies such as wind and solar are a crucial component however these intermittent sources are inherently unreliable. Thus, advancements in clean energy generation and storage technologies are critical.

In this respect, hydrogen is regarded as one of the most important energy carriers for the future. It has one of the highest specific energy densities of any fuel ($\sim 142 \text{ MJ kg}^{-1}$, three times that of petrol²) and can be cleanly combusted without detriment to the environment, as the only by-product is water. At present, hydrogen is most commonly produced from natural gas through a process known as steam reforming. However this technique is innately damaging to the environment, causing the release of large quantities of carbon dioxide. A cleaner alternative for hydrogen production is through the catalytic water splitting reaction, where an input of electrical energy is used to electrochemically decompose water (H_2O) into oxygen (O_2) and hydrogen

(H₂) gas, represented as follows:



Importantly, the energy supply used to drive the reaction can be from any number of renewable sources, such as wind, hydro or solar, thus avoiding the use of fossil fuels. The advantages here are; (i) the earth’s atmosphere can provide the feedstock of H₂O needed and (ii) the power generated from these unreliable natural resources during excess or off peak times can be stored as a fuel (H₂) and later used for load balancing of the energy grid. Furthermore, this renewable energy storage solution can lead to a hydrogen based economy, thus enabling future sustainable technologies such as fuel cell electric vehicles.

For this ‘hydrogen-economy’ to become a reality the development of efficient and cost effective electrocatalysts is paramount. Electrocatalysts play an important role in reducing the energy requirements for the reaction and increasing the reaction rate. Typically platinum group metals (PGM) are the best electrocatalysts for this reaction, however high scarcity and cost makes these materials inadequate for widespread adoption.³ The next generation of catalysts requires the identification of materials which are abundant, non-toxic, cheap and can generate hydrogen at competitive rates.

Many efforts have been made to develop new, sophisticated and often complex materials with exceptional activity towards the water splitting reaction. However to solve this problem in addition to developing superior electrochemical methods, there are material science issues that need to be resolved. In this regard it is widely accepted that nanoscience has an important role to play in the next stages of development of efficient electrocatalysts.⁴⁻⁶ Nanostructuring a material from bulk macroscopic states can change its properties in a myriad of way, in particular increasing the density of catalytically active sites, which generally reside at defects location, such as the edges of nanostructured crystals.

Thesis Outline

In this thesis I present a strategy for developing highly active catalyst electrodes using systematic material science methodologies. This includes investigations into the effects of nanostructuring, maximising catalyst thickness (or mass loading per area) and creating composite films with 1D nanoconductors. This is achieved through the use of liquid phase exfoliation (LPE), a method for exfoliating bulk layered materials into two dimensional nanosheets (2D), in a processible liquid form.

The initial chapters of this thesis introduce and discuss the background theory and relevant terms regarding the electrolysis of water and electrocatalysis. Layered transitional metal dichalcogenides (TMDs) and layered double hydroxides (LDHs) are promising catalytic materials. These are discussed and a comprehensive overview is given to the current landscape of electrocatalysts literature. The benefits of creating nanomaterial composites, particularly 1D:2D composites are also outlined. Following this, the experimental methods employed in this report are presented and sufficient technical detail for each method is provided. Large quantities of nanomaterials are created using LPE and fabricated into films by stacking nanosheets to create networked films, using vacuum filtration.

A straightforward yet oft ignored method of improving catalyst activity is by increasing the thickness of catalyst films. This is investigated, and a procedure is developed to maximise electrode thickness which can be applied to any solution-processable, nanoparticulate catalyst material. Taking a systematic approach allows for a quantitative model to be developed which relates nanosheet edge and film thickness to catalytic activity.

The versatility of this model is demonstrated and is used to identify active regions of new catalyst materials. Thus, through nanostructuring and high mass loading active site densities can be increased, leading to high performing electrocatalysts. Finally, hindering further development are the intrinsically poor electrical and mechanical properties of nanosheet networked films. This is mitigated through the development of composite materials, mixing 1D carbon nanotubes with 2D nanomaterials. Ultimately this approach provides a road-map for catalytic improvement and demonstrates that a cheap, relatively poor catalyst material can be enhanced

to be competitive to state-of-the-art electrode materials.

Chapter 2

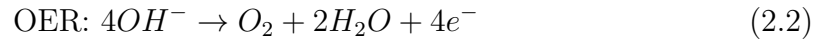
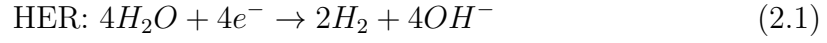
Electrochemical water splitting

A good understanding of the water splitting process is undoubtedly necessary for one to offer direction for the design and synthesis of electrocatalysts. This chapter will begin by giving a brief overview to the water splitting reaction, leading to a more in-depth discussion of the electrode-solution interface. From this, a better understanding of electrode potentials and reaction thermodynamics is possible. To reduce operating potentials an effective electrocatalyst is required and information on electrode kinetics are introduced. Finally this chapter concludes with a discussion of the parameters used to evaluate electrocatalyst performance, which thus allows one to choose effective catalyst materials.

2.1 Water electrolysis cell

A typical water electrolysis cell, shown in figure 2.1A, consists of two electrodes, a cathode and anode submerged in a conductive aqueous electrolyte. When a sufficient voltage is applied across the electrodes, electrons flow through the circuit to the cathode while charge carrying ions travel through the electrolyte enabling the electrolysis reaction. At the cathode a reduction reaction occurs, the hydrogen evolution reaction (HER), and H_2 gas is generated, while at the anode the oxidative oxygen evolution reaction (OER) takes place, producing O_2 . The reaction proceeds in either acidic or alkaline conditions, which contribute a high concentration of ionic charge carriers (protons/hydronium ions or hydroxide ions), facilitating an efficient

reaction⁷. In alkaline solution, the HER and OER can be described by the following reaction pathways:



While in acidic conditions the reactions are represented by:

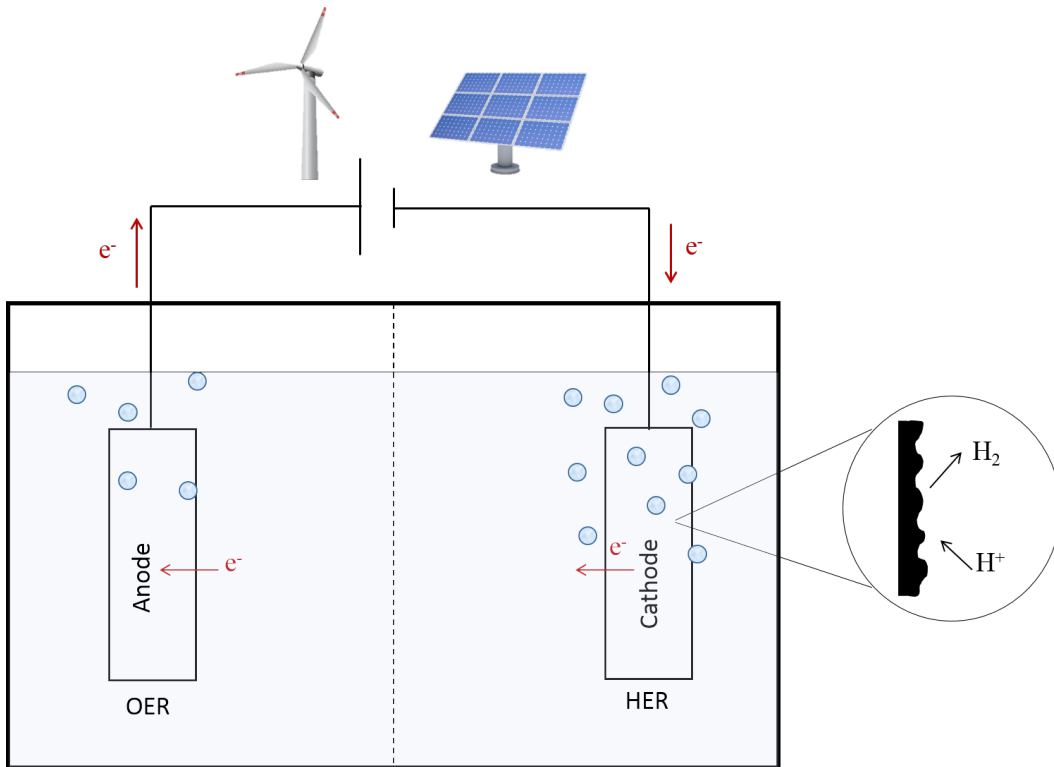
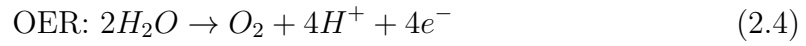


Figure 2.1: A pictorial representation of a water electrolysis cell. Hydrogen is evolved at the surface of the cathode and oxygen at the anode

Table 2.1: *Industrial electrolysis; AEL versus PEM*^{18,19}

	Alkaline electrolysis	PEMs
Electrolyte	30 wt %KOH	Solid acid polymer
Electrodes	Ni/Fe electrodes (Raney)	Noble metals (Pt, Ir,..)
Temperature	50-80 C	RT – 90 C
Pressure	< 30 bar	< 150 bar
Lifetime	> 100,000 h	< 40,000 h
Current density	0.2 – 0.4 A/cm ²	0.6 – 2 A/cm ²

2.1.1 Electrolyte and industrial electrolysis

The choice of acidic or alkaline electrolyte can affect many conditions of the electrolysis reaction such as gas purities, reaction mechanisms, and stability and activity of electrocatalysts. Choice of catalyst material depends largely on the reaction medium, where low cost transition metals such as cobalt, nickel and iron are very stable in alkaline conditions,^{8–10} while in an acidic regime typically more expensive platinum group metals are used.^{10–12}

On a commercial level, the two most common water splitting technologies are liquid alkaline electrolysis (AEL) and acidic polymer electrolyte membrane electrolysis (PEM). Of these, AEL is currently the most mature technology, with reasonable efficiencies and impressive lifetimes.^{13,14} PEM electrolyzers on the other hand are generally even more efficient and can operate at larger current densities when compared to AEL.^{13,15,16} Their low durability and shorter lifetimes however lead to much higher operational costs.¹⁷ A comparison between these two technologies is found in table 2.1.

The field of commercial water splitting is continuously evolving and improving, with new technologies such as high temperature steam electrolysis (HTEL) being developed which have the potential for even greater efficiencies than conventional low temperature AEL or PEM.¹³

2.1.2 Electrodes and the electrode/solution interface

The electrodes of the water splitting cell are typically comprised of a highly conductive current collecting substrate, for example Ni plates or carbon paper²⁰, coated with a film of catalyst material anywhere from a few nanometres to 100s of micrometres thick.^{13,21,22} This catalyst film can be highly porous which enables electrolyte to penetrate deep into the large internal surface. At the electrode surface an important phenomenon occurs; mobile ions in the electrolyte solution near the interface, due to effects of the electrode, can form layers of charge known as an electrical double layer.²³

Every electrochemical reaction caused by an applied potential to an electrode, is initiated by a charge transfer reaction that occurs across the electrode-electrolyte boundary and thus the properties of this double layer region can have a considerable effect on the kinetics of a reaction. An understanding of the dynamics at the electrode-solution interface is therefore crucial to the understanding of electrode potentials and kinetics.

At a basic level, the boundary of the solid-liquid interface can be modelled as an electrical double layer consisting of sheets of positive or negative charge at the electrode surface and a layer of opposite charge next to it in solution.²⁴ The exact properties governing the nature and formation of this double layer have been examined using electrocapillary studies²⁵ however are beyond the scope of this report. Of more interest are the current models used to describe the double layer; two of which are the Helmholtz layer model and the Gouy-Chapman model. Both of these interpretations rely on the principle that a conducting electrode holds a charge density arising due to an excess or deficiency of electrons at the surface. Ions of opposite charge to the electrode surface will thus cluster close to it and act as counter charges, while ions of the same charge are repelled from it. These interactions between ions in solution and on the electrode surface are also assumed to be electrostatic.

In the Helmholtz layer model,²⁶ mobile ions surrounded by solvent molecules arrange themselves along the surface of the electrode, but are kept a distance, H ,

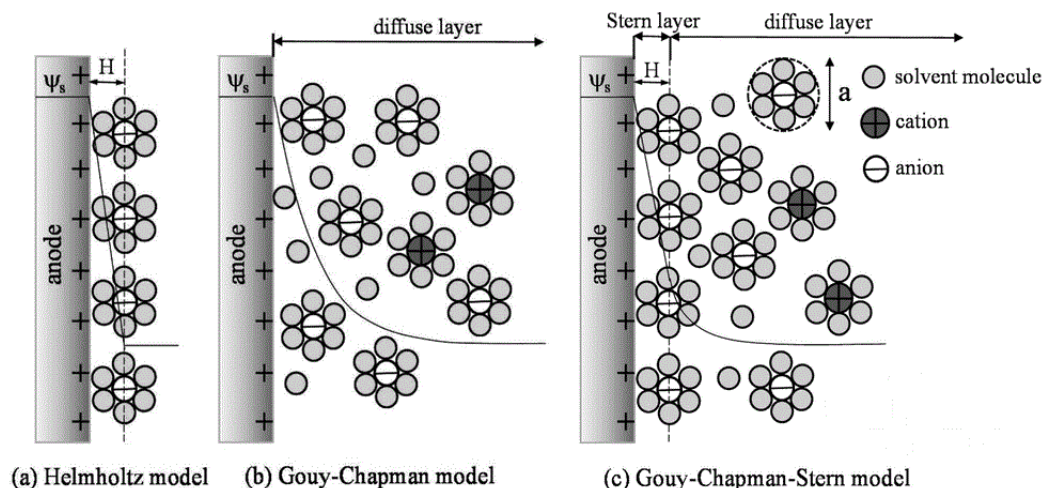


Figure 2.2: Illustrative representation of the electrical double layer as described by (A) The Helmholtz model, (B) Gouy-Chapman model and (C) The Gouy-Chapman-Stern model. Ψ_s is the Galvani potential difference across the double layer

away due to their hydration spheres (see figure 2.2A). These form a sheet of ionic charge known as the outer Helmholtz plane (OHP).^{23,24} The double layer formation is a non-faradic process and the two layers of separated charges (surface and OHP) are analogous to an electrical parallel plate capacitor separated by a dielectric medium.²³ This is responsible for the electrode surface having measurable capacitance (double layer capacitance), which can contribute charging currents when measuring the rate of the HER or OER (see example in Chapter 7).

Solvated ions in the OHP are said to be nonspecifically adsorbed and can be disrupted and break up due to thermal motion in the solution, creating a diffuse layer in three dimensions.²³ This concept is described by the Gouy-Chapman model of the diffuse double layer,^{27,28} as shown in figure 2.2B. Later, the Helmholtz layer model and the Gouy-Chapman model were combined in both the Stern model and the Grahame model to give a more complete picture of the actual interface (figure 2.2C).²³

The significance of this double layer arrangement is rooted in the creation of an interfacial potential difference between the electrode and the solution, known as the Galvani potential difference (Ψ_s).²³ Depending on the conditions, this potential drop can change linearly (Helmholtz) or exponentially (Gouy-Chapman) with distance from the electrode. The Galvani potential difference depends specifically on the

energy and density of electronic states of the two phases in contact,^{23,29} and can be measured as the electrode potential as described below.

It should be noted however before proceeding that the above models and discussions assume the electrode material to be a metal. This is not always the case (as for the materials discussed in this thesis) and the exact properties of the double layer region will depend on whether the electrode is a metal, semiconductor or insulator. Differences in electrical properties, such as the presence of a band gap and lower charge carrier concentrations, will have an effect on the interfacial potential difference. In a semiconductor for example, charge is spread over a 3D space charge region, not just concentrated all at the surface, thus the electrode potential extends further into this layer.³⁰

2.2 Cell potentials

2.2.1 Electrochemical thermodynamics

The thermodynamic stability of water is well known. As a result it requires an input of energy to separate water molecules to form hydrogen and oxygen gas. In other words, for a charge transfer reaction to occur at each electrode (HER or OER) a minimum input voltage is required, the value of which is dictated by the thermodynamics of the electrochemical reaction. At equilibrium, with no net current flowing, the potential at an electrode ($E_{0,electrode}$) is described by the Nernst equation and depends on the concentrations or activities (a_i) of the reactants as:²⁹

$$E_{0,electrode} = E_{electrode}^0 + \frac{RT}{n_e F} \sum_i n_i \ln a_i \quad (2.5)$$

Where R is the gas constant, T is the temperature, n_e and n_i are the stoichiometric coefficients of the electrons and reactants respectfully, F is the Faraday constant and E^0 is known as the standard potential; the equilibrium electrode potential under standard conditions of $a_i = 1$, $T = 298$ K, and pressure $p = 1.013 \times 10^5$ Pa. For the reduction of hydrogen (HER) this standard electrode potential, E_{H^+/H_2}^0 is universally defined as 0 V and is known as the standard hydrogen electrode (SHE).

The SHE is used as a reference potential against which other potentials can be compared (see Chapter 4). For the OER the standard potential, E_{O_2/H_2O}^0 , is approximately +1.23 V versus the SHE. Therefore to generate hydrogen and oxygen at each electrode, a voltage must be applied across the cell which at least overcomes the standard electrode potentials. This cell voltage is the fundamental operating potential of water electrolysis and is given by:²⁴

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 = E_{H^+/H_2}^0 - E_{O_2/H_2O}^0 = -1.23 \text{ V} \quad (2.6)$$

This value is related to the thermodynamics of the reactions such that:

$$\Delta G^0 = -n_e F E_{cell}^0 \quad (2.7)$$

Where ΔG^0 is the standard Gibbs free energy change of the overall cell reaction. Substituting -1.23 V into equation 2.7, it is seen that for the electrolysis of water $\Delta G^0 = +237.2 \text{ kJ mol}^{-1}$ and is the minimum amount of electrical energy required to generate hydrogen.³¹

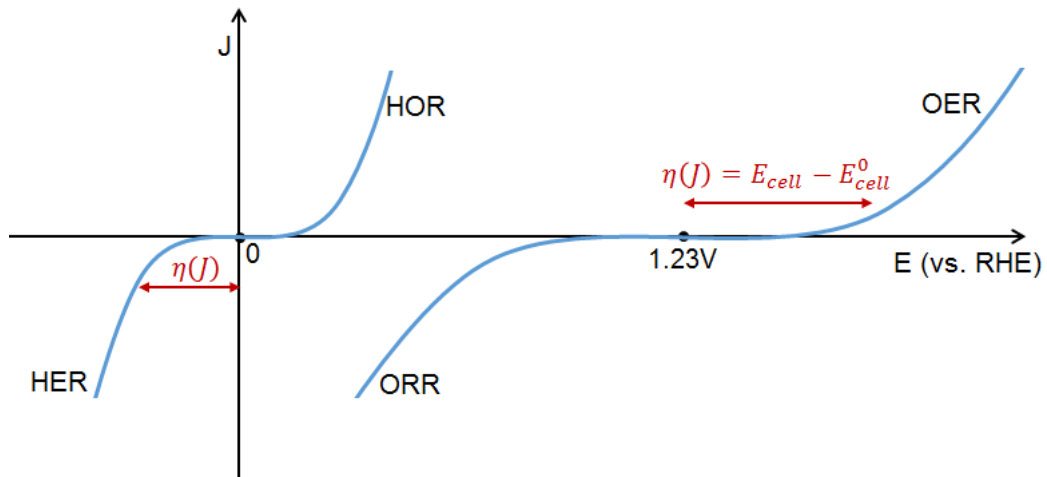


Figure 2.3: Representation of the current-potential relationship for hydrogen evolution and oxidation (HER and HOR) and for oxygen evolution and reduction (OER and ORR).

2.2.2 Cell overpotentials

Beyond the thermodynamic requirements of the water electrolysis reaction, other factors such as poor electrode conductivity, sluggish charge transfer kinetics and ionic and gas diffusion limitations lead to additional potential requirements.^{23,32} This additional potential is often referred to as the overpotential, η . Therefore to drive the electrolysis reaction (and generate a current response) a voltage, E_{cell} , is applied across the two electrodes of the cell such that:

$$E_{\text{cell}} = E_{\text{cell}}^0 + \eta_A + |\eta_C| + \eta_{\Omega, \text{cell}} \quad (2.8)$$

Where η_C and η_A are the cathodic (HER) and anodic (OER) overpotentials respectfully, arising from inefficient kinetics of the reaction, and, $\eta_{\Omega, \text{cell}}$ is additional potential required to compensate for Ohmic losses in the cell.³³ Of note, η_A , η_C and $\eta_{\Omega, \text{cell}}$ are all functions of current. Here $\eta_{\Omega, \text{cell}} = iR_{\text{cell}}$ where i is the current through the cell and R_{cell} is the sum of all the electrical resistances of the cell, such as resistance through the cell membrane, resistance due to bubble formation, electrolyte resistance and resistances in the cell wiring and electrodes.^{13,34} A representation of these potentials is shown visually figure 2.3.

The efficiency of the electrolysis system is reflected in the ratio of $E_{\text{cell}}^0/E_{\text{cell}}$ i.e. the degree to which E_{cell} deviates from 1.23 V.¹³ As a result of the extra overpotentials required, real world industrial water electrolyzers operate at potentials far exceeding this minimum, typically around 1.8 – 2.0 V at current densities of 1000 – 300 A m⁻².¹³ Consequently, with current technology the production of hydrogen through water splitting is uncompetitive compared to fossil fuels. To become economically viable, operational costs must be decreased, meaning reductions in both the HER and OER overpotentials are vital. This can be achieved through the development of inexpensive and efficient electrocatalysts.

2.3 Electrocatalysis

An electrocatalyst can be defined as a material which reduces the overpotential of an electrochemical reaction without itself being consumed in the process.²⁹ Electrocatalysts play a key role in energy conversion technologies such as water electrolysis, as they increase the efficiency and accelerate the rate of the particular chemical reaction.³ To discuss electrocatalysis, an understanding of the electrode overpotentials, the rates of reaction and the current-voltage relationship must first be established. Following this, the activity parameters used to measure the performance of catalysts are introduced. Finally, consideration of the reaction mechanisms of the HER and OER at the electrode surface lead to a discussion on choosing the optimum catalyst material.

2.3.1 Electrode overpotentials

To drive either the HER at the cathode or OER at the anode the electrode potential must be increased beyond its zero-current value, by an overpotential, η_C or η_A , as well as by a contribution due to resistive losses, η_Ω , such that equation 2.8 can be rewritten for each electrode as:

$$E_{HER} = E_{H^+/H_2}^0 + |\eta_C| + \eta_{\Omega,HER} \quad (2.9)$$

$$E_{OER} = E_{O_2/H_2O}^0 + \eta_A + \eta_{\Omega,OER} \quad (2.10)$$

An effective electrocatalyst works by reducing the electrode overpotential η_C and η_A , and to a large extent has no effect on the equilibrium or Ohmic potentials[†]. As a result, when measuring the activity of an electrocatalyst these values must be taken into account and compensated for (see Chapter 4).

[†]This is not strictly true regarding the Ohmic overpotential, as Ohmic resistances due to the catalyst film can contribute to this value. However these are usually much smaller than resistances due to the supporting electrode, electrolyte, etc. This is discussed further in Chapter 4.

2.3.2 The rate of the reaction

Faraday's law tells us that the number of moles of electrolysed species (products) in an electrochemical charge transfer reaction, N , is related to the total Coulombic charge transferred, Q , by:²³

$$N = \frac{Q}{n_e F} \quad (2.11)$$

Where n_e is the number of electrons involved in the reaction and F is the Faraday constant (96485.332 C mol⁻¹). Following this, the rate (ν) of the reaction can then be expressed as dN/dt (mol s⁻¹) and in terms of the total reaction current ($i = dQ/dt$) as:

$$\nu = \frac{dN}{dt} = \frac{i}{n_e F} \quad (2.12)$$

Another common way to consider ν is as the amount of material produced over a region of the electrode surface in a period of time and so can be normalised by the area of the electrode, A :

$$\nu_A = \frac{i}{AnF} = \frac{J}{n_e F} \quad (2.13)$$

Where ν_A is expressed in mol s⁻¹cm⁻² and J is the current density, usually expressed in units of mA cm⁻². This expression is significant and shows that the reaction rate can be quantified by the current density. In other words, the amount of product generated per second is directly proportional to the measured current. This is worth highlighting, as more often than not when discussing the amount of H₂ or O₂ being generated from a catalyst, the value being discussed is the current density and not the actual mass or moles of gas produced.

2.3.3 Current-potential relationship: The Butler-Volmer equation

As discussed, the application of a sufficient electrode potential initiates the electrode reaction. The rate of the electrode reaction, and so of gas evolution, must therefore

be strongly dependent on the applied potential (or overpotential). From this understanding, a relationship between overpotential and current density can thus be established. Pioneering work by Polanyi and Horiuti^{35,36} into theoretical approaches to electrochemistry have led to the development of such relationships and detailed reviews and derivations can be found elsewhere.^{23,37-39} They are however far beyond the scope of this introduction. Instead, without going into needless detail some important terms should be introduced to help contextualise this relationship.

To simplify the discussion, consider only the case of a one-step, one-electron reaction at the electrode surface. The rate of the reaction, alternatively to equation 2.13, can be expressed in terms of the concentration of the reactants at the electrode surface by:²⁴

$$\nu_{OX} = k_c[Ox] \text{ (rate of reduction of Ox)} \quad (2.14)$$

$$\nu_{Red} = k_a[Red] \text{ (rate of oxidation of Red)} \quad (2.15)$$

Where [Ox] and [Red] are the molar concentrations of the oxidised and reduced materials (mol cm^{-3}), respectfully and k is the rate constant (a coefficient of proportionality) for the reaction with units cm s^{-1} . Following this, from transition state theory the rate constant can also be written as:²⁴

$$k = Be^{-\Delta^\ddagger G/RT} \quad (2.16)$$

Where $\Delta^\ddagger G$ is the activation Gibbs energy and B is a constant with the same dimensions as k .²³ The activation Gibbs energy is related to the Galvani potential difference ($\Delta\Psi_S$) across the electrode solution interface (introduced previously) as:

$$\Delta^\ddagger G_C = \Delta^\ddagger G_C(0) + \beta_C F \Delta\Psi_S \quad (2.17)$$

$$\Delta^\ddagger G_A = \Delta^\ddagger G_A(0) - \beta_A F \Delta\Psi_S \quad (2.18)$$

Where $\Delta^\ddagger G(0)$ is the value it has in the absence of a potential difference across

the double layer, and β_A and β_C are the anodic and cathodic transfer coefficients ($\beta_C = 1 - \beta_A$). These terms are symmetry factors which lie in the range of 0 to 1 (usually 0.5) and describe the fraction of potential across the double layer which reduces the activation barrier for the reaction.²⁹ The Galvani potential is also related to the electrode overpotential by $\Delta\Psi_S = E^0 + \eta$.²⁴

Finally, the net current density at an electrode can be expressed as the difference between $J = J_a - J_c$, where when $J_a > J_c$, $J > 0$ and the current is anodic and when $J_c > J_a$, $J < 0$ and cathodic current flows. Thus, combining equation 2.14,2.15,2.16,2.17 and 2.19 together and putting it in terms of current density using equation 2.13, an expression that relates the applied electrode potential to the current density can be formed:²⁴

$$J = J_0 \left[\exp\left(\frac{\beta_A \eta F}{RT}\right) - \exp\left(\frac{-\beta_C \eta F}{RT}\right) \right] \quad (2.19)$$

Where J_0 is known as the exchange current density, a measure of current at equilibrium when $J_a = J_c$ and $\eta = 0$. This is known as the Butler-Volmer equation and describes the relationship between the overpotential at an electrode and the net cathodic or anodic current density. For a multi-step charge transfer reaction ($n_e > 1$), such as the OER or HER, the reaction transfer coefficients, β , can be converted to α , which contain information about the number of electrons transferred before and after the rate determining step,^{32,37} and the Butler-Volmer equation can be re-expressed as:

$$J = J_0 \left[\exp\left(\frac{\alpha_A n_e F \eta}{RT}\right) - \exp\left(\frac{-\alpha_C n_e F \eta}{RT}\right) \right] \quad (2.20)$$

At low overpotentials close to E^0 both the cathodic and anodic terms of equation 2.20 have an influence on J . Far from equilibrium however, at larger positive or negative potentials one term of the Butler-Volmer equation dominates and equation 2.20 can be rewritten as:

$$J = J_0 \exp\left(\frac{\alpha_A n_e F}{RT} \eta\right) = J_0 \times 10^{(\eta/b)}, \text{ OER } (J > 0, \eta > 0) \quad (2.21)$$

$$J = -J_0 \exp\left(\frac{-\alpha_C n_e F}{RT} \eta\right) = -J_0 \times 10^{-(\eta/b)}, \text{ HER } (J < 0, \eta < 0) \quad (2.22)$$

Where $b = \frac{2.303RT}{\alpha n_e F}$ is known as the Tafel slope and will be discussed in more detail later in this work.

The overpotential associated with a given current in the Butler-Volmer equations serves solely to provide the activation potential required to drive the reaction, at a rate reflected by the current density.²³ The more sluggish the kinetics, the larger the activation overpotential must be for a given current. Figure 2.4A shows an example current-voltage diagram for the oxygen evolution reaction. From this diagram it can be seen that the current rises exponentially with overpotential at moderate potentials, following the Butler-Volmer equation. However as the potential increases further the relationship expressed in equation 2.21 breaks down and no longer describes the reaction. At this point the current is becoming diffusion limited.

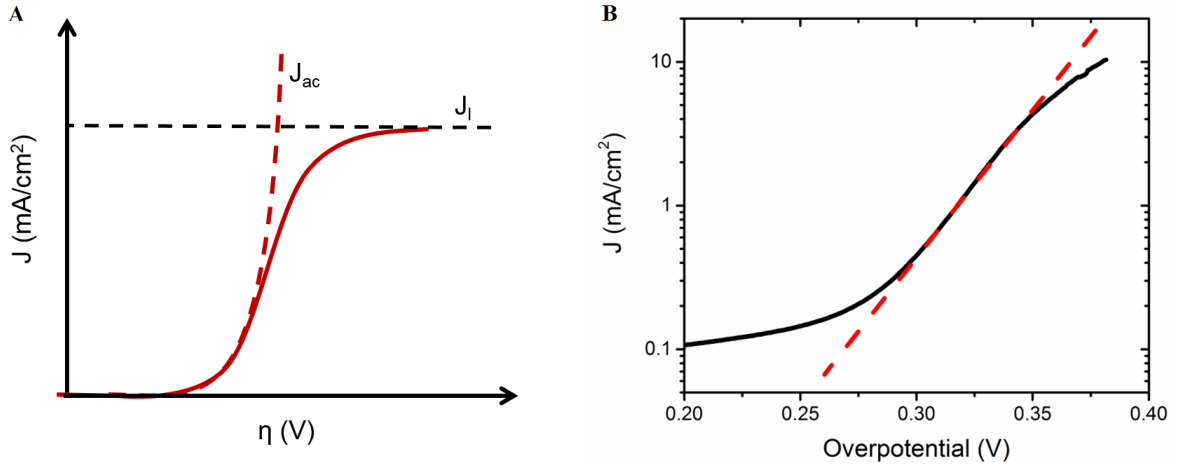


Figure 2.4: (A) J - E polarisation plot illustrating the OER response of an ideal and real system. The dashed red line is purely activation controlled and is totally described by equation 2.21. The solid red line is reflective of the actual current that would be measured in a real system, reaching a limiting current at high rates due to mass transport limitations. (B) Tafel plot of $\log(J)$ versus overpotential, showing the linear Tafel region represented by the red dashed line. J_0 can be found from the intercept and b from the inverse slope of this line.

Diffusion limitations

In reality the overpotential expressed in equation 2.9 and 2.10 is made up of two components:

$$\eta = \eta_{ac} + \eta_{diff} \quad (2.23)$$

Where η_{ac} is the contribution from the activation kinetics of the reaction (the overpotential described by the Butler-Volmer equation) and η_{diff} results from limiting diffusion rates, i.e. slow mass transport of reactants and/or products to and from the electrode surface. The diffusion overpotential, η_{diff} , can result in a limiting current, J_l (figure 2.4A); the maximum current obtainable when the charge transfer reaction is completely mass transfer controlled. At this point the current becomes potential independent and becomes reliant on the concentration of electroactive species in the bulk electrolyte. As a result, this implies the maximum output of an electrolysis cell is ultimately hinged on the diffusion of reactants and products to and from the catalyst surfaces, and thus this diffusion limit must be reduced to operate at maximum current densities. This can largely be managed through effective cell design, for example with the use of stirring equipment to aid in the mass transport.

However the optimisation of other design features of electrocatalysts can also have an effect of reducing the diffusion overpotential. At high potentials the rate of gas production is very fast. As a consequence, gas molecules being produced in the internal surfaces of a catalyst do not have time to escape and can combine together to form larger bubbles. These bubbles can become trapped (anchored) along the surfaces of the catalyst, shielding active catalytic sites from participating in the reaction. Effective engineering of the catalyst morphology, such as producing highly porous catalysts, can reduce this gas shielding effect and raise the limiting current.

2.3.4 Tafel equation and activity parameters

For the HER and OER η_{diff} is typically only important at high overpotentials, when significant amounts of H_2 or O_2 are being generated. Under ideal conditions, where diffusion limiting effects are at a minimum, $\eta_{ac} \gg \eta_{diff}$ and $\eta \approx \eta_{ac}$. Expressing

equation 2.21 and 2.22 logarithmically reveals a linear relationship between $\log(J)$ and η :

$$\log(J) = \log(J_0) + \eta/b \text{ (OER)} \quad (2.24)$$

$$\log(J) = \log(-J_0) + -\eta/b \text{ (HER)} \quad (2.25)$$

This is known as the Tafel equation and plotting it, as shown in figure 2.4B, allows for values of b and J_0 to be extracted. The Tafel slope and exchange current density are often looked at as identifiers of the activity of a particular catalyst electrode. The following section will introduce various parameters used throughout literature (and this thesis) to evaluate the activity of different materials. Some of these parameters provide information about the intrinsic per site activity of a material, while others supply information about the total electrode activity. These values tend to complement each other and researchers should attempt to report on most, if not all of these parameters to give a complete picture of catalyst performance.

Turn-over frequency

An important metric in electrocatalysis is the specific activity at a given overpotential, the turnover frequency (TOF). This is the number of H_2 or O_2 molecules produced per catalytically active site per second (units s^{-1}).^{10,29} The TOF gives an insight into the fundamental reactivity of each catalytic site, and in general is a useful parameter when attempting to compare the intrinsic activity of catalysts with different surface areas or loadings.⁴⁰ Notably however, the TOF relays no information about the density or number of active sites and thus can be a slightly misleading value if the catalyst material has a very low density of sites.

The TOF can be calculated as follows:⁴¹

$$\text{TOF} = \frac{1}{N_s} \times \frac{dN}{dt} = \frac{i_E}{nFN_s} \quad (2.26)$$

Where N_s is the number of catalytic active sites (given here in mol), i_E is the current at a given potential and everything else is as previously stated. The number

of catalytic active sites in a sample is a notoriously difficult parameter to measure accurately.⁴⁰ While some studies use scanning tunneling microscopy⁴² or probe molecules that absorb selectively to active sites,⁵ the most practical method to obtain N_s is by using the voltammetric charge.^{43,44} By integrating the area under an oxidation or reduction peak to extract the charge and by assuming one electron transferred per site, one can obtain the total number of redox sites.^{41,45} A problem with this technique however is that there is no way to guarantee that the sites available for oxidation or reduction are also available for the OER or HER, and typically the calculated value of N_s overestimates the actual number of active sites. This leads to most reported values of TOF being conservative estimates of the actual per site TOF.

Exchange current density

The exchange current density is a measure of the electron transfer activity at equilibrium, i.e. at zero overpotential. At this potential forward and reverse reactions occur at the same rate ($J_a = J_c$), and the magnitude of the exchange current density reflects the intrinsic rates of electron transfer at the catalyst, where a large J_0 indicates a more active catalyst.⁴⁶ To report J_0 the current can be normalised using a variety of techniques, with the most common method in literature being to normalise using the geometric surface area of the electrode.⁴⁷ For reporting on intrinsic activities of the catalyst this method is the least accurate way to present the current density as it does not take into account morphology of the material, however it is the primary method used in this report, partly to aid with comparison to the literature. Other normalisation methods include per actual surface area (using BET measurements)^{48,49}, per mass loading (or active metal mass)⁵⁰ or using the electrochemically active surface area (ECSA),⁴⁸ with the latter method being most correct. One popular technique to calculate the ECSA involves measuring the double layer capacitance in a non-redox active potential window and converting capacitance to area using a standard conversion factor for that material.^{40,48,51} This can be difficult however if a conversion factor is not available for the particular material.

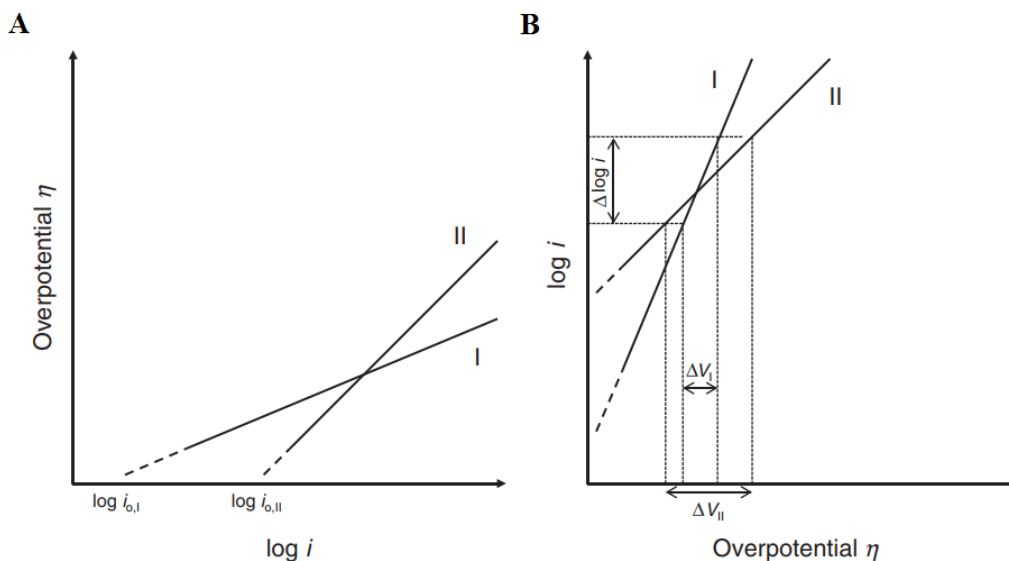


Figure 2.5: (A) and (B) Diagrams illustrating the significance of both Tafel slope and exchange current density for evaluating catalyst activity. Reproduced from Conway et al⁵²

Tafel slope

The Tafel slope, b , is a multifaceted parameter which can give various insights into the efficiency of a reaction. It is often a difficult parameter to interpret as it can depend on several factors including the reaction pathway, the adsorption conditions and the active catalyst site.⁴⁷ Primarily, the Tafel slope can be thought of as a sensitivity function which indicates the magnitude of potential required to increase the current by a factor of 10 and thus is typically expressed in units of mV dec^{-1} .³² In addition, the value of b has also been used to suggest a possible rate determining step (r.d.s) for the HER or OER. The rate determining step is considered a single step in a sequence of elementary steps of a mechanism that is much more sluggish than all others, in such a way that it controls the rate of the overall reaction.²³ The value of the transfer coefficient, α , can change depending on the order of the r.d.s and this is reflected in the Tafel slope (see HER and OER mechanisms below for more details).

Reporting on either J_0 or b alone as a measure of activity for electrocatalysts drastically devalues their utility, as the two parameters are inherently linked. This concept is illustrated as Tafel plots in figure 2.5A which presents two catalysts, (I) and (II). Here $J_{0,I} > J_{0,II}$ thus catalyst (I) could be considered more active relative

to catalyst (II). Conversely $b_I < b_{II}$ therefore reporting solely the Tafel slope would lead to the opposite conclusion. In reality, each catalyst is superior in a different potential range, thus reporting both J_0 and b for each catalyst gives a more complete picture.^{32,52}

Systems may also need to operate at a range of current densities, depending on demand. Therefore the rate of change of current density with overpotential is also of practical importance. This is reflected in the inverse Tafel slope, given as the slope of equation 2.24 and 2.25. Figure 2.5B shows that for an equal increase in current density, catalyst (I) requires a much smaller change in overpotential than catalyst (II). Thus further emphasising the importance of Tafel slope as an indicator of efficient electrocatalysts activity.³²

Overpotential and current density

Perhaps the most common performance metrics for analysing electrocatalysts for the HER or OER are the overpotential at a fixed current density, $\eta@J$, or vice versa, $J@\eta$. Describing the reaction rate through parameters such as J_0 can be effective to show the intrinsic activity of a material, however this only refers to kinetics at the zero overpotential mark and thus does not characterise the kinetics of the electrode at higher, more practical current densities.³² Quoting $\eta@J$ or $J@\eta$ at rates more appropriate to real world applications can thus be highly advantageous.

Furthermore, as discussed the performance of a catalyst electrode is not dictated solely by the kinetics at the anode and cathode but also by the rates of mass transport. The design of the catalyst electrode itself is partly responsible for reducing the diffusion overpotential (other than cell design). Therefore to accurately evaluate a device under practical conditions sometimes currents or potentials outside of the linear region of the Tafel plots must be presented. Because of this $\eta@J$ or $J@\eta$ can often give the clearest snapshot of a catalysts' ability. In this regard, normalising current density using geometric area is a sufficient way to accurately reflect the total electrode activity and is useful for practical device performance comparisons.

When reporting the overpotential of a catalyst, one common potential of interest is the onset potential. This is considered the potential at which gas begins to evolve,

or where current is first observed.⁴⁰ Caution must be taken when reading this value however as there is no strict definition of onset potential, and thus the same label can be assigned to many different values of current density depending on the observer. In general onset potential should be reported in the range of 0.05 - 1 mA cm⁻². Due to this ambiguity overpotential should always be defined with a corresponding current density. A more practical criterion for comparing catalysts is the overpotential required to achieve 10 mA cm⁻² current density (per geometric area) and is by far the most common figure of merit used to compare electrocatalysts for the HER and OER. This somewhat arbitrary value is approximately the current density expected at the anode in a 10% efficient solar water-splitting device under 1 sun illumination, which is the order of efficiency required for cost effective photoelectrochemical water splitting.^{10,40}

2.4 Mechanisms of the HER and OER

To develop a more complete picture of the catalysed water splitting reaction it is useful to understand both the HER and OER mechanisms that take place at the electrode/electrolyte interface. In this report, investigations into electrocatalysts for the HER and OER are conducted under acidic or alkaline conditions respectfully. Thus for the sake of brevity and clarity, the mechanisms related to each reaction will be discussed for those electrolyte conditions only. For either reaction the general procedure follows five steps, where any one of these points can be the rate determining step;²⁹

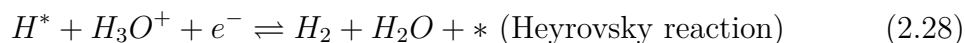
1. Transfer of reactive species ($\text{H}_3\text{O}^+/\text{H}^+$ or OH^-) from the electrolyte solution to the catalyst electrode surface
2. Adsorption onto the surface
3. Charge transfer reaction steps at the surface or chemical rearrangement
4. Surface diffusion
5. Desorption as H_2 or O_2 gas

2.4.1 HER

It is generally accepted that the HER follows one of two reaction pathways^{53,54} with a pictorial representation of these pathways is presented in figure 2.6. For the HER in acidic media these pathways occur via two steps; initially the Volmer reaction, where a proton is adsorbed onto the electrode surface (proton discharge step);



followed by either the Heyrovsky reaction;



where the adsorbed hydrogen atom bonds directly to a hydrated proton, or the Tafel reaction;



where two adsorbed hydrogens diffuse along the electrode surface and combine. These give either the Volmer-Heyrovsky or Volmer-Tafel mechanism.⁵³ In the above equations, * indicates the catalytic active site.

Either the first (equation 2.27) or second (equations 2.28 or 2.29) reaction step in the mechanism is the rate determining step of the reaction. According to Conway⁵³ the dominating mechanism will depend on the surface coverage of adsorbed hydrogen, H_{ads} , on the electrode. Here the Tafel slope can be used as a tool to evaluate the dominant mechanism. For the case of high surface coverage of adsorbed hydrogen, a Tafel slope close to 40 mV dec⁻¹ or 30 mV dec⁻¹ suggests the Heyrovsky or Tafel reaction dominates. When surface coverage of H_{ads} is relatively low the Volmer reaction dominates and a Tafel slope of 120 mV dec⁻¹ is observed. It should be noted however that the precise value of the Tafel slope can be altered by other influencing factors and can vary significantly for preparations of the same material.^{32,47} The values above generally only appear when there is a clear r.d.s and often no step is much slower than the rest. Hence it is not always well understood why a

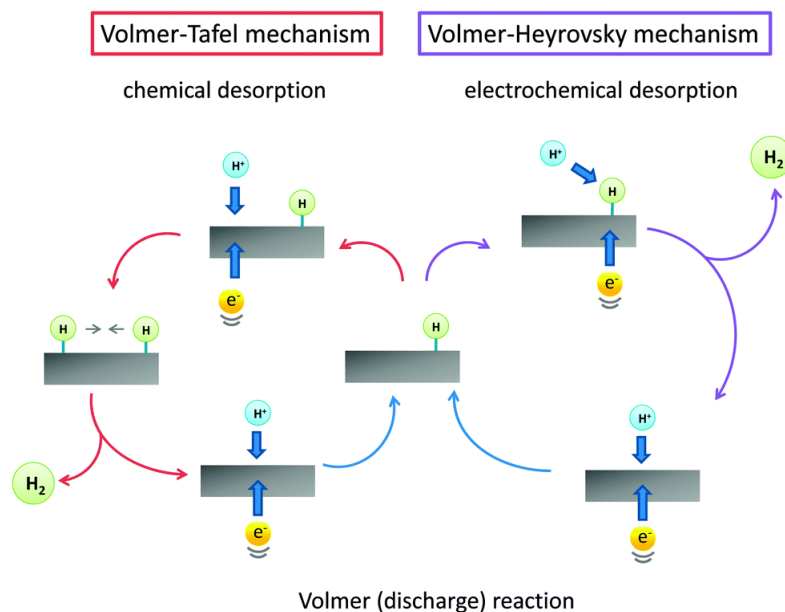


Figure 2.6: *The mechanisms of hydrogen evolution in acidic media*⁵⁵

material will have a particular Tafel slope.

2.4.2 OER

Unlike the HER the oxygen evolution reaction is a more complex process involving the transfer of 4 electrons. There are a large number of possible reaction intermediates for the OER and consequently the exact reaction mechanistic pathway are less well defined.⁵⁶ Over time there have been many possible mechanistic schemes suggested for the OER and in 1986 Matsumoto and Sato⁵⁷ summarised some of the different proposed schemes, shown repeated figure 2.7.⁵⁶ In general, the steps of the OER involves the initial adsorption of an OH^- species on the catalyst surface and the intermediate reaction steps differ but usually involve several other surface adsorbed intermediate.⁵⁶ Due to the ambiguity in reaction pathways, the precise identification of rate determining steps for the OER can be tricky.

Alkaline solution**Electrochemical oxide path**

- (a) $S + OH^- \rightarrow S-OH + e^-$
- (b) $S-OH + OH^- \rightarrow S-O + H_2O + e^-$
- (c) $2S-O \rightarrow 2S + O_2$

Krasil'shchikov path

- (a) $S + OH^- \rightarrow S-OH + e^-$
- (b) $S-OH + OH^- \rightarrow S-O^- + H_2O$
- (c) $S-O^- \rightarrow S-O + e^-$
- (d) $2S-O \rightarrow 2S + O_2$

Bockris path

- (a) $S + OH^- \rightarrow SOH + e^-$
- (b) $SOH + OH^- \rightarrow S-H_2O_2 + e^-$
- (c) $S-H_2O_2 + OH^- \rightarrow S-O_2H^- + H_2O$
- (d) $S-H_2O_2 + S-O_2H^- \rightarrow H_2O + OH^- + O_2$

S represents a surface active site

Oxide path

- (a) $S + OH^- \rightarrow S-OH + e^-$
- (b) $2S-OH \rightarrow S-O + S + H_2O$
- (c) $2S-O \rightarrow 2S + O_2$

Yeager's path

- (a) $S + OH^- \rightarrow S-OH + e^-$
- (b) $S^Z-OH \rightarrow S^{Z+1}-OH + e^-$
- (c) $2S^{Z+1}-OH + 2OH^- \rightarrow 2S + 2H_2O + O_2$

Figure 2.7: Possible reaction mechanisms for the evolution of oxygen in alkaline media, as originally reported by Matsumoto and Sato⁵⁷. Note here S represents a catalytically active site.

2.4.3 Choosing a catalyst material

Following from research into the mechanistic pathways of the HER and OER a lot of attention has been devoted to the concept of a universal descriptor for catalyst activity; a single microscopic parameter that governs the activity of different electrocatalytic materials.^{3,43,58-60} Taking the simpler case of the HER, regardless of whether the mechanism follows the path 2.27 and 2.28 (Volmer-Heyrowsky) or 2.27 and 2.29 (Volmer-Tafel), the reaction proceeds through hydrogen adsorption at the electrode surface, H_{ads} . If the hydrogen binds to the surface too weakly, the adsorption (Volmer) step will limit the reaction rate, while if it is too strongly bound the reaction will be limited by the desorption step (Heyrowsky/Tafel). Thus, the overall rate of the HER and by association catalytic activity, is largely influenced by the free energy of hydrogen adsorption, ΔG_H .^{3,59} This was initially demonstrated by Parsons,⁵⁹ Conway and Bockris⁶¹ and later by Gerischer⁶² and Trasatti.^{63,64}

In the case of the OER, while less straightforward than the HER, pioneering studies by Bockris, Otagawa⁵⁸ and by Trasatti⁴³ proposed correlations between electrocatalysts activities and the bonding energies of OH, and later studies by Man⁶⁵ between activities and the energy states of reaction intermediates.

Plotting measured catalytic activity (such as J_0 , Tafel slope or TOF) as a function one of these descriptive parameters for various different catalyst materials usually revealed a ‘volcano’ type relationship, examples of which are shown in figure 2.8A and B for the HER and OER respectfully. These volcano plots tend to be symmetric around the centre and showed that the most active catalysts had moderate binding energies (optimum HER catalysts have adsorption energies close to $\Delta G_H = 0$)^{3,47,66,67}. This reflects the so-called Sabatier principle,⁶⁸ which states that reactants should be moderately adsorbed on the catalyst surface. Too strongly or too weakly bound leads to low electrocatalytic activity. Ultimately, an understanding of how to manipulate these binding energies of reaction intermediates on the catalyst surface is the key to designing materials with improved per site performance.³

Currently for the HER in acidic conditions, precious metals such as Pt, Rh, Ir and Re^{18,53,69,70} have been demonstrated to have optimal bond strength and thus maximum catalytic activity. In particular Pt has proven to be the most efficient and most stable electrocatalyst material, having a near 0 V onset potential and sitting right at the top of the hydrogen volcano curve.^{3,14}

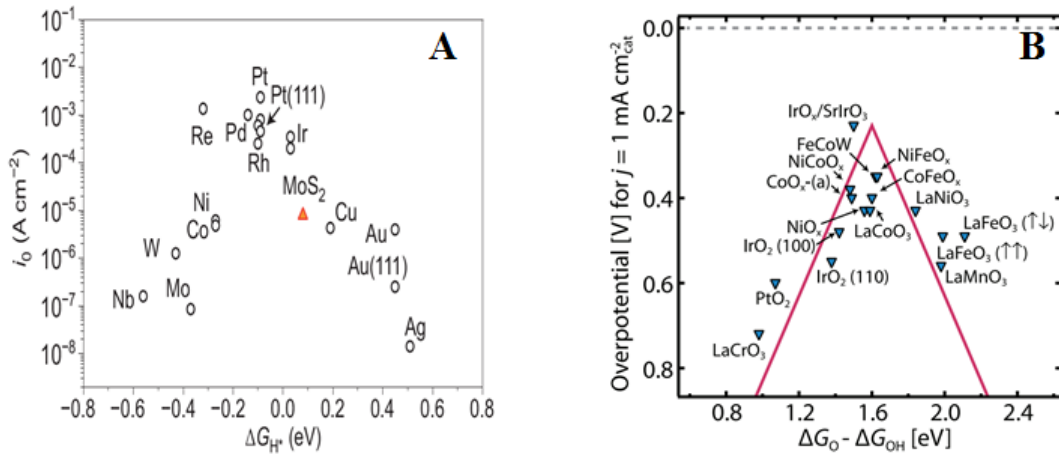


Figure 2.8: (A) HER volcano plot of catalyst activity (I_0) as a function of DFT-calculated Gibbs free energy (ΔG_H^*) of adsorbed atomic hydrogen for various pure metals and nanoparticulate MoS_2 . Pt resides at the top of the curve while MoS_2 is below on the shoulder.⁴² (B) OER volcano plot of onset potential versus the difference in Gibbs free energy of OER reaction intermediates, for various metal oxide surfaces obtained by reference³.

For the OER the best catalyst materials tend to be metal oxides or hydroxides, as represented in figure 2.8B (volcano curve). These include rutile, perovskite, spinel, rock salt and bixbyite oxides.^{3,10,65,71–74} Currently considered the benchmark catalyst are made from Ru and Ir, which both reside close to the top of the volcano curves. These materials exhibit some of the lowest overpotentials for the OER at practical current densities.^{75–77}

When choosing a material to be a good electrocatalyst for the HER or OER, volcano curves can provide a valuable insight. However, it is not sufficient for a material to simply have optimal binding energies, and other criterion must be considered when choosing an optimum catalyst material for the future. Some of which include:

- **Cost:** While precious metal-based catalyst such as Pt, RuO₂ and IrO₂ can achieve large reaction currents at low overpotentials, their scarcity and high cost makes them far from the ideal catalyst material.
- **Activity:** Efficient electrocatalysts need to be highly active, meaning maintaining low overpotentials at high current densities. Overall catalyst activity is important and not just per site activity (TOF). It should be possible to engineer the morphology of such catalysts electrodes to cluster a high density of active sites together, with a large exposed (accessible) surface area i.e. nanoscale catalyst.
- **Processibility:** Materials should be manufacturable on large scale, in a flexible processing manner that caters for adoption into a variety of electrode technologies. Flexible and transparent electrodes are potential future applications and catalyst material should not be a limiting factor when deciding on particular substrates. Furthermore, the ability to form composite catalysts from a collection of different materials with complementary properties is also highly desirable.

On top of this, materials that are environmentally safe and have low toxicity levels are other important requirements that must be considered when developing future catalyst. As a result of many of these influencing factors, alternatives to Pt, Ru and

Ir are being extensively investigated.^{3,4,6,18,56} At the forefront of this development is nanoscience research, where catalysts made of nanostructured materials can fulfil many of the above requirements. One such class of nanomaterial that has developed into a thriving research community is the class of two dimensional materials.⁷⁸ Harnessing the potential of 2D materials and combining them with other well-known materials such as 1D carbon nanotubes has the potential to revolutionize energy storage technologies. These are the class of materials utilized in this thesis and the following chapter will give a comprehensive introduction to them and their place as potential catalysts for the production of hydrogen.

Chapter 3

Materials for Electrocatalysis

The objective of this thesis is to present research investigating the catalytic properties of networks of 2D nanomaterials and 2D:1D nanocomposites for the evolution of hydrogen and oxygen. The materials featured are 2D nanosheets of molybdenum disulphide (MoS_2) and cobalt hydroxide ($\text{Co}(\text{OH})_2$) for the HER and OER respectively, and 1D carbon nanotubes (CNTs) for composites electrodes. In this chapter, general information on their structure, properties, synthesis and applications as electrocatalysts are reviewed. An overview of the general catalyst landscape for acidic HER and alkaline OER is also presented, with a discussion on common research strategies employed for optimising the catalytic activity. This gives context to the motivation for improving catalytic performance presented in chapters 5, 6 and 7. Finally, a detailed discussion on the properties and benefits of 1D:2D composite devices is also provided.

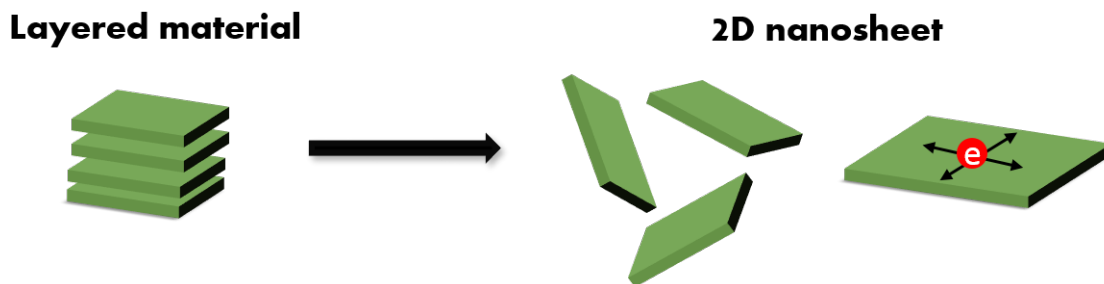


Figure 3.1: *Picture representing the exfoliation of bulk layered materials into 2D nanosheets. 2D materials restrict electron movement to a two dimensional plane*

3.1 Layered materials and 2D nanosheets

Two dimensional (2D) nanomaterials are those in which one dimension of the material is small enough ($< \text{nm}$) that electron movement through it is confined to a two directional plane. Perhaps the most well-known 2D material is graphene, a monolayer graphite. It consist of an atomically thin array of sp^2 -hybridized carbon atoms jointed in a honeycomb lattice.⁷⁹ Initially believed to be unstable in a free state,⁸⁰ graphene was successfully isolated by Geim and Novoselov in 2004^{79,81} through the delamination of layered graphite, and with it came an explosion of research into other layered and 2D nanomaterials.^{78,82–84}

The excitement around 2D nanomaterials stems from the fact that many layered inorganic systems have interesting properties linked to their anisotropy.⁸⁵ These layered crystals typically consist of an array of covalently bonded atoms in-plane, stacked together by van der Waals forces out-of-plane to form a layered structure. Breaking these weak out-of-plane bonds can result in the formation of 2D nanomaterials often referred to as nanosheets (see figure 3.1).^{78,83} Nanosheets consist of a small number of stacked layers, from monolayer to ~ 10 layers thick (few layer nanosheets). Restricting the dimensionality of a material into 2D can lead to remarkable changes in the electronic, optical and mechanical properties comparted to the bulk counterpart.⁸⁶

2D nanomaterials span a wide range of diverse families, with potential applications in a variety of technologies. Layered materials such as boron nitride,⁸⁷ transition metal dichalcogenides (MoS_2 , WS_2 , etc)^{78,84}, transition metal oxides (MnO_2 , MoO_2 , etc),⁸⁸ semiconducting III-VI compounds (GaS , InSe , etc.)^{89,90}, layered double hydroxides ($\text{Ni}(\text{OH})_2$, NiFe , etc)^{91,92} and exotic structures such as black phosphorous⁹³ can all be exfoliated into 2D nanosheets. Promising applications for these materials include energy storage and generation,⁹⁴ water purification,⁹⁵ mechanical reinforcement,⁹⁶ gas barriers⁹⁷, strain sensors,⁹⁸ printed electronics,⁹⁹ transistors,¹⁰⁰ photodetectors¹⁰¹ and the list goes on.

In particular for the area of energy generation and storage 2D nanomaterials have a lot to offer. This is an expansive field including technologies such as solar cells, fuel cells, batteries, supercapacitors and water splitting electrocatalysis. Nanostructuring a material drastically increases its specific surface area, lending itself to be highly useful in applications requiring many surface sites. Notably, the field of electrocatalysts is being transformed with the introduction of 2D materials.⁷⁸ Transition metal dichalcogenides (TMDs) have gained significant attention as catalyst electrodes for the hydrogen evolution reaction, while layered double hydroxides (LDHs) are paving the way forward as new OER catalysts. The following sections will discuss both these classes of materials in more detail.

3.2 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are a class of inorganic layered compounds that have received a significant amount of research attention in the field 2D nanoscience.^{83,84} TMDs have the general chemical formula MX_2 ; where M denotes a transition metal from group 4 to 10 and X is a chalcogen atom of sulphur, selenium or tellurium (see figure 3.2A).^{84,86} The family of TMDs spans a wide variety of combinations of M and X, and can behave as metals (e.g. NbSe_2), insulators (e.g. HfS_2) or semiconductors (e.g. MoS_2) depending on the coordination of the metal atom.¹⁰²

A single TMD monolayer has a structure consisting of three covalently bonded atomic sheets, X-M-X, in sequence forming a trilayer, as shown in figure 3.2B. In bulk, these sheets form a 3D layered structure, held together in stacks by van der Waals interactions. The structural coordination of TMDs can be either trigonal prismatic or octahedral leading to two general polytypes, 2H and 1T respectfully (the stacking sequence of these layers can however lead to other arrangements, such as 3R). Here the first digit indicates the number of layers in the unit cell and the letter indicates the type of symmetry with H standing for hexagonal, and T for tetragonal.⁸⁵ In general, for Group 6-based TMDs such as Mo and W the 2H phase is the most thermodynamically stable and more commonly found in nature.⁸⁵

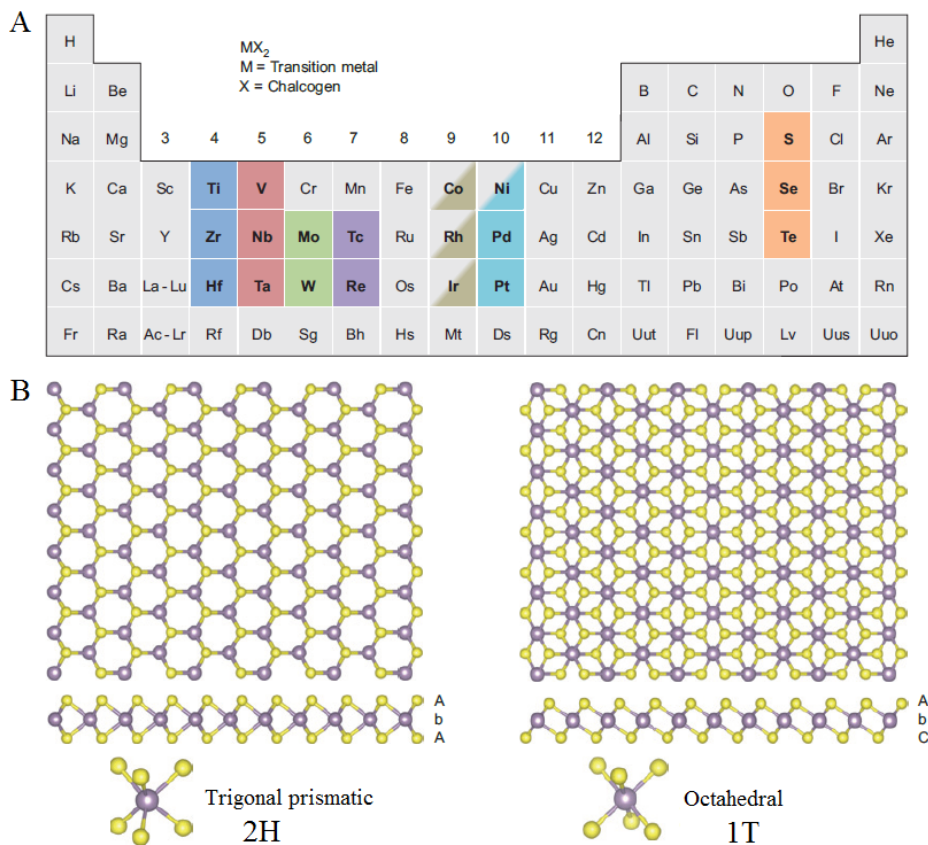


Figure 3.2: (A) Periodic table highlighting transition metals from group 4-10 which can be combined with the three chalcogen atoms to form a variety of TMD combinations. (B) Top and side view of the structure of a single layer TMD with trigonal prismatic (left) and octahedral (right) coordination. Purple atoms = metal, and yellow = chalcogen.⁸⁴

Similar to other layered compounds, exfoliating TMDs from bulk into 2D nanosheets can dramatically change the properties of the material leading a host of potential new application. For example, the indirect bandgap of MoS_2 (~ 1.3 eV) becomes direct in monolayer nanosheets (~ 1.9 eV).^{103,104} TMD nanosheets have been identified for applications in electrochemical energy storage devices such as battery electrodes,^{105–107} supercapacitors^{108,109} and electrocatalysts for fuel cells and hydrogen production.^{3,40}

In this regard, TMD nanosheets have been extensively examined as electrocatalyst for the HER in acid, with group 6 TMDs such as MoS_2 , WS_2 , $MoSe_2$ and WSe_2 showing the most promise.⁸⁴ Of all, MoS_2 has received the most attention and its catalytic activity has been well characterised. The following paragraphs will discuss the use of TMDs, in particular MoS_2 , as emerging catalysts materials for the HER in acidic conditions, giving an overview to the various strategies employed to improve

the catalytic activity. However it should be noted that, as is often the case, the rules for improvement of MoS₂ can generally be applied to other TMDs, and often MoS₂ acts as a sort of model system for HER catalysis research in general.

3.2.1 HER materials: MoS₂

Platinum is currently the most active HER catalyst, however with an earth crust abundance of only 0.005 mg kg⁻¹,^{47,110} and an annual average price of \$35 per gram in 2016¹¹¹, this high price and scarcity makes it far from ideal for large scale production of hydrogen. Bulk MoS₂, which occurs naturally as the mineral molybdenite, was the subject of early electrocatalytic studies, pioneered by Tributsch^{47,54} and others in the 1970s. At the time results suggested that MoS₂ was not an active HER catalyst, with exceedingly high values of Tafel slope of ~692 mV dec⁻¹, likely due to high internal resistance in the bulk semiconductor.

Interest in MoS₂ as a HER catalyst however was revived when density functional theory (DFT) studies emerged comparing MoS₂ to the active centres of natural hydrogen evolving enzymes. Hinnemann and co-workers were inspired by the enzymes nitrogenase and hydrogenase, both of which are highly active hydrogen evolving catalysts that contain an iron sulphur (Fe-S) cluster in their active centres, bound with an Mo atom.¹¹² Taking a biomimetic approach, they performed DFT calculations on MoS₂ edges, revealing the sulfide[1010] Mo-edges, containing uncoordinated S sites, had a highly advantageous hydrogen binding energy (figure 3.3A and B).^{112,113} At 50% hydrogen coverage, it possesses a ΔG_H of 0.08 eV, very close to the optimal value of 0 eV (see volcano curve figure 2.8).

Experimental confirmation that the edges of MoS₂ crystals are the catalytically active sites was performed by Jaramillo et al in 2007.⁴² Single sheet 2H MoS₂ nanoparticles were carefully grown on an Au[111] surface under ultra-high vacuum, where the basal plane to edge site ratio was systematically varied (figure 3.3C). The predominant exposed edge site in the MoS₂ crystal was the same[1010] structure predicted by DFT to be highly active.^{112,114,115} Indeed, the activity was found to

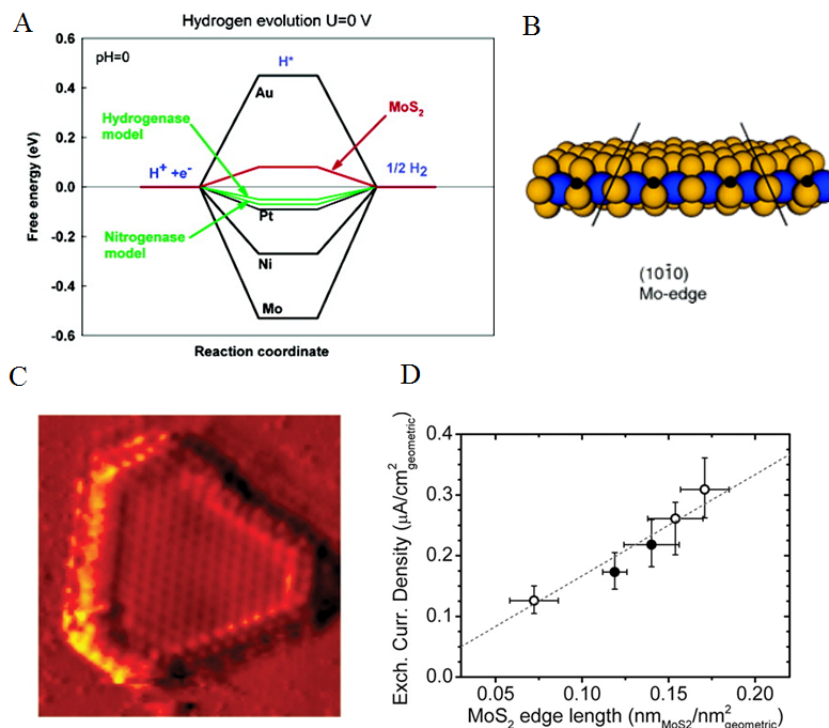


Figure 3.3: (A) DFT calculated free-energy diagram of hydrogen adsorption. (B) MoS₂ side view depicting the Mo-edge. Yellow atoms are sulphur, blue are Mo and black are hydrogen atoms.¹¹² (C) Single MoS₂ particle on an Au(111) surface, atomically resolved using STM. (D) Plot of exchange current density versus MoS₂ edge length, revealing the linear dependence of catalyst activity with edge length.⁴²

scale linearly with the perimeter length and not surface area, confirming the edges are the active sites of the MoS₂ crystal (figure 3.3D). This is a significant finding, implying that nanostructuring MoS₂, such as into nanosheets, to increase the number of edge sites should result in a highly efficient HER catalyst.

Since this revelation research into nanostructured MoS₂ and other TMDs as HER catalysts has continued to gain momentum, with the key challenge being to design catalysts competitive with Pt activities (or at least activity/€). This means reducing overpotentials required for large current densities while keeping production costs low. Three primary strategies in for achieving this are;^{18,47}

1. Optimise intrinsic activity; lower the binding energy of hydrogen at surface sites
2. Increase active site density; i.e. the number of active sites per unit area.

3. Improve conductivity; boost the electrical transport properties of the catalyst.

Perhaps the most obvious route to maximising MoS₂ activity is to improve the intrinsic reactivity of the material.^{47,85} In chapter 2 it was stated that an active HER catalyst should have a hydrogen binding energy such that the hydrogen is not too strongly nor too weakly bound to the catalyst surface.^{59,70} Theoretical studies by Tsai et al have suggested that enhancing the coupling between the supporting substrate and the active material can alter the hydrogen binding energy.¹¹⁶ It was shown that for the Mo-edge, strong adhesion of the catalyst onto the support can lower the energy of hydrogen adsorption, leading to improved performance. Alternatively Voiry et al proposed, based on first principle calculations, that straining nanosheets of 1T WS₂ can tune the hydrogen adsorption energy on the flake surface, showing a $\Delta G_H = 0$ eV at strain of 2.7%.^{5,117} Doping the MoS₂, for example with Co has also proven successful.¹¹⁸ DFT calculations showed that incorporating Co into the S-edge decreases the hydrogen binding energy from 0.18 to 0.10 eV. However while many of these reports boast impressive results, implementing these strategies is often not straightforward and experimental evidence of their efficacy is often lacking.

Instead, a more practical approach to maximising the electrocatalytic activity is to simply increase the total number active sites in a given electrode area. In general this involves increasing the density of exposed edge sites. A number of authors have approached this problem. Kong et al¹¹⁹ and others^{120–123} have grown films of vertically aligned MoS₂ nanosheets thereby maximizing the number of exposed edge sites (figure 3.4A). Reducing the particle size (figure 3.4B) to optimize the ratio of edge to basal plane atoms has also proven to be an effective strategy.^{124–128} Alternatively, introducing defects into the MoS₂ basal plane increases the number of active edge sites^{45,129} as has the use of amorphous instead crystalline MoS₂.^{41,130–133} Engineering the morphology of MoS₂ nanostructures to expose a high density of active edge sites such as single-crystal MoS₂ nanobelts,¹³⁴ nanotubes,⁴⁷ three dimensional MoS₂ spirals¹³⁵ or double-gyroid structures¹³⁶ is another effective method to improve HER activity (figure 3.4C).

Other approaches to increasing the density of active sites go beyond just increasing number of flake edges. Approximately only one quarter of MoS₂ edge sites

are actually active for HER.⁸⁴ Together with basal plane sites this means a relatively large percentage of a given nanosheet's surface is potentially wasted. This was considered by the Chhowalla group, where it was found that by tuning the contact resistance between the support and catalyst surface in 2H MoS₂, the inert basal planes could be 'turned-on' to participate in the HER.¹³⁷ Similar basal plane activities were realised by straining the MoS₂ nanosheet to form surface sulphur vacancies.¹³⁸

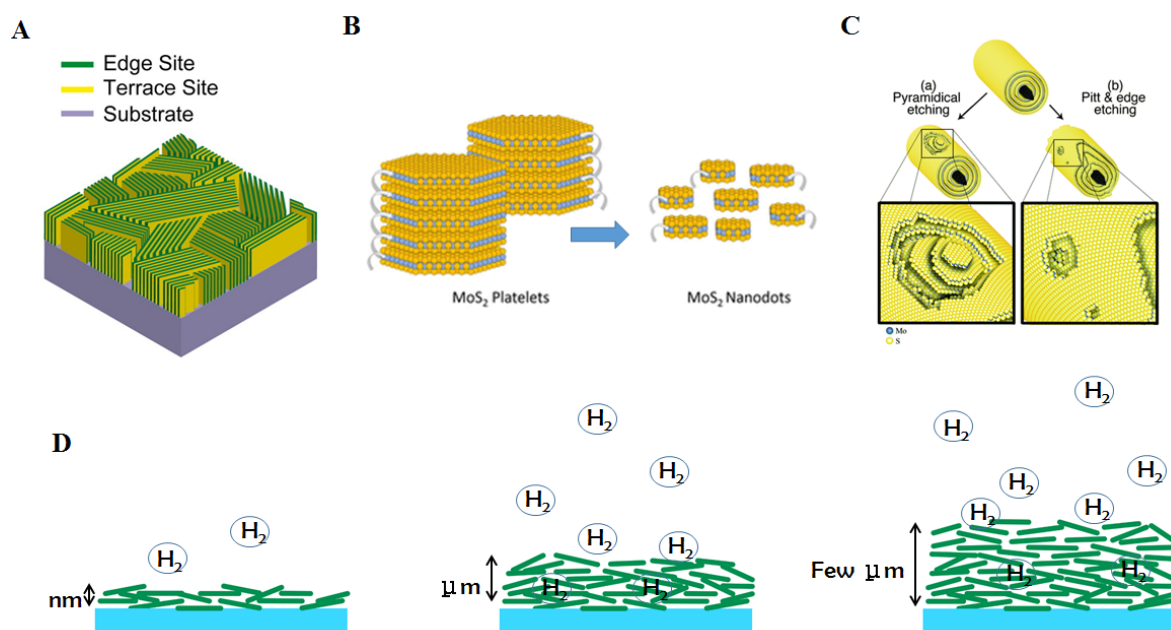


Figure 3.4: (A) Edge terminated MoS₂ nanosheets aligned perpendicular to the substrate.¹¹⁹ (B) MoS₂ platelets exfoliated into nanoparticles to increase the number of edge sites.¹²⁸ (C) MoS₂ nanotubes with etched surfaces to increase the number of exposed edge sites.⁴⁷ (D) Stacking MoS₂ nanosheets on a planar substrate to increase the film thickness. The thicker film have a higher number of active sites thus evolve more H₂

Another method for achieving highly active catalysts is to use thicker (i.e. higher catalyst mass loading) electrodes to increase the overall number of available active sites.^{45,118,122–124,130,131,133,139–143} Thicker electrodes should improve activity so as long as electrolyte is free to move throughout the material (i.e. films are porous) and there is good electrical contact between the current collector and the active sites. One way to achieve high mass loading is by utilizing a conductive 3D support, such as 3D carbon fiber paper, which gives impressive performances at high

loading.^{121,133,139,143} This method however means a significant mass percentage of the electrode is taken up by inactive support material. It can also limit the choice of substrate and electrolyte and may not be suitable for certain cell designs. A more flexible and straightforward method is to use a flat planar substrate and stack material to increase the mass per area (M/A) (figure 3.4D). This creates a porous network of interconnected nano-objects (sheets, particles, belts etc.). This has been attempted by many in the literature, however with limiting success. While the hydrogen production rate initially increases as the catalyst mass is increased, it invariably peaks at some loading level before falling off at higher M/A .^{45,118,130,141,142} Unfortunately, this reduction often occurs at quite low mass loadings,^{45,130,139,142} limiting the performance of the catalyst.

Finally, a third general strategy for enhancing catalytic performance is to improve the electrical properties of the catalyst films. For low conductivity electrode materials, performance can be limited by difficulties in transporting electrons from the external circuit to active sites. This is particularly likely in electrodes fabricated from interconnected nanosheets where, for example MoS_2 can give films with out-of-plane conductivity as low as $\sim 10^{-9} \text{ S m}^{-1}$.¹⁰¹ This is in part due to the intrinsically low conductivity of 2H MoS_2 , as well as to a large number of inter-flake junctions, increasing resistance.¹⁴⁴ To address this a common method involves synthesizing MoS_2 on various conductive materials, typically allotropes of carbon, including graphene sheets^{124,132,145–148}, carbon nanotubes,^{149–152} or carbon fibers.¹⁵³ One of the lowest non-nobel metal catalysts values reported has been demonstrated with an MoS_2 /nitrogen-doped reduced graphene oxide composite where the N-RGO is used as an anchoring site to synthesis the MoS_2 nanosheets. Values of only 56 mV overpotential to achieve 10 mA cm^{-2} , and superior exchange current densities of $7.4 \times 10^{-4} \text{ A cm}^{-2}$ were reported.¹⁵⁴ Additionally it has also become popular to decorate MoS_2 sheets with noble metal nanoparticles, such as Au or Pt.^{155,156} These integrated metal particles can improve the catalytic activity by enhancing the charge transport along the interplanar directions

Another highly successful approach has been to improve the intrinsic electrical conductivity of the material through phase transformation from the semi-conducting

2H to the metallic 1T polytype.^{123,139,155,157,158} Intercalating lithium ions into the van der Waals gaps of MoS₂ can promote this transformation^{5,157,158} and while less stable, this leads to enhanced catalytic performance.^{123,157,159} Interestingly, not only does 1T MoS₂ improve the transport of charges but it has been suggested by Voiry et al¹⁵⁸ that the improvements in HER activity are also due to the basal plane of the 1T MoS₂ becoming catalytically active. Catalyst electrodes were examined, made from a network of either 2H or 1T MoS₂ nanosheets, with flake edges electrochemically oxidised to block their involvement in the reaction. As expected the oxidized 2H-MoS₂ had reduced catalytic activity, however the HER performance of 1T were mostly unchanged, suggesting basal plane activity. Currently 1T MoS₂ is considered the most active form of the material, however it should be noted that even after transformation there is generally still a high percentage of 2H MoS₂ present. On top of this generally the 1T phase is meta-stable and often the structure is dynamically unstable.^{18,160}

Finally it is worth considering how the activity of other TMDs compares to that of MoS₂. This was investigated by Tsai et al who examined the intrinsic activity of various group 6 TMDs by DFT calculations.¹⁶¹ The edges of the TMDs were shown to have a ΔG_H close to zero, with the exception of the W edge in WSe₂ and S edge in MoS₂ which bound hydrogen too weakly or too strongly respectfully. Of the TMDs investigated MoSe₂ was predicted to be the most active catalyst based on these intrinsic measurements. This has been confirmed experimentally. A comprehensive study by Gholamvand et al¹⁶² compared the performance of six TMDs (MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂ and WTe₂) as HER catalysts with results showing a clear hierarchy of performance with selenides > sulphides > tellurides, and with MoSe₂ outperforming other materials. Beyond group 6 TMDs, monolayer VS₂ has also shown potential as an active HER catalyst, reaching close to Pt level activates.¹⁶³

3.3 Layered double hydroxides

Layered double hydroxides (LDH) are a family of ionic compounds composed of positively charged monolayers layers stacked together with charge balancing counterions and solvation molecules interlayered between them.⁹⁴ A structural model of a typical LDH is presented in figure 3.5 showing sheets of octahedrally coordinated metal cations in the centre and hydroxide groups at the vertexes. The chemical formula of LDHs can be represented by the general formula:¹⁶⁴

$$\left[M_{1-x}^{2+} M_x^{3+} (OH)_2 \right]^{x+} \left[A_{x/n}^{n-} \right]^{x-} \cdot mH_2O \quad (3.1)$$

where M^{2+} and M^{3+} are divalent (commonly Ni^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , or Zn^{2+}) and trivalent (commonly Fe^{3+} , Al^{3+} or Mn^{3+}) metal cations which make up the positive charge layer, and A^{n-} is a charge compensating inorganic or organic anion, such as CO_3^{2-} , Cl^- and SO_4^{2-} that reside between the layers. The value of x is generally in the range of $0.2 - 0.4$.^{165–167}

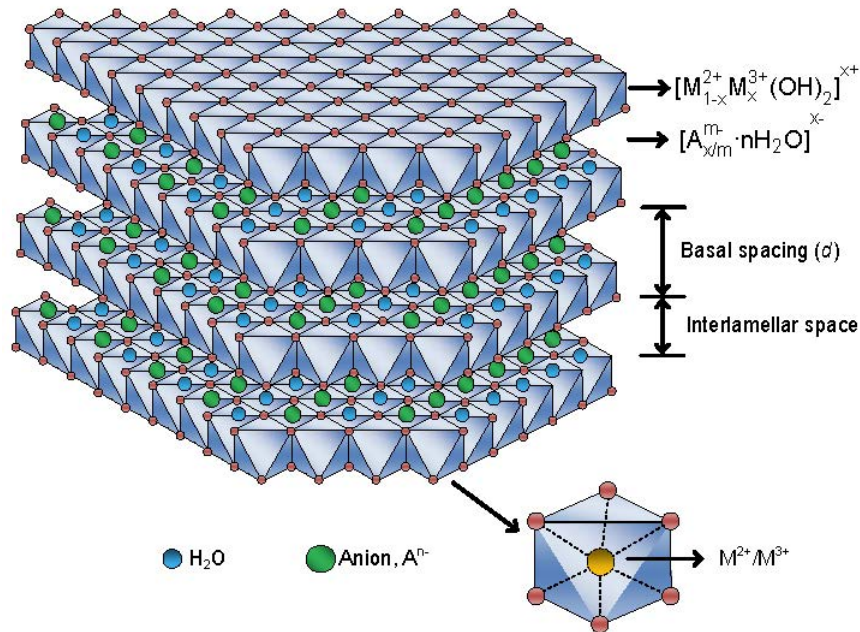


Figure 3.5: *Schematic representation of the LDH structure. Yellow = metal atom and red = hydroxide group.*

It is possible to loosely categorise LDHs into two groups; single or bi-metallic hydroxides, where the latter are those described by equation 3.1 and contain both divalent and trivalent cations. Much simpler are single metal hydroxides which contain just one transition metal (i.e. $x = 0$ in equation 3.1) and have the form $[M(OH)_2]$. In this form the basal plane is typically not charged thus no counter-ions are needed. This facilitates the exfoliation of LDHs into nanosheets without the need for intercalating ions (see synthesis section below). Common examples of these include $Ni(OH)_2$, $Mg(OH)_2$ and $Co(OH)_2$.

Of primary interest in this thesis is cobalt hydroxide. $Co(OH)_2$ can be found as two phases, α - $Co(OH)_2$ and β - $Co(OH)_2$, analogous to $Ni(OH)_2$ which can also be found in α or β form.¹⁶⁸ For $Co(OH)_2$ each phase is easily recognisable by their distinctive colouring, α - a green colour and β - a pastel pink.¹⁶⁹ β - $Co(OH)_2$ is a largely anhydrous phase made of the typical hexagonal stacking of neutral brucite-like layers (layer spacing of $\sim 4.6\text{\AA}$). α - $Co(OH)_2$ on the other hand is a hydrated phase, with water molecules intercalated in the sheet structure $(M(OH)_{2-x}(H_2O)^{x+})$.^{168–170} α - $Co(OH)_2$ sheets also have a positive charge and contain charge compensating anions (layer spacing $>7\text{\AA}$).¹⁶⁹

LDH nanosheets have found uses in a diverse variety of applications; as precursors for preparing CO_2 adsorbents,¹⁷¹ fire retardant additives,¹⁷² drug delivery hosts,¹⁷³ cement additives,¹⁷⁴ electrochemical supercapacitors,^{91,175} and electrocatalysts.^{78,94,176} In particular, for the oxidation of water in alkaline LDHs are a promising class of materials.^{18,56}

3.3.1 Materials for the OER: LDHs

The OER is a kinetically sluggish reaction, typically requiring higher overpotentials than the HER due to the complex 4-electron transfer process.¹⁸ Fortunately cheap transition metal oxide/hydroxides are emerging as stand out catalyst materials, beyond the usual platinum group metals.^{3,10,11,73,177–183} In particular LDH nanosheets containing Ni, Co and/or Fe are comparable or even outperforming benchmark Ru or Ir based oxides in alkaline conditions.^{78,92,184–187} To understand the landscape of non-noble metal OER catalysts it is useful to discuss current trends and research

strategies in the literature.

Active site

As discussed, the catalytically active sites of TMD nanosheets for the HER have been theoretically and experimentally identified as the edges. Subsequent research thus involved engineering materials with a high density of active sites. For metal oxide/hydroxide nanosheets the situation is not as straightforward and fundamental understanding of the active sites is lacking. Part of the difficulty lies in the diversity of active oxides/hydroxides materials, and the fact that these materials become oxidised under anodic potentials. Even for the subset of LDH materials no conclusive results have been reported. Theoretical evaluation from Chen and Selloni¹⁸⁸ and others¹⁸⁹ using DFT has suggested that defects in the layered LDH structures, particularly at steps, are the likely sites of catalytic activity. Similarly Mattioli and co-workers found using DFT-U calculations that the vertexes of Co-based cubane-like units were the most active sites of the catalyst.¹⁹⁰ However to date no adequate experimental analysis has been conducted to confirm these finding.¹⁹¹ Song et al⁹² found that by exfoliating a variety of layered hydroxides such as NiFe, CoCo and NiCo from bulk crystals into 2D nanosheets OER current density improved 3.5 fold on average and lowered Tafel slopes (note; the abbreviation NiFe etc. refers to the metals in the centre of the LDH structure in equation 3.1). This improvement was largely attributed to the increased number of edge sites associated with the nanosheets (see figure 3.6), however it was made clear that a rigorous investigation to prove this correlation was still required in literature.

With uncertainty surrounding precise active sites an alternative approach is to develop catalysts with a large surface area. This is done by highly nanostructuring the morphology for example into nanosheets,^{92,192–195} nanoparticles¹⁹⁶, nanowire,¹⁹⁷ or obscure shapes such as honey-combs¹⁹⁸ or nano-flowers.¹⁹⁹ This can result in highly active catalysts, with CuO/Co₃O₄ sea anemone-like nanostructures structures obtaining 10 mA cm⁻² at a very low 227 mV.²⁰⁰ 3D Ni foam substrates are also

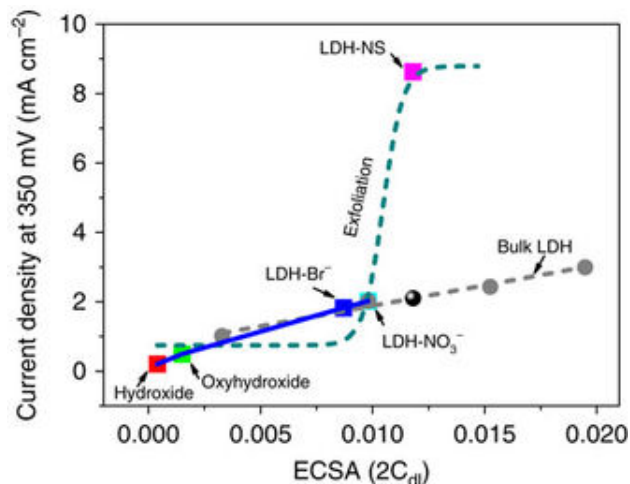


Figure 3.6: Current density at 350 mV overpotential plotted versus the electrochemically active surface area (ECSA) of CoCo-based materials. Solid blue square shows bulk LDHs and pink, exfoliated nanosheets (both 0.07 mg cm^{-2}). Upon exfoliation the ECSA of the material increases only slightly, while the activity increases by much larger extent. This increase in activity was attributed to an increase in the number of edge sites for the exfoliated nanosheets.⁹²

incredibly common, having large surface area while also physically supporting the materials.^{92,177,184,193,196,201} It is important to highlight however that the specific surface area of a catalyst is not necessarily the same as the active surface area and thus might not actually correlate to a high density of active sites.⁵⁶

Increasing surface area (or number of active sites) through increasing the film thickness is an obvious strategy however is rarely presented in OER, perhaps due to difficulties that arise with thicker films. For solution cast particulate films at higher thickness mechanical stabilities can be an issue. Akin to mud cracking, a state can be reached known as the critical cracking thickness, above which films inevitably crack upon drying, limiting the achievable thickness. Ghanem et al showed the activity of high surface area mesoporous cobalt hydroxide improves with mass loading on a planar substrate.²⁰² Current density rises by $>100 \text{ mA cm}^{-2}$ and overpotentials decrease by $\sim 100 \text{ mV}$ as loading is increased from $0.14 - 2.1 \text{ mg cm}^{-2}$. Further mass however resulted in reduced performance due to the catalyst physically detaching from the substrate. Others have shown similar trends of initial increase followed by decreases in performance with rising film thickness due mechanical, electrical, or diffusion problems.^{3,185,201,203-205} Often however these difficulties arise on

very thin, low mass films,^{185,204–206} and quantitative investigations into the relationship between film thickness and activity are never conducted. Instead of increasing film thickness, large $M/A_{\text{geometric}}$ films are examined typically using Ni foams in an attempt to achieve high performing catalysts.¹⁹⁹

Beyond nanostructuring, the most common approach in the literature for improving OER catalysts is to focus on discovering new chemical compositions and structural phases.⁹² This can result in novel catalyst materials with superior intrinsic activity. However, advancements with this approach can often seem unsystematic. Catalyst are prepared via an optimal synthetic route with a single nominal mass being deposited onto a support and tested, with little regard for the physical features of the film.^{183,207,208}

Typically the most successful metal combinations for oxide/hydroxide catalysts involve the incorporation of iron, usually as some derivative of NiFe or CoFe. The ideal stoichiometric ratio of Fe to Ni or Co is a debated topic but usually lie in the range of 5 – 35 %Fe.^{205,209} Highly active catalysts have been reported. Xu and co-workers developed a strategy to create NiFe hydroxide using a metal selenide as a nanostructured templating precursor.¹⁸⁴ The highly porous $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$ nanoplates achieved a current of 10 mA cm^{-2} at an impressively low 195 mV and a Tafel slope of just 28 mV dec^{-1} with a film of 4.1 mg cm^{-2} catalyst material. More recently Zhang presented a ternary FeCoW gelled oxy-hydroxide catalyst, showing extremely active performance.¹⁷⁷ Based on information gathered from DFT calculation, the unique addition of tungsten with FeCo oxy-hydroxide modulated the electronic and coordination structure providing a near-optimal adsorption energy for OER intermediates. This resulted in an overpotential of 191 mV to achieve 10 mA cm^{-2} current, the lowest value at the time.

Many varieties of Co based OER catalysts have been examined including metal oxides^{182,210} and hydroxides,^{194,210–212} perovskites,²⁰³ sulphides,^{213,214} nitrides,²¹⁵ and phosphates.²¹⁶ In terms of single metal cobalt oxides/hydroxides most reported are outperformed by the more sophisticated double or triple metal alternatives. Many have onset potentials well above 300 mV^{10,92,181,196} and most require overpotentials in the range of 350 – 450 mV to produce 10 mA cm^{-2} current,^{10,92,194,196,203,210–214,216,217}

with only a handful achieving it below 300 mV.^{198,200,218} The most active reported single metal Co-catalysts are those combined with conductive carbon additives. Cobalt oxide nanoparticles dispersed on N-doped carbon nanosheets were reported to obtained impressive overpotentials reaching 10 mA cm⁻² at 260 mV.²⁰¹

Similar to TMDs for the HER, poorly conducting oxide/hydroxide materials are often combined with conductive carbon, proving a successful recipe to boost performance.^{176,219} It should be noted however, unlike in the HER, carbon materials are more easily corroded at the high oxidising potentials of the OER. Generally carbon can be oxidised at potentials as low as 207 mV,²²⁰ which will obstruct the experimentally measured current in an OER investigation. More stable forms of carbon however, such as carbon nanotubes or graphene have better electrochemical corrosion resistances and are usable composite materials. In many works, carbon nanomaterials such as graphene,^{221–223} nanotubes^{185,201,213,224,225} and carbon black²²⁶ have been used to improve the electrical conductivity across the film. The carbon materials are usually used as anchoring sites for the catalyst nanoparticles, where chemical bonds are formed between materials. Most commonly carbon is oxidized to create defect bonding sites which are then used as nucleation sites to synthesize active material. Rarely are nano-conductors simply mechanically mixed to form composite films.²¹⁹ Finally, while the OER improvement associated with these conductive composites are well reported, investigations into the ideal quantity of non-active conductive material are generally missing.

3.4 Synthesis techniques

Whether examining properties on a lab scale or for use in large industrial applications the synthesis and production of 2D layered materials is of tremendous importance. Depending on the procedure, control over the composition, morphology, size and shape of the nanomaterials can vary, with the appropriate method generally dependent of the required application. For example, experiments on fundamental material properties may call for pristine single crystals, while battery or catalyst electrodes may require less stringent quality but prioritise a higher yield. On an

industrial level, a more scalable technology is often required combined with strict quality control, for example in the production of electrical circuits. At present there are a plethora of different synthesis and production techniques are available each with its own specific pros and cons. In general theses can be divided up into two classes; bottom up and top down synthesis. Bottom up methods involves growing a crystal, sometimes over a large area, by the stacking of smaller constituent blocks, such as atoms or molecules, onto each other. These create monolayer crystal planes which can further stack into a few layer nanosheets. Top down methods refer to taking a larger, macroscopic bulk layered material and shredding it down onto the nanoscale, by breaking the weak-out-of plane bonds, to form 2D nanosheets. A sample of these methods will now be discussed with particular attention paid to common techniques for the formation of 2D nanosheets of TMD and LDHs.

3.4.1 Mechanical exfoliation (scotch tape method)

This is a straightforward procedure based on peeling away layer upon layer of bulk crystal using adhesive tape, until monolayer nanosheets remain.^{227,228} The adhesive forces in the tape are strong enough to break the inter-layer van der Waals interactions to produce atomically thin flakes which are then identified by light interference.^{229,230} This method was pioneered by Frindt in 1963²³¹ on MoS₂ but popularised by Geim and Novoselov in 2004⁸¹ to obtain single crystal graphene from bulk graphite and has since been applied to many other materials, such as TMD's²²⁷ and BN.^{228,232} Very high purity, large single layer nanosheets can be obtained that are ideal for fundamental analysis of intrinsic properties.^{103,233–235} However low yield limits this to lab scale use.

3.4.2 Liquid phase exfoliation

Liquid phase exfoliation (LPE) is a straightforward, low cost production technique for creating liquid dispersions of suspended nanosheets under ambient conditions. This technique was first introduced by Coleman et al in 2008,²³⁶ exfoliating graphite into graphene in surfactant solution and is the method employed throughout this

thesis for exfoliating MoS_2 , Co(OH)_2 and CNTs. A more in-depth review of the techniques used are presented in chapter 4. In a nutshell, layered crystals in powder form are agitated through application of mild energy in the form of sonic waves^{82,237} from an ultrasonicator or high sheer forces from an industrial mixing unit.²³⁸ This causes the interlayer bonds to break, which are then stabilised against aggregation by matching surface energies of the nanoparticles with suitable solvents²³⁹ or through coating the nanoparticles in surfactant molecules.²³⁷ The resulting dispersion of suspended nanoparticles are quite stable over time and can be produced in large volumes (>100 s of litres)²³⁸ with concentrations exceeding 1 g L^{-1} .²⁴⁰ Both few layer (typically <10) and mono-layer nanosheets can be obtained through this method, although yield of individualized monolayers is low compared to other methods.

LPE is a highly versatile technique having been successfully applied to an ever-growing catalogue of layered materials, from graphene,^{236,241} BN,⁸⁷ TMOs,^{242,243} TMDs,^{82,244} GaS,⁹⁰ phosphorene^{93,245} and MXenes.²⁴⁶ Typically, LPE has not been used to exfoliate charged crystals such as the family of layered double hydroxides. However LDHs such as Ni(OH)_2 or Co(OH)_2 have a neutral basal plane, and thus have no counter-ions. As such theses LDHs have been successfully exfoliated using LPE in both solvent and surfactant environments.⁹¹

The main advantage of LPE, other than the quick and simple nature of the process is that the dispersions of suspended nanosheets are highly malleable, meaning techniques such as centrifugation can be applied to manipulate the average flake size of a dispersion, or spectroscopic techniques can be used to identify key features of the nanosheets.^{247,248} LPE is also compatible with solution processing techniques, such as spray casting or ink jet printing, and can be used to easily form composite dispersion of various nanomaterial. Finally LPE is also highly scalable and has even been demonstrated to work with a simple kitchen blender and Fairy Liquid soap.²⁴⁹

3.4.3 Chemical exfoliation

Chemical exfoliation is a broadly used term describing an exfoliation procedure typically performed in liquid phase involving some chemical or electrochemical interaction that assists in the delamination process. This includes electrochemical

exfoliation of graphene in suitable electrolytes,²⁵⁰ exfoliation of layered TMDs such as MoS₂ using ion intercalation,^{251,252} and ion exchange exfoliation of layered oxides and hydroxides.²⁵³

Ion intercalation involves adsorbing lithium ions between the van der Waals gaps of a bulk TMD crystal under inert conditions.^{251,252,254} Introducing water then causes the lithium ions to react, evolving hydrogen gas and in turn expanding the inter-layer spacing of the material, weakening the van der Waals bonds. The dispersion is then sonicated to complete exfoliation and the lithium ions pass into solution as hydrated Li⁺ ions. This method has the advantage of producing a high yield of monolayer nanosheets in a liquid suspension as well as changing the structural and electronic properties of the material (2H to 1T).⁸⁴

Delamination of layered oxides or hydroxides can be difficult due to strong inter-layer electrostatic interactions but may occur through the process of ion-exchange exfoliation. First reported by Adachi-Pagano et al in 1999,²⁵⁵ this involves modifying the interlamellar environment of the LDH by exchanging existing charge balancing anions with bulkier guest species, for example substituting in larger dodecyl sulphate.⁹⁴ This results in a high degree of swelling between the crystal layers, enlarging the interlayer distance and weakening the cohesive interactions, allowing for exfoliation using e.g. sonication or shaking. The liquid is typically a highly polar solvent such as formamide^{92,192} or water²⁵⁶ which is able to solvate the hydrophobic tails of the intercalated anions making exfoliation thermodynamically favourable.^{94,257} The disadvantage of chemical exfoliation is that it can be time consuming, sensitive to environmental conditions and incompatible with many solvents.²⁴⁰

3.4.4 Chemical vapour deposition

Alternatively to the other methods outlined, chemical vapour deposition (CVD) is a bottom up processing technique involving the decomposition/reaction of one or more gas phase compounds to give a non-volatile solid that builds up on a substrate. This can produce very high quality thin films and single crystal monolayer 2D materials, such as graphene or MoS₂.²⁵⁸ For MoS₂ CVD samples are typically grown by sulfurization of evaporated metal films in a high temperature (>500 C) furnace,

producing few layer or monolayer films.²⁵⁹ CVD is the most suited technique for high-end applications that require pristine electrical grade quality and uniformity over relatively large areas.

3.5 1D materials: Carbon nanotubes

Analogous to 2D materials, one dimensional (1D) materials restrict electrons movement to only one direction. These come in many forms such as gold nanowires or ZnO nano-swords, but perhaps the most well-known 1D material is the carbon nanotube (CNT). CNTs were initially observed in 1991 by Iijima;²⁶⁰ while attempting to build C₆₀ fullerenes he discovered tube like structures were also produced. These structures were made up of concentric cylinder shells, between 2 – 50 layers, separated by 0.35 nm which became known as multi-walled carbon nanotubes (see figure 3.7A). Later single-walled variants (SWNTs) were also produced.²⁶¹ SWNTs can be thought of as a single 2D sheet of graphene (i.e. hexagonally bonded sp²-hybridised carbon atoms) rolled up to form a cylinder of varying diameters (usually 1-2 nm) as in figure 3.7B. Since their discovery, CNT have created a huge amount of excitement in the material science community owing to their unique electrical, mechanical, magnetic, optical and thermal properties.^{262–267}

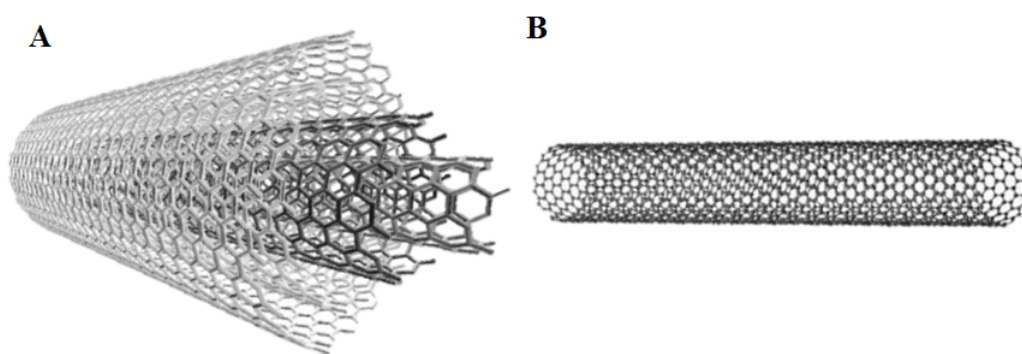


Figure 3.7: *Illustration of (A) a multi-walled and (B) a single-walled carbon nanotube.*

The electronic structure of CNTs can vary dependent on the chirality of the “rolled-up” graphene sheet. As shown in figure 3.8A, CNTs can be uniquely iden-

tified by their circumference (wrapping) vector, $\hat{C}$, which is specified by a pair of integers (n,m) that relate $\hat{C}$ to the unit vectors $\hat{a}_1$ and $\hat{a}_2$ ($\hat{C} = m\hat{a}_1 + n\hat{a}_2$).²⁶⁷ Three basic nanotube types exist depending on the values of (n,m) and angle θ ; armchair, zig zag or chiral tubes (see figure 3.8B). When n-m is divisible by 3 the tubes are metallic (about 1/3 of the time), otherwise they are semiconducting and thus have a band gap, E_g which inversely scales with tube diameter.^{267,268}

Due to the 1D nature of CNTs they possess outstanding electrical properties; charge carriers can travel through tubes with no scattering (ballistic transport),²⁶⁹ which leads to high current carrying capacities of $\sim 10^7$ A cm⁻².²⁷⁰ Furthermore, DC conductivities can reach greater than 200,000 S cm⁻¹,²⁷¹ and carrier mobilises as high as 10⁵ cm² V⁻¹ s⁻¹ have been recorded.²⁷²

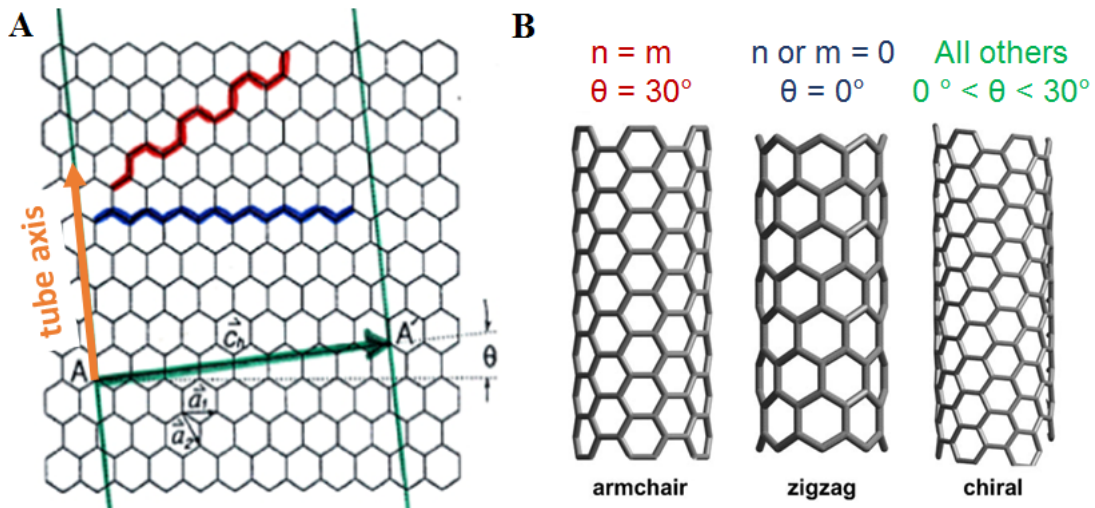


Figure 3.8: (A) To make a nanotube, take a strip defined by the green lines and roll it along the direction of the tube axis such that $A \rightarrow A'$. The angle θ is the chiral angle and is defined by the wrapping vector $\hat{C}$. (B) Depending on the values of (n,m) and θ the nanotubes are either armchair, zigzag or chiral.

While the diameter of CNTs are on the nanoscale, their lengths can extend far greater, up to a few centimetres,^{273,274} giving aspect ratios of 1000s or more. This high aspect ratio leads to incredible mechanical properties. Nanotubes can have a Young's modulus of over 1 TPa and an outstanding tensile strength greater than 60 GPa, orders of magnitude stronger than carbon fibres or high strength steel wire (steel wire only has 210 GPa and 4.4 GPa respectively).^{269,275,276}

Synthesis

There are three main ways to synthesis CNTs: Arc discharge, laser ablation and CVD. Arc discharge involves the vaporisation of catalyst-containing graphite electrodes by forming an electric arc between them, under inert conditions.²⁷⁷ This can create fullerenes, MWNTs and SWNTs on the metal catalyst. Alternatively, laser ablation involves the removal of material from a graphite/catalyst target using a pulsed laser.²⁷⁸ The vaporised material is transported by a carrier gas to condense as a soot, containing CNTs. Finally, CVD, the most common method used, involves the decomposition of vapour phase metal-catalyst/gaseous hydrocarbon mixtures at high temperature.^{279,280} These interact, initiating the growth of CNTs.

As produced, tubes typically contain a mixture of lengths, diameters and chiralities, as well as impurities such as amorphous carbon and metal contaminants from the catalysts. Developing production techniques to control chirality (i.e. produce solely metallic or semiconducting tubes) is a current pursuit of many CNT synthesis research. Typically, impurities in the CNT powder can be removed through refluxing in acids, however this can damage the CNT and leave unwanted functional groups on the surface which can alter the tube properties.²⁸¹

Commercially available CNTs generally come as a powder, containing bundles of closely tied tubes. This aggregation is due to attractive van der Waals interactions present between the highly flexible nanotubes.²⁶⁹ For many applications it is desirable to separate CNTs, for example into a liquid dispersion. This can be achieved using similar LPE techniques described previously for the exfoliation of layered materials. Through manipulation of surface energies nanotubes can be stabilised in a number of liquids environments, such as organic solvents,^{282–284} aqueous-surfactant media²⁸⁵ and polymers matrixes.²⁶⁶ Furthermore, functionalising the CNTs can change the surface-solution interactions allowing tubes to be dispersed in other liquids such as water without stabilising agents.²⁸⁶ This is commonly achieved by oxidising the CNT surface in an acid which allows for hydrogen bonding.²⁸⁷

Once in solution form CNTs can be deposited using liquid processing techniques such as printing, spray casting or membrane filtration. Deposited CNTs generally arrange into interconnecting conductive networks which, on their own, may be useful

for a number of applications such as transparent conductors. Even more useful however is combining CNTs with other nanomaterials, such as 2D nanosheets, to form composite films with a combination of properties. These are now discussed.

3.5.1 Composites

Inorganic layered compounds, such as those described above, possess a range of exciting physical and chemical properties, particularly when exfoliated on the nanoscale. Often however, devices built from layered materials suffer from low electrical conductivities and poor mechanical integrity, limiting the performance.^{144,288,289} This is especially the case for thick or high mass loading electrodes, required for practical applications.^{13,21,22} For example, 2D metal oxides have high capacitance, ideal for achieving high energy densities ($E = CV^2/2$) in the next generation of supercapacitor electrodes, however their low conductivity means high resistance, reducing the power density ($P = V^2/4R_s$) and limiting performance. Low power density is also a limiting factor in Li battery electrode, partly due to low electrical conductivity in cathode. In addition, these electrodes have the tendency to crack due to stresses caused by Li intercalation during charge/discharge cycles.

For nanosheet electrocatalyst, such as those for the HER and OER the requirements for high electrical conductivities and strong mechanical properties are obvious. Efficient transport of charges to or from the conductive support to the outer regions of the catalyst electrode is critical for reducing kinetic barriers and lowering overpotentials. Mechanical stability during gas evolution is another important factor vital for optimising catalyst electrodes. As bubbles are generated and flow through the porous material cracking can occur damaging the electrode, ultimately leading to failure (figure 3.9). On top of this, increasing mechanical properties, e.g. toughness, increases the critical cracking thickness.

A straightforward solution to overcome many of these shortcomings is to form composite devices of two or more materials with complementary properties (figure 3.9).²⁹⁰ This concept is nothing new. Mixing straw with mud to form mechanically

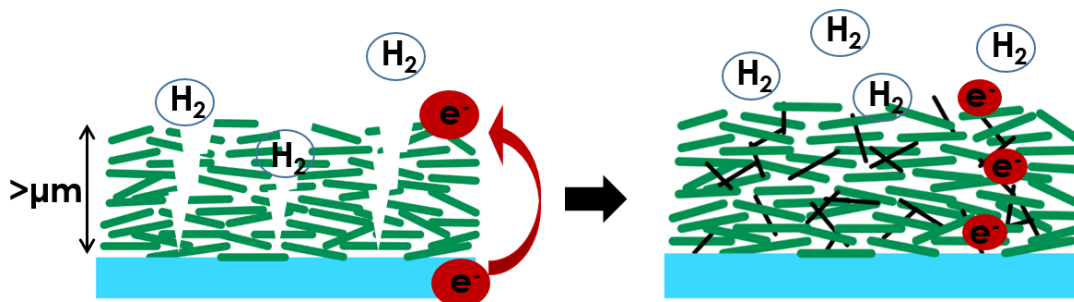


Figure 3.9: *Thick films of stacked nanosheets can become limited by poor charge transport from the current collecting substrate to the outer regions of the film. Mechanical weaknesses can also lead to cracking, particularly during gas evolution. The addition of CNTs to the nanosheet film aids in transporting charges and acts as a binder keeping the film mechanically stable.*

stable bricks has been known for thousands of years. In the world of nanoscience, composites films are often composed of materials of varying dimensionalities. Mixing 2D nanomaterials with 0D, 1D or 2D fillers has been investigated for Li battery systems,^{291–296} supercapacitor system,^{242,288,297–301} and electrocatalysts.^{129,289,302–308}

In particular 1D:2D composites have proven advantageous. The high aspect ratio of 1D materials means they can easily span a connected network through a 2D matrix, requiring only small amounts for beneficial gains (see percolation section below). In this regard 1D carbon nanotubes, with excellent mechanical and electrical properties, are ideally suited for composites with inorganic 2D nanosheets. In addition, both CNTs and layered materials can be exfoliated in the same liquids using LPE, facilitating the formation of hybrid films by simple solution mixing. This is a powerful technique and allows for the conductivity of films to be tuneable over a wide range.

Individually CNTs may be metallic or semiconducting but when formed into bulk networks they form a pseudometal with conductivities in the range of 10^5 S m^{-1} .^{309,310} When combined with 2D materials these CNTs form a conducting network that spans through the 2D matrix. The conductivity of these hybrid films are typically lower than CNT networks alone due to higher junction resistances³⁰⁹ nonetheless show drastic improvements, for example $\times 9$ orders of magnitude difference from MoS_2 only to an MoS_2/SWNT hybrid.¹⁴⁴

Percolation theory

For composites of 2D:1D it has been shown that electrical improvements to the film follows percolation scaling law^{144,293}. Percolation theory is a mathematical model which describes the behaviour of networks of randomly varying connections, and is used to characterise transitions in materials properties, such as metal/insulator transitions.³¹¹

In its simplest form imagine a square lattice with grids that are either occupied, “on” or not occupied, “off” and where the fraction of occupied sites are denoted p . Two sites are connected if there is a continuous unbroken path of “on” sites between them, and a group of connected sites forms a cluster. If a cluster grows large enough that there is a connected path from one end of the lattice to the other, a threshold is reached known as the percolation threshold. The fraction of occupied sites at the percolation threshold is denoted p_c , the critical fraction. Above p_c , the number of connections continues to grow and $p \rightarrow 1$.³¹²

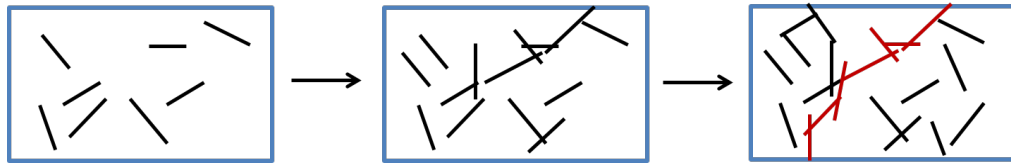


Figure 3.10: *The black rods represent CNTs. As more CNTs are added, initially clusters are isolated until eventually a path is formed connecting one end of the container to the other. This is the percolation threshold.*

For a composite network of 1D:2D nanomaterials each “off” square is a 2D nanosheet and each “on” square is a highly conductive nanotube, such that the percolation threshold now describes the point at which there is a continuous connection of nanotubes forming a conductive path from one end of the insulating 2D matrix to the other (see figure 3.10). Around the percolation threshold any random site that is now occupied by a nanotube, is very likely to coalesce two unconnected clusters of tubes when compared to the limit of high or low site occupancy (p). Thus at this point there are very rapid changes in cluster size and so conductivity,

as p increases above p_c . Above the percolation threshold the conductivity of the composite depends on p and p_c as:

$$\sigma \propto (p - p_c)^n \quad (3.2)$$

Where the exponent n is known as a critical exponent and reflects a remarkable aspect of percolation theory; the behaviour of a material property (around the percolation threshold) scales independently of the structure or property being measured and is only dependent on the dimensionality of the system i.e. 2D, 3D, etc.³¹¹

As a result of percolative scaling of conductivities in systems with 1D nano-conductors, only a small volume of CNT is needed, usually < 10 vol% to reach percolation threshold.^{144,242,289,293,309} This is advantageous as not only does it allow more space to be filled with active material, it means less nano-conducting fillers are required which can save costs.

As well as provide enhanced conductivities, the high strength and stiffness of nanotubes can also be useful to improve composite mechanical properties. CNTs have been employed as a filler to reinforce mechanically unstable systems, such as in polymer composites^{313,314}, Li barriers^{107,292,293}, supercapacitors^{242,288} and even in some commercial tennis rackets. An advantage of both mechanical and electrical improvements with CNT means there is no longer a need for polymeric binders or supporting substrates. This allows free-standing films to be made that can be both flexible and have a high mass of active material.

Chapter 4

Experimental Methods and Characterisation

In this chapter the experimental procedures used to fabricate, characterise and test catalyst films of 2D and 1D nanomaterials are outlined and a brief description of the theoretical background for each technique is also provided. Bulk layered materials are processed into large quantities of 2D nanosheets using liquid phase exfoliation. Carbon nanotube dispersions are prepared in a similar fashion. Centrifugation is used to manipulate and control the nanosheet dimensions and dispersions are characterised using UV-vis spectroscopy and transition electron microscopy (TEM). Nanosheet/nanotube network thin films are created using vacuum filtration and electrode devices are prepared using contact based transfer methods. Catalyst devices are characterised using scanning electron microscopy (SEM), profilometry and 4-wire electrical analysis. Finally, electrochemical analysis is performed using impedance spectroscopy and linear voltage sweeps in a 3-electrode electrochemical cell.

4.1 Dispersion preparation and characterisation

4.1.1 Liquid phase exfoliation

Sonication

To produce 2D nanosheets from a bulk layered material, layers must be stripped away from the parent crystal and stabilised from aggregation. Similarly, nanotubes must be separated out of bundles to obtain the benefits from their high aspect ratios. As previously discussed, this is achieved through the process of liquid phase exfoliation (LPE).^{82,83} This is a simple process whereby the attractive van der Waals forces between nanoparticles are broken through an input of energy and stabilised in the presence of a suitable liquid.^{237,239} This energy input is either in the form of ultrasonic pressure waves from a sonicator or through sheer forces using sheer mixing equipment (rotor stator mixers or even kitchen blenders). While sheer mixing allows for industrial scaling,²³⁸ ideal for applications with a commercialization focus, the nanomaterials presented in this thesis have been prepared through sonication, using a high power sonic tip (VibraCell CVX; 750 W, 60 kHz)

This process is illustrated in figure 4.1 and involves mixing a carefully chosen quantity of starting material (in powder form) with a suitable stabilising liquid and immersing the sonic (probe) tip into the solution. A piezoelectric converter induce mechanical vibrations in the probe, which in turn create high frequency ultrasonic sound waves (>16 kHz) in the presence of a liquid. These longitudinal waves cause water molecules to oscillate around a mean position, compressing and stretching their molecular spacing. Eventually the cohesive forces in the liquid breaks down and voids are created, known as cavitation bubbles.³¹⁵

These cavitation bubbles expand and then collapse violently on compression, creating high temperatures and pressure. This in turn imparts shear forces to exfoliate the nanomaterials surrounding them.⁸² Delamination of layers or debundling of nanotubes results in a dispersion of separated 2D or 1D nanomaterials. Sonication however rarely produces single isolated particles such as monolayer nanosheets,

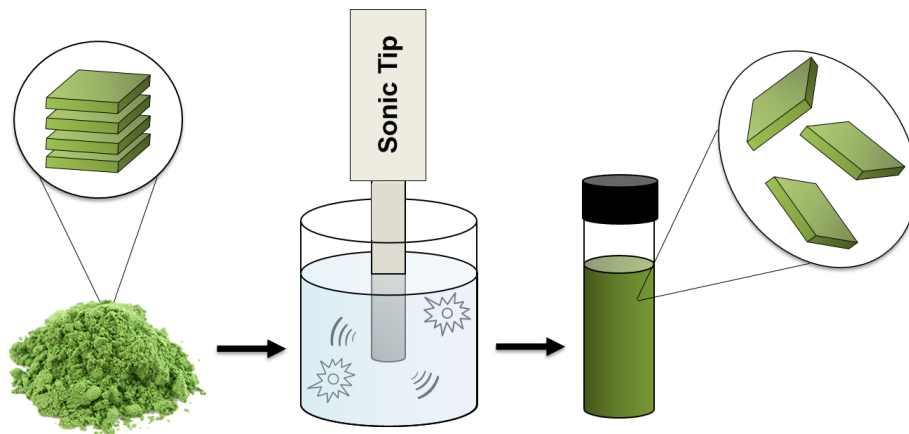


Figure 4.1: *Illustration of the liquid phase exfoliation procedure.*

rather few layer nanosheets or a range of nanotube bundle thickness are obtained.

Sonication can also induce scission of nanosheets whereby the in-plane covalent bonds of the flakes can be broken, shortening their lateral size.^{316,317} Here the mean flake length, L , is proportional to the sonication time, t , as $L \propto t^{-1/2}$.³¹⁸ This relationship holds for MoS_2 ,¹⁰⁴ $\text{Ni}(\text{OH})_2$,⁹¹ and 1D carbon nanotubes.³¹⁷ This is advantageous for electrocatalysts as it allows for a high yield of nanosheets with large edge to basal plane ratios, although for 1D nanotubes this shortens the aspect ratio.

All nanomaterial dispersions presented in this thesis were prepared using tip sonication, typically producing ~ 80 mL of dispersed material for a given process. Bath sonication is also possible however is far less powerful and is instead used to ‘freshen’ older samples by separating any re-aggregated particles, or to help blend mixed dispersions of nanosheets and carbon nanotubes.

Stabilisation

Upon exfoliation the newly dispersed nanomaterials must then be stabilised against re-aggregation and sedimentation. This is done through the choice of exfoliating liquid, generally either a suitable organic solvent or an aqueous surfactant. In either case interactions at the nanosheet/liquid interface reduce the net exfoliation energy and impede flocculation. Solvent stabilisation is described in the context of solubility parameters, such as surface tension and Hansen parameters. Effective solvents are

found by matching these parameters with those of the solute and the nanoparticles reach an energy minimum and become stabilised.^{318–320} This allows nanomaterial such as carbon nanotubes, MoS₂ and others to be exfoliated in common solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) or isopropanol (IPA) and remain in stable dispersions for a long time.

Another common approach is to exfoliate nanomaterials in water and surfactant.^{237,241,321} This coats the surface of the nanomaterials with surfactant, preventing it from re-combining through electrostatic interactions. Surfactant stabilisation is well documented for MoS₂,²⁴⁹ CNTs,³²² and some LHDs such as Ni(OH)₂.⁹¹ Common surfactants include sodium dodecyl sulfate, sodium dodecylbenzene sulfonate and sodium cholate (SC), the latter of which is used for all dispersions in this thesis.

Surfactants are amphiphilic molecules, generally made up of long alkyl chain tail groups and ionic head groups. The tail groups coat the non-polar nanomaterial through London interactions, while the ionic head group dissociates from the tail due to Brownian motion and forms a diffuse cloud of counter ions around the particle, creating an electrical double-layer.³²³ Neighbouring particles are stabilised by Coulomb repulsion, characterised by the Zeta potential (ζ); the electrical potential at the interface between the layer of bound surfactant and the bulk fluid (generally in the range of 25–65 mV).³²⁴ There are also non-ionic surfactant, such as Triton X, that prevent re-aggregation through steric hindrance of the tail groups.³²⁴ Stabilising dispersions with surfactants generally gives highly reproducible, long-term stable, high quality dispersions.

For many applications high boiling point and toxicity make the use of solvents undesirable. In comparison surfactant solutions are both non-toxic and environmentally benign. This makes dispersion preparation and film formation much more straightforward. It can however be difficult to fully remove surfactant from the nanosheet surface which may block surface sites of the nanomaterial and thus block potential catalytic activity. Thus during film formation, steps must be put in place to remove as much surfactant as possible. Nonetheless some surfactant will remain, even after processing becoming trapped between restacked nanosheets.²⁴⁰

4.1.2 Centrifugation

Upon exfoliation the resulting dispersions tend to be highly polydisperse, containing a wide distribution of nano to micron sized objects. This can mean a variety of bundle diameters for 1D nanotubes or a range of flake lengths and thicknesses for 2D nanosheets, as well as larger unexfoliated material. For many applications it is often highly desirable to control the size of the material under consideration; the optoelectronic properties of nanosheets can change with layer number,⁸⁶ electronic properties change with size⁸¹ and electrocatalytic properties can change with the fraction of edge to basal plane sites.⁴² Dispersions with well-defined nanoparticle sizes can be readily achieved using centrifugation.

Centrifugation works by rotating a liquid dispersion at high speed around a fixed axis for a period of time. The centripetal force acts perpendicular to the axis of rotation and proportionally on each particle depending on its mass. This results in particulate content being separated out along the radial direction of the container toward the base, with larger aggregates or unexfoliated particles sedimenting out faster than lighter constituents. Thus, at a given time different sized particles will either be in the supernatant or sediment.

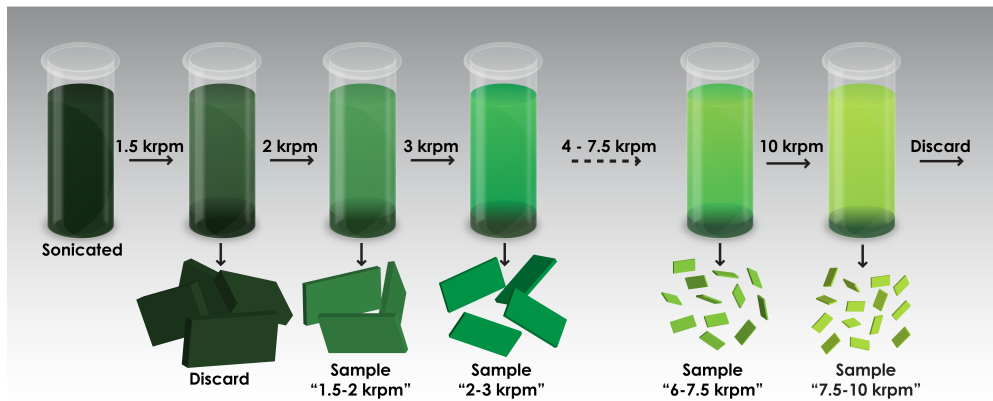


Figure 4.2: *Size selection scheme for liquid cascade centrifugation*

Liquid cascade centrifugation

Centrifugation can be used to separate out exfoliated material into segments containing well defined crystallite sizes. This is done using a technique called liquid cascade centrifugation (LCC).²⁴⁸ As shown in figure 4.2, this is a multi-step procedure whereby progressively faster rotation speeds are used to trap different sized particles between centrifugation stages. The resulting sediment can then be redispersed in fresh surfactant to retrieve the sample. This is a simple yet versatile procedure that has been applied to many systems such as MoS₂,²⁴⁷ WS₂,²⁴⁸ Ni(OH)₂,⁹¹ GaS,⁹⁰ black phosphorus⁹³ and graphene.³²⁵ Determination of the particle size and dispersion concentration can then be achieved using absorption spectroscopy, TEM and AFM analysis.

4.1.3 UV-vis spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy is a multipurpose analytical technique which can be used to determine characteristics of colloidal dispersions, such as concentration and average nanosheet length and thickness.^{247,248} A reference sample is placed in a quartz cuvette and irradiated with a parallel beam of monochromatic light of altering wavelength from 200 – 800 nm. The intensity of the incident and transmitted light is measured using a photodetector. The reference is then replaced by the colloidal dispersion and the incident and transmitted light intensity (I_0 and I), is recorded, as in figure 4.3. If $I_0 > I$ a portion of light has been absorbed and/or scattered by the sample and the extinction, Ext can be defined as:

$$Ext = -\log(I/I_0) \quad (4.1)$$

Absorption occurs when photons match the energy gap of the atoms or molecules in the sample, exciting the outer electrons and causing transitions to higher energy states (excitations).³²⁶ For molecules this is from the HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) and for solids the valence to conduction bands. By recording the attenuation of light for various wavelengths an extinction spectrum is obtained which is made up of components

of both the absorption and scattering spectrum.^{91,247} After removing the extinction spectrum of the reference sample, the remaining spectrum is directly dependent on the number of light absorbing/scattering particles which itself relates to the concentration of the dispersion, C . It is also dependent on the path length, d , which is typically between 1 – 10 mm for standard cuvettes. This is described in the Beer-lambert law for particulates in a liquid, such that:²⁴⁷

$$Ext = \varepsilon C d \quad (4.2)$$

Where ε is known as the extinction coefficient and is a function wavelength. Once $\varepsilon(\lambda)$ is known for a particular material determination of concentration becomes straightforward.^{247,322}

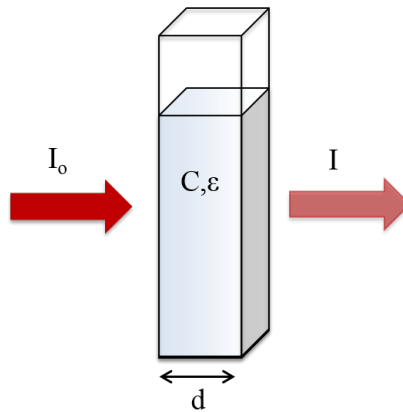


Figure 4.3: *Monochromatic light of intensity I_0 passes through a quartz cuvette of length d , containing a collide dispersion. The nanomaterial in the dispersion adsorbe and scatter light, proportional to the concentration, such that the transmitted light intensity is reduced to I .*

Recently it has also been shown that determination of average nanosheet flake length (L) and number of layers (N) for MoS_2 nanosheets can simultaneously be extracted using UV-vis.^{247,248} MoS_2 has well documented excitonic transitions that appear as broad peaks in the extinction spectrum.³²⁷ It was found that the relative intensity of the B-exciton and energy of the A-exciton shifted systematically with nanosheet size. By measuring these changes values for $\langle L \rangle$ and $\langle N \rangle$ can be determined using:

$$\langle L \rangle (\mu m) = \frac{3.5Ext_B/Ext_{345} - 0.14}{11.5 - Ext_B/Ext_{345}} \quad (4.3)$$

$$\langle N \rangle = 2.3 \times 10^{36} e^{-54,888/\lambda_A} \quad (4.4)$$

These shifts in the excitonic transitions are a result of electron edge and confinement effects on exfoliation, which results in a change of electronic band structure of layered materials. However these models break down at very large (>350 nm) or very small (<70 nm) nanosheet sizes. This technique has since been demonstrated on nanosheet dispersions of WS_2 ,²⁴⁸ black phosphorus,⁹³ $Ni(OH)_2$ ⁹¹ and graphene.³²⁵

4.1.4 Transmission electron microscopy

Transmission electron microscopy (TEM) was used in this thesis to characterise 2D nanosheets; confirm their exfoliation state, measure their lateral size and aspect ratio. All TEM imaging and analysis was performed by Dr Andrew Harvey. A coherent, monochromatic stream of electrons is formed by an electron source, through thermionic or field emission and accelerated towards a thin (<200 nm) electron transparent specimen. The stream is confined and focused using apertures and magnetic lens systems into a thin focused beam that interacts with the sample. Transmitted electrons are then magnified using a lens systems onto a detector.

These electrons can be of three forms. Zero energy loss or slightly scattered electrons are those used to create a traditional TEM image. The slight scattering cause a spatial variation of the transmitted e^- intensity, which is used to make a 2D projected image of the nanosheet. Energy loss electrons lose energy by exciting a core shell electron in the material. This energy loss can be used as a finger print to identify elements. Highly scattered electrons can be detected at a given angle and are used to make up a dark field image. Electron diffraction patterns can also be detected, created at the back focal plane of the objective lens. This is due to electrons having wavelengths similar to typical lattice spacing.³²⁸ TEM typically uses accelerating voltages of 100-400 kV (200 kV for all TEM images in this thesis) and magnifications from 50 – 1,000,000 and have a resolution of ~ 0.2 nm. Resolution

is limited by aberration.

4.2 Film formation

Liquid dispersions are highly processable and can be readily converted into thin films. There are a plethora of liquid phase processing techniques developed to form thin films, including spin coating, dip coating, Langmuir-Blodgett coating, ink jet printing, rotogravure printing, spray casting, drop casting, vacuum filtration, screen printing, doctor blading and freeze drying. Many factors influence the choice of film formation technique and each offer a unique set of advantages and disadvantages depending on the desired application. The method of deposition can effect film morphology, porosity, electrical and mechanical properties, uniformity and surface roughness. Also of importance is the ability to mix-and-match materials to form composite films, flexibility in shape, design and feature size of the film, as well as the ability to deposit onto a variety of substrates.

Depending on the application film thickness must be considered. For this thesis thin electrocatalysts, ~ 100 nm thick are required as well as thick micron sized free-standing films. Thus vacuum filtration combined with contact transfer methods were chosen as the most useful method to create our catalyst films.

4.2.1 Vacuum Filtration

Vacuum filtration is a straightforward process whereby liquid dispersions are drawn through a porous membranes via the application of a pressure gradient, as outline in figure 4.4A. As liquid is sucked through the membrane nanomaterial is deposited on the surface, creating a thin film. Spatially uniform films formed of restacked nanosheets tend to deposit horizontally in-plane, as depicted in figure 4.4B. Uniformity occurs because the vacuum filtration process is inherently self-regulating. Localised flow-rate is limited by the thickness of deposited material at a given point. If one area becomes too thick then deposition rates at that point are reduced relative to another spot. This guarantees an even distribution of material across the membrane.

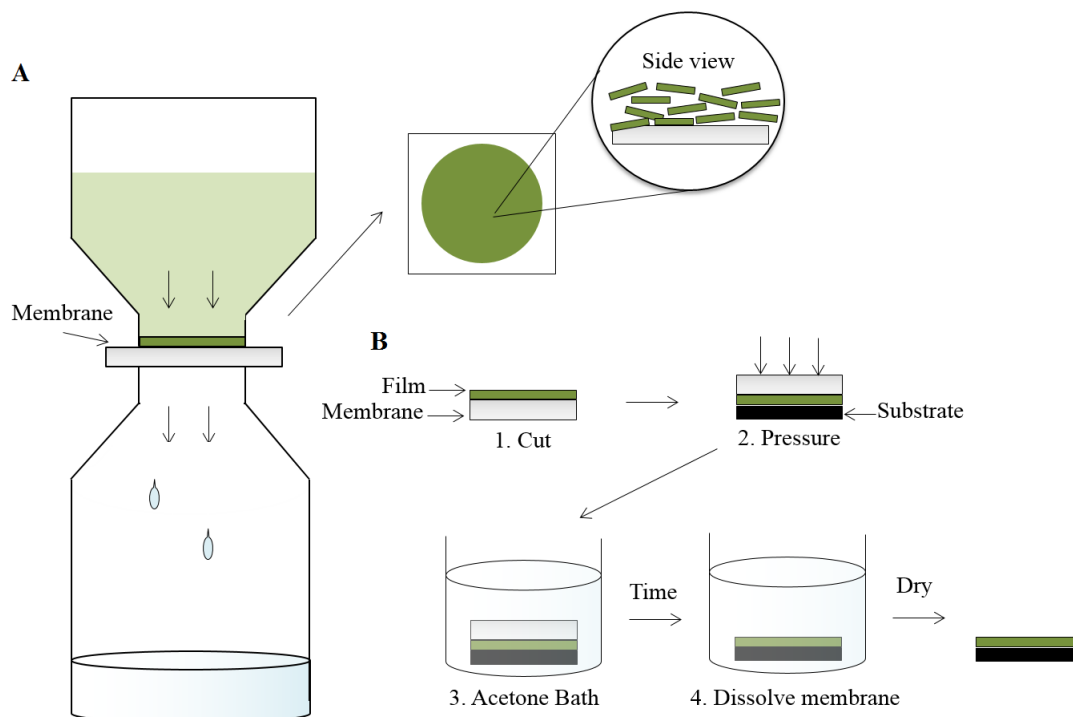


Figure 4.4: (A) Illustration of filtration apparatus. Dispersions are filtered through a porous membrane, creating a film of stacked, interconnected nanosheet networks. (B) Transfer process whereby films are cut to a desired shape, pressed onto a substrate and placed in a series of acetone baths to remove the membrane.

Vacuum filtration provides excellent control over the mass of deposited material and facilitates the production of films with a wide range of mass loadings. By filtering precise volumes of dispersions with known concentrations the mass per unit area (M/A) of films can easily be calculated. Once film thickness (t) is measured this allows for film density, ρ , to be found using $M/A = t \times \rho$. Another key advantage is the ease at which composite films can be produced by simply mixing dispersions of two different materials. Crucially the precise ratio of mixture can be readily controlled by altering the volumes.

To prepare a dispersion for vacuum filtration it is initially bath sonicated for a short period to reverse any minor re-aggregation that may have occurred, as well as to mix combined materials thoroughly. A suitable filter membrane is chosen depending on the intended purpose. Typically nitrocellulose membranes with a pore size of 25 nm are used as they can be easily dissolved in acetone during the trans-

ferring process (described below). To make free-standing films, polyester (PETE) membranes are used as they offer the least resistance when removing the film. After filtration there may exist excess surfactant residual remaining in the film which must be removed. Filtering large volumes of deionised water through the porous film can remove much of the remaining surfactant.

4.2.2 Film transferring

Films must be then converted into an electrode device by transferring the film onto an appropriate substrate via an acetone bath transferring technique. This is outlined in figure 4.4B and involves removal of the cellulose membrane from the film with a series of acetone baths and through application of pressure, transferring the film onto a supporting substrate. The versatility of this technique is apparent as the film shape can be cut into any design and the substrate can be any number of flat surfaces such as glass slides, ITO, glassy carbon, metal foil, SiO₂, etc.

4.3 Film characterisation

4.3.1 Profilometry thickness measurements

A contact profilometer was employed to accurately measure the thickness of the transferred films. This instrument is used to measure surface profiles, giving information such as surface roughness and step height. The film must be prepared on a smooth, rigid substrate for example a glass slide, which is placed on a centre stage. A stylus is dragged laterally across the surface of both the substrate and sample film with a constant force, recording information about the surface topography. Variations in the stylus height as a function of position are measured and converted into a digital signal which can be read as a surface profile. From this the film step height can be recorded. Profilometry is relatively non-destructive, allowing for catalyst films thickness to be measured before electrochemical experiments.

4.3.2 Scanning electron microscopy

A scanning electron microscope (SEM) can be used for imaging surface structures and analysing chemical composition of samples. In this work SEM was used to examine morphological features of the nanomaterial films, such as film uniformity, porosity, nanosheet alignment, or the degree of mixture of nanotube/nanosheet composites. Similar to TEM an electron beam is formed through either thermionic or field emission and directed toward a sample. SEM however typically operates at much lower energies, of the order of 100 eV – 50 keV. Electron beam size is ~ 1 nm and it rasters across the sample building up a picture point-by-point. Figure 4.5A shows a detailed breakdown of an SEM apparatus, which contains an anode, a system of magnetic lens and apertures (condenser and objective), scanning coils (used to raster scanning) and detectors. The condenser lens systems are used to control beam spreading while the objective lens is used for focusing.

Electrons that are emitted in the backward direction are detected (i.e. not transmitted electrons). As a result, to avoid charging effects samples must be either conductive or made conductive by a thin (few atoms) coating of metal particles. When the beam strikes a sample, electrons are scattered and loose energy due to collisions with atoms in the sample.³²⁹

The volume inside the sample where electrons interact has a tear drop shape (figure 4.5B), and signals that are collected from this volume include:

1. Secondary electrons: Low energy (inelastic) electrons that have been knocked out of an atom. With a very short range these are highly surface sensitive and give detailed topographical information about the sample.
2. Back scattered electrons: Electrons that have been elastically back scattered and leave the sample with high energy. Originating deeper in the sample they are less surface sensitive but are strongly dependent on sample atomic number and are thus useful for picking out areas of heavier elements (higher contrast).

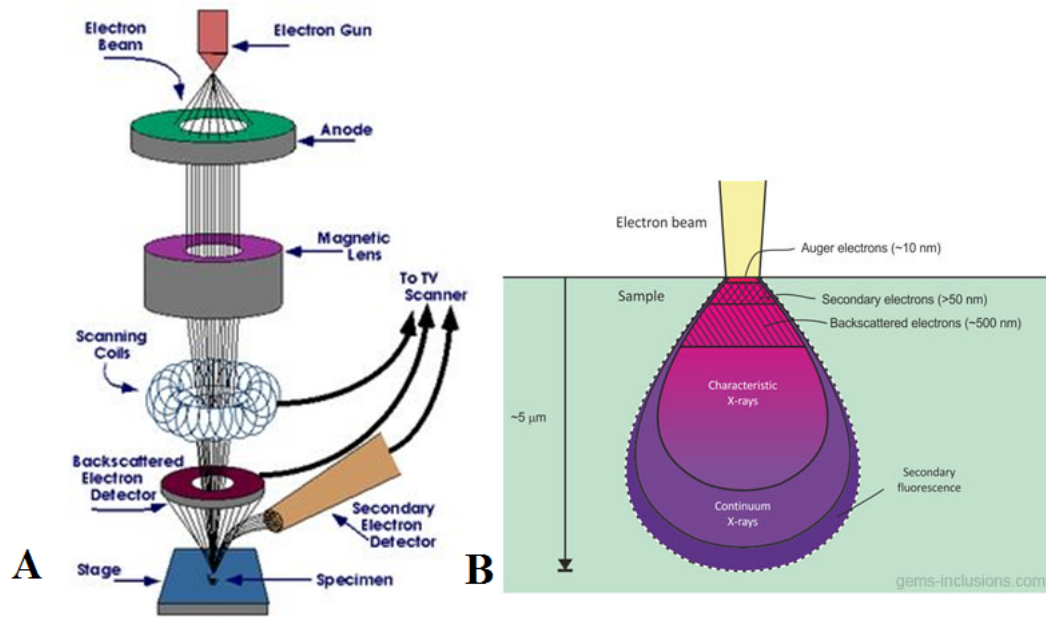


Figure 4.5: (A) Components of an SEM instrument. (B) Interaction volume; the size of the tear drop depends on the atomic number of the sample as well as its density and electron acceleration energy

3. Auger Electrons and characteristic X-rays: These are used to give compositional information (elemental analysis). Core electrons can get excited and transfer energy to another electron which is emitted or can relax by emission of photons.

Each emitted signal is collected by a separate detector and counted to build up an image. The resolution is typically a few nanometres.

4.3.3 Electrical measurements

The electrical conductivity of films is measured using a 4-wire measurement technique. Wire contacts are attached to the film as shown in figure 4.6, spaced at known distances apart. A constant current is supplied across the outer two wires (1 and 4) while a voltage drop is measured across the inner wires (3 and 4) using a high impedance volt meter. The advantage of using a 4-wire set-up is that error due to contact resistances is reduced as no current flows through the voltage measuring contacts.

Current-voltage (I-V) curves are collected and display Ohmic behaviour for all

materials ($V = IR$). Values for resistance, R , can then be determined via;

$$\frac{V}{I} = R = \frac{\rho L}{wt} \quad (4.5)$$

Measuring the length (L), width (w), and film thickness (t), allows for the calculation of bulk film resistivity (ρ). From this the electrical conductivity of the film can be determined ($\rho = 1/\sigma$). Importantly, conductivity measured here is the in-plane DC conductivity of the film. Measuring the out-of-plane conductivity would also provide very useful information relating the catalyst films however was not found to be practical to measure and is thus absent from this report.

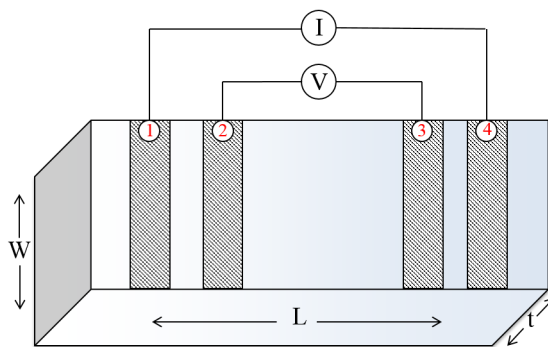


Figure 4.6: *Four wire electrical measurement of a thin film.*

4.4 Electrochemical measurements

To examine the electrocatalytic behaviour of different 2D nanomaterials for the HER and OER, a number of electrochemical measurement techniques were carried out. In general, these involve recording the electrical response of a catalyst to an applied potential. From this current-potential behaviour important kinetic properties can be extracted such as the exchange current, Tafel slope, overpotentials and electrode resistances. To examine the I-V characteristics of a system a potentiostat instrument is used (Gamry Instruments), which supplies a driving potential to the electrochemical cell and measures the corresponding current flow. Within the potentiostat is a digital signal generator which is used to supply a variety of outputs.

4.4.1 Three electrode cell

A simple electrochemical cell used for analysing a catalyst is shown in figure 4.7 and consists of three electrodes; firstly a working electrode (WE), which is the primary electrode of interest and contains the catalyst film under investigation. A counter electrode (CE) is used to complete the electrical circuit. The CE must have a larger surface area than the WE so as not to limit the reaction rate and is often prepared from graphite or platinum. Together the WE and CE make up the cathode and anode of the cell. However to experimentally study the capabilities of an electrocatalyst, the reactions at the cathode and anode must be accessed individually. This is done using a reference electrode (RE) which is placed close to the WE and allows either the cathodic or anodic potential to be measured independently, with respect to the reference electrode. All electrochemical experiments conducted in this work were carried out using this standard three electrode cell, at room temperature (unless otherwise stated). The three electrodes are connected to the potentiostat and immersed in an electrolyte solution; 0.5 M H_2SO_4 for HER and 1M NaOH for OER. These electrolytes were chosen to allow for easy comparison to literature.

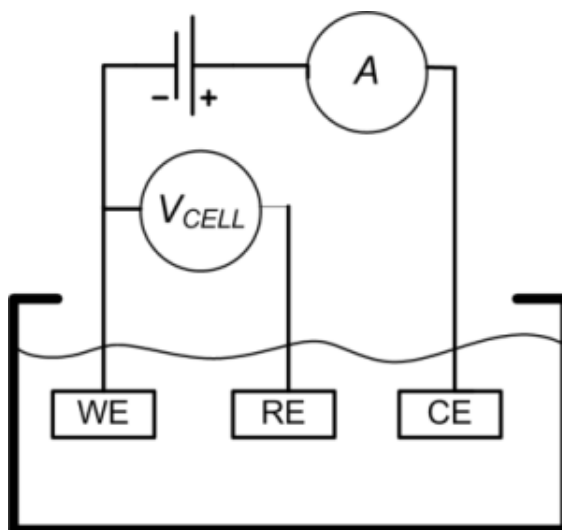


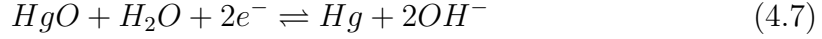
Figure 4.7: *Three electrode electrochemical cell.*

4.4.2 Reference electrode:

The reference electrode is used to monitor the potential difference across the WE interface by providing a fixed potential against which the WE potential can be measured. The choice of reference electrode in this work was dependent on the electrolyte and reaction being examined. For the HER in 0.5 M H_2SO_4 (pH = 0) acidic conditions a reversible hydrogen electrode (RHE) was used. This consists of a thin platinum/palladium wire (HydroFlex) which facilitate the redox reaction:



For the OER in 1 M NaOH (pH = 14) alkaline conditions a mercury-mercuric oxide (Hg/HgO) electrode (CH Instruments, cat no CHI 152) with aqueous 1.0 M NaOH filling solution was used as the reference standard due to its strong chemical stability in alkaline solutions, with redox reaction:



To simplify understanding and comparison to the literature, all measured potentials in this work are quoted as overpotentials. For the HER this is straightforward. Because the redox reaction in the reference RHE electrode is the same as the reaction under investigation any potential deviations from the reference can be measured directly as overpotential (additional potential required after the thermodynamic potential) as:

$$\Delta E_{\text{WE/RHE}} = \eta + iR_u \quad (4.8)$$

Where iR_u is the potential drop due to the uncompensated solution resistance between the WE and RE (see EIS section below). For the OER measuring the overpotential however it is less straightforward and requires the measured potentials using the reference electrode to be converted into overpotential using the standard reaction potentials. Typically, the potential of references electrodes are measured and quoted versus the standard hydrogen electrode (SHE).

The SHE is the standard reaction potential for the reduction of hydrogen, under standard conditions, defined as 0 V at all temperatures. This is referred to as the universal reference electrode, against which potentials of any other reference electrode can be compared. In this regard the difference between the RHE and SHE can be confusing. The SHE is a theoretical concept and is defined under IUPAC as a platinum electrode in contact with an acidic solution of unit H^+ activity, and saturated with pure H_2 gas with a standard pressure (or more precisely, fugacity) of 10^5 Pa. Compared to SHE the RHE can be considered as a reference hydrogen electrode that is pH dependent. The potentials of each electrode are related through the Nernst equation;

$$E_{RHE} = E_{SHE} + \frac{RT}{nF} \ln \left(\frac{[H^+]^2}{P_{H_2}/P_0} \right) \quad (4.9)$$

Where $[H^+]$ is the concentration of H^+ ions and is related to the pH ($pH = -\log[H^+]$), P_{H_2} is the partial pressure of the hydrogen gas, P_0 is the standard pressure of 10^5 Pa and all other symbols are their usual meanings. Assuming standard H_2 partial pressure equation 4.9 can be simplified to;

$$E_{RHE} = E_{SHE} - 0.059 \times pH \quad (4.10)$$

And as E_{SHE} is defined as 0 V, E_{RHE} becomes;

$$E_{RHE} = -0.059 \times pH \quad (4.11)$$

From 4.10 it is clear to see that the RHE is the same as the SHE at $pH = 0$, however its value changes vs. SHE with increasing pH. This concept is represented visually in figure 4.8 and shows that as the pH increases, the potentials of the HER and OER decrease versus the SHE but remain separated by the thermodynamic potential of water splitting, 1.23 V. Therefore at pH 14, $E_{RHE} = -0.828$ V vs. SHE. The potential of the Hg/HgO reference electrode thus can be calculated from thermodynamic data (or given from manufacturer specifications) as $E_{Hg/HgO} = 0.098$ V vs SHE in pH 14. Combining these equations gives, $E_{Hg/HgO} = 0.926$ V vs RHE and thus the thermodynamic onset potential of the OER is 0.303 V vs Hg/HgO. Therefore any

potential measured above 0.303 V is considered overpotential as:

$$\Delta E_{WE/H_2O} = 0.303 \text{ V} + \eta + iR_u \quad (4.12)$$

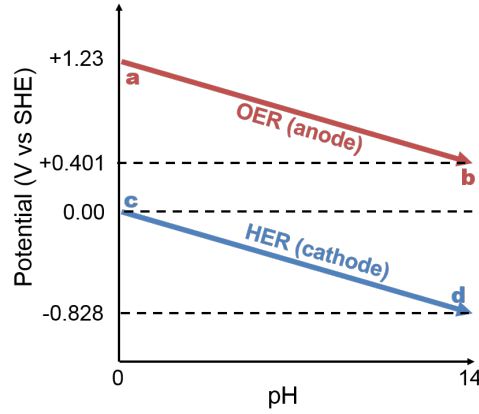


Figure 4.8: Graph showing potential versus the SHE of the OER and HER changing with pH. Adapted from reference³³⁰.

To probe the electrocatalytic activity of nanomaterial network films the primary electrochemical measurement techniques employed are, linear sweep voltammetry (LSV), chronopotentiometry and electrochemical impedance spectroscopy (EIS).

4.4.3 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is the most common technique employed to evaluate the current response of catalysts to applied voltages. This is a straightforward technique which consists of a single unidirectional voltage sweep, from an initial potential V_i , to a final potential V_f , in a time t . An example of the applied waveform is shown in figure 4.9A. The resulting I-V response of the catalyst creates the familiar polarisation curves as shown in figure 4.9B.

The shape of this current response is dictated by the slowest kinetic process at a given potential i.e. either by the kinetics at the interface during a charge transfer reaction or by diffusion transport of species to and from the surface. Initially as

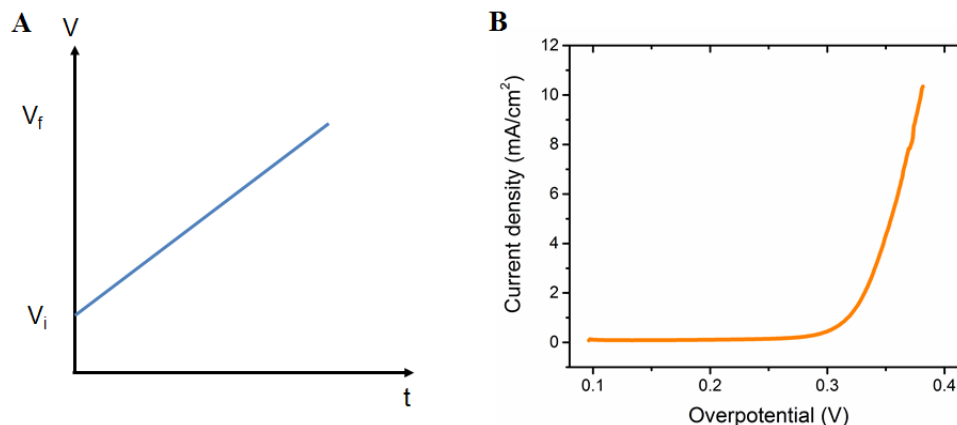


Figure 4.9: (A) Waveform of a linear voltage sweep. (B) Typical polarisation curve obtained after applying an LSV for the oxygen evolution reaction.

potential is applied the current density is low, until the required thermodynamic and onset overpotentials are reached. Afterwards increasing the potential increases the current density and the cathodic or anodic Butler-Volmer equation is used to describe the I-V relationship of the initial potential region before diffusion limitations.

To measure the kinetics parameters accurately steady state conditions must be reached, where the appearing signal is mainly controlled by the kinetics of the reaction. A system is in steady state when the applied potential at the WE gives a resulting current that is independent of time. This will depend on the scan rate dV/dt (mV s⁻¹), which must be slow enough to allow a system to reach steady state before increasing to the next potential step. Scan rates of less than 5 mV s⁻¹ are typical of electrocatalytic experiments.

4.4.4 Chronopotentiometry

In electrocatalysis chronopotentiometry is used to study the stability of gas evolution systems. In this technique one applies a fixed current density, which corresponds to a fixed rate of gas production, while the corresponding potential required to generate this is measured as a function of time. The current density is generally high (10 – 100 mA cm⁻²) to simulate real operational use. The more inefficient a system is, the larger the potential required to generate a given current. The potential increasing

over time is often an indication of the catalyst becoming unstable due to cracking or physical detachment from the electrode.

4.4.5 Electrochemical Impedance spectroscopy

Electrochemical Impedance spectroscopy (EIS) is a highly versatile tool for probing the electrochemical response of a system to an applied alternating potential. For the purpose of this thesis EIS is used to calculate the charge transfer resistance of the reaction (HER or OER) and to measure the uncompensated solution resistance. The main concepts of EIS follow the principle that an electrochemical cell behaves as an electrical circuit and thus can be modelled as such. Initially a small sinusoidal (AC) voltage is supplied to the cell, and the resulting current response is acquired, for a range of different frequencies (usually ten Hz or below). This allows an equivalent electrical circuit to be determined that mimics the behaviour of the cell. Finally components of the equivalent circuit can be related to key physical or chemical characteristics of the electrochemical system.³³¹

Similar to resistance, impedance (Z) is a measure of the ability of a circuit to resist the flow of electrical current ($Z = E/I$) where the supplied potential, E and responding current, I are frequency dependent sinusoidal signals. Initially a DC signal is supplied with a small (1 – 10 mV) AC perturbation superimposed:

$$E = E_0 \cos(\omega t) \quad (4.13)$$

Where E_0 is the amplitude of the perturbation, ω is the angular frequency, and t is the time. Typically, electrochemical I-V responses are non-linear (Butler-Volmer) however focusing at a small enough portion of the I-V curve, it appears linear. Thus as the applied AC voltage is kept small the I-V response is (pseudo-) linear, meaning the measured current is at the same frequency, however it may be shifted in phase and amplitude:

$$I = I_0 \cos(\omega t - \phi) \quad (4.14)$$

Where I_0 is the amplitude of the response and ϕ is the phase angle shift. The

corresponding impedance gives information relating to the system and is measured for a range of frequencies as the chemical and physical characteristics of the cell will vary with frequency, and thus the amplitude and phase of the response will as well. To facilitate analysis the impedance can easily be converted into complex notation; in Cartesian coordinates by $Z = Z_{real} + iZ_{imag}$ (i.e. on the real and imaginary axes) and in polar coordinates by $Z = |Z|, \arg(Z)$ where $|Z|$ is the modulus, in Ohms, and $\arg(Z)$ is the argument or phase angle in radians.

Equivalent circuit

If the I-V response is purely Ohmic (i.e. not phase shifted) then the impedance can be modelled as a resistor, typical of a poorly conducting solution, and $Z = E/I = R$. If the current is $+90^\circ$ out of phase with the potential the response is purely capacitive, typical of the solid-liquid interface (double layer) and $Z = E/I = -i/\omega C$. In a real electrochemical system the I-V response is made up of a combination of resistors, capacitors, and other elements.

These impedance responses can be represented on either a Bode or Nyquist plot. In Bode representation (figure 4.10A), the magnitude, $\log|Z|$, and phase angle (ϕ) are plotted versus the frequency as $\log(f)$ (i.e. polar coordinates). Plotting the imaginary ($-Z_{imag}$) and real (Z_{real}) terms of the impedance against each other generates a Nyquist plot (i.e. Cartesian coordinates), where every point corresponds to a particular frequency (figure 4.10B). Depending on the shape of the impedance plots, equivalent circuits can be built using components such as resistors, capacitors, and more complex components such as constant phase elements or Warburg elements (see figure 4.10C). From these equivalent circuits, important parameters of the reaction can be measured, including the charge transfer resistance (R_{ct}) or the uncompensated solution resistance (R_u).

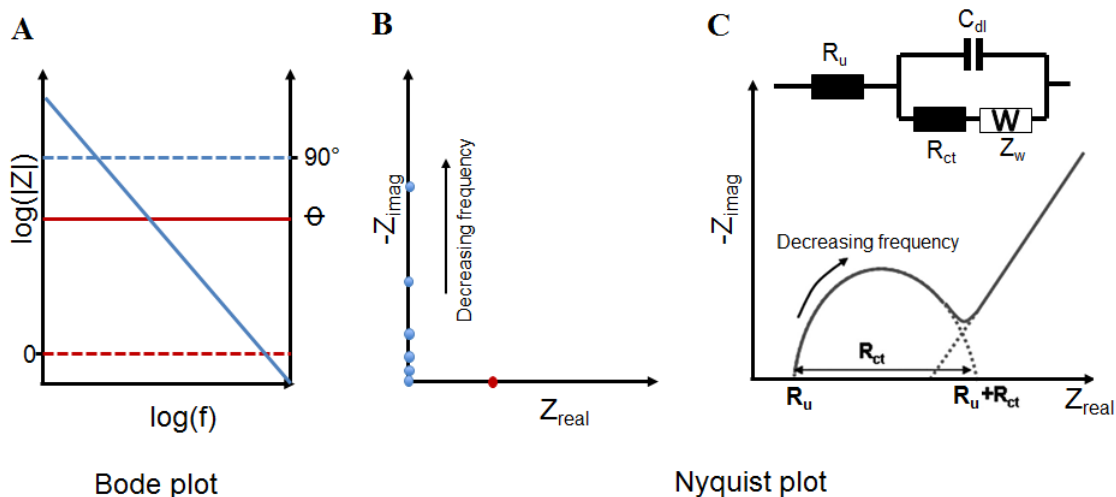


Figure 4.10: (A) Bode plot showing the impedance response of a system that can be represented by a simple resistor (red) or capacitor (blue). The $|Z|$ is shown with a solid line and phase angle, ϕ , with a dashed line. (B) Nyquist plot of the same resistor (red) or capacitor (blue) system. Each point corresponds to a different frequency. (C) Nyquist plot the impedance response of a system which can be represented by the equivalent circuit shown. This circuit is known as a Randles circuit and can be typically used to describe a simple reversible electron transfer at electrode/electrolyte interface. The component Z_w is known as the Warburg impedance and can model the mass transfer resistance of a system.

4.4.6 IR compensation

It was shown in equation 2.9 and 2.10 that part of the driving potential of electrochemical system is made up of contributions from Ohmic resistances. This resistant overpotential, η_Ω , is largely independent on the catalyst material however can still decrease the rate of charge transfer between the anode and cathode. Consequently when evaluating a catalysts activity η_Ω must be removed so as not to overcompensate the catalyst overpotential. The resistance overpotential, η_Ω , is the result of Ohmic resistances, R_u , in the electrolyte solution and electrode wiring and follows Ohm's law:

$$\eta_\Omega = iR_u \quad (4.15)$$

Where R_u is known as the uncompensated solution resistance which depends on the position of the reference electrode, conductivity of solution and geometry of electrode and is found from electrochemical impedance spectroscopy (EIS) meas-

measurements. Corrections to the experimentally measured overpotential are done by subtracting the Ohmic drop IR_u according to:

$$\eta_{corr} = \eta_{measured} - IR_u \quad (4.16)$$

Accurately measuring R_u is essential for obtaining valid Tafel plots, especially when passing large current. A straightforward method of measuring R_u exists without having to model the entire electrochemical system with an equivalent circuit, which can often be difficult and time consuming. By choosing a potential region where no Faradaic reaction occurs, the electrochemical system can be modelled by a simple resistor and capacitor in series, where the capacitor comes from the double layer and the resistance is R_u . Thus at high frequencies, the capacitor acts as a short circuit and the measured impedance is solely representative of R_u . Thus R_u can be measured from the high frequency plateau of the Bode plots or the high frequency intercept of Nyquist plots.

It should be noted however that the resistance of the catalyst film itself (R_{film}) can sometimes be included as part of R_u . This will depend on the material, and whether it has a capacitance value. If the material has appreciable capacitance then the impedance response to film is usually modelled by a resistor and capacitor in parallel and therefore is not included in the value of R_u .^{33,2} However if this is not the case some component of R_u will be made up of the R_{film} and thus the catalyst material will have an effect on the resistance.³⁴ Correcting for this value when presenting overpotential will therefore overcompensate the actual overpotential due to the catalyst material. This is typically not an issue however as the values of R_{film} are usually $\ll$ than the resistances due to the solution, supporting electrode, etc. and fall within the experimental error.³⁴

Chapter 5

Thickness Dependence of Hydrogen Production Rate in MoS₂ Nanosheet Catalytic Electrodes

5.1 Introduction

The use of nanomaterials as catalysts for the generation of hydrogen have potential to lower costs and enable future technologies. This is generally achieved through the hydrogen evolution reaction (HER) in acidic media: $2H^+ + 2e^- \rightleftharpoons H_2$. Currently, while platinum is the most efficient catalyst for the HER, its high price makes it far from the ideal material. To address this by replacing platinum will require the identification of a material which is abundant, non-toxic and cheap and of course can generate hydrogen at competitive rates at low overpotential. Finding a nanomaterial that can fulfill these requirements has created much interest within the research community.⁴⁻⁶

In this regard 2D transition metal dichalcogenides (TMDs), in particular molybdenum disulfide (MoS₂), have surfaced as potential candidates. Nanostructured MoS₂, such as exfoliated nanosheets, are efficient HER catalysts. Usually found in

two polytypes: semi-conductive 2H and metallic 1T, the 2H form is most commonly encountered in nature. Importantly, the HER active sites of 2H MoS₂ has been identified as the uncoordinated disulphides at the nanosheet edge^{42,112,333} (unlike 1T which is basal plane active). As a result, an effective strategy for creating highly active MoS₂ catalysts involves maximizing the amount of edge sites present in a given electrode.

This is a common approach taken by many authors as outlined in chapter 3. Increasing the density of active sites improves the performance while also reducing the catalytic footprint, thus reducing costs. This can be achieved using high mass loading electrodes made by stacking nanomaterial into thick porous films, which serves to increase the overall number of available active sites per electrode area.^{45,118,122–124,130,131,133,139–143} However, this tactic is not perfect and requires optimization. Performance of thick electrodes tend to become limited as mass per area (M/A) is increased. Limitations can arise due to diffusion effects of transporting mass into the interior surface, mechanical robustness problems such as cracking,⁸² as well as electrical transport limitations occurring in poorly conducting thick films. These effects will eventually limit the production rate, canceling out any gains due to increased M/A. As a result, and while many papers in the literature report impressive data for thin film electrodes, the corresponding data for thick films is often not given. In fact, it is quite uncommon to find nanosheet catalytic electrodes made with mass loading of 0.5 mg cm⁻² (or ~1.7 μm for MoS₂) or higher and currently there is no well-established threshold at which electrode performance becomes thickness limited. There is clearly a lack of understanding of the relationship between film thickness and activity and a detailed analysis has yet to be reported.

To investigate this the production of large quantities of high quality MoS₂ nanosheets is required. This can be achieved quickly and easily using liquid phase exfoliation (LPE).^{83,238,249,334} LPE is scalable²³⁸ and gives dispersions of suspended MoS₂ nanosheets in a processable form. Additionally, advanced centrifugation and spectroscopic techniques can be used to control and measure the nanosheet thickness and size,²⁴⁷ thus allowing for the selection of small nanosheets with greater numbers of edge sites. Using LPE, nanosheet dispersions can easily be formed into porous

films consisting of disordered arrays of nanosheets.⁸² Such films have great potential for thick hydrogen evolution catalysis as their porous nature will facilitate access of the electrolyte throughout the interior of the electrode.⁹⁰

In this chapter, we investigate the enhancements in catalytic performance associated with maximizing electrode thickness, using porous electrodes of randomly restacked MoS₂ nanosheets as a model system. We show that the current density, and thus H₂ production rate, rises linearly with increasing thickness up to 5 μm , much higher than previously shown in literature. Above 5 μm however improvement tends to saturate with rising thickness. Through quantitative analysis a simple model is developed linking catalytic activity parameters to both electrode thickness and flake length, which perfectly predicts this linear increase. From this we extract a new catalytic figure of merit, and propose it as a more complete measure of a catalysts performance compared with the often used the turnover frequency (TOF).

5.2 Experimental Procedure

5.2.1 MoS₂ dispersion preparation and characterisation

Exfoliation

Dispersions of MoS₂ nanosheets stabilized in in surfactant solution were prepared as described previously.²⁴⁷ Two stock solutions of sodium cholate (SC, Sigma-Aldrich) in deionised water were made with SC concentrations of 12 mg mL⁻¹ and 3 mg mL⁻¹. MoS₂ powder (MoS₂, Sigma-Aldrich, used as supplied) was added to 80 mL of the 12 mg mL⁻¹ SC solution at a concentration of 30 mg mL⁻¹ and sonicated in a high power sonic tip (VibraCell CVX; 750W, 60kHz) for 1 hour at 60% amplitude, and with a pulse rate of 6 s on 2 s off. The formed dispersion was then immediately centrifuged (Heraeus Multifuge X1) at 5500 rpm for 99 min and the supernatant was discarded. This initial pre-treatment step was required to remove very small nanoparticles and impurities from the dispersion, and results in a higher yield of exfoliated nanosheets. The collected sediment was then redispersed in the 3 mg

mL⁻¹ sodium cholate solution to a volume of 80 mL and exfoliated using a sonic tip for 8 hours at 60% amplitude, pulse rate 4 s on 4 s off. The dispersion was then let sit for 2 hours to allow large aggregates (unexfoliated material) to settle.

Flake size selection

Controlling the average MoS₂ flake size was possible using liquid cascade centrifugation (LCC), outlined in chapter 4. The MoS₂ dispersion was first centrifuged initially at 5000 rpm for 2.5 hours and the supernatant, containing very small flakes, was removed and discarded. The sediment was redispersed in the 3 mg mL⁻¹ SC solution and centrifuged at 2000 rpm for 2.5 hours. This step separates out larger flakes from the desired flake size. The supernatant was retrieved and formed a stable dispersion.

UV-Vis analysis

Using UV-vis spectroscopic metrics, reported by Backes et al.²⁴⁷ we were able to extract values for the dispersion concentration as well as the average nanosheet lateral size and number of layers per flake. The concentration of exfoliated MoS₂ was determined from extinction spectra at wavelengths of 345 nm using a Varian Cary 6000i. Using the Beer-Lambert relation: $C = Ext/\epsilon d$, the dispersion concentration, C, was found, using an extinction coefficient, of $\epsilon_{345} = 69 \text{ mL mg}^{-1} \text{ cm}^{-1}$, and a cell length, $d = 1 \text{ cm}$. The average flake length and number of layers per flake of the exfoliated MoS₂ was then calculated from the extinction spectrum using equation 4.3 and 4.4.

5.2.2 Film formation and device characterisation

Films of stacked MoS₂ nanosheets were made by a combined process of vacuum filtering liquid dispersions onto a membrane and then transferring the films onto a suitable substrate. Details of these filtration and transfer techniques are outlined in chapter 4. Dispersions of MoS₂ in SC were vacuum filtered through porous mixed cellulose ester filter membranes (MF-Milipore membrane, hydrophilic, 0.025 μm pore size, 47 mm diameter). Precise control over the mass per unit area (M/A) of

filtered material was achieved by filtering known volumes of a dispersion with known concentration. This resulted in spatially uniform films ranging in M/A. To remove the remaining surfactant films were “washed” by filtering 200 mL of deionised water through the porous network. The resulting films (diameter 36 mm) were left to dry overnight. Once dry, they were cut to the desired dimensions and transferred onto a pyrolytic carbon (PyC) substrate for electrochemical testing, SEM imaging and profilometry thickness. The cellulose membrane was removed by applying pressure to the film, wetting it with acetone vapour and subjecting it to a series of acetone baths. The acetone dissolves the cellulose membrane and leaves the films behind on the substrate surface (see for example ref³³⁵). Pyrolytic carbon was grown by CVD as described previously.³³⁶

Film thickness

Film thickness was measured using a Dektak 6M, Veeco Instruments profilometer. Step profiles were taken at four different locations to get an average film thickness for each electrode. Films ranged in thickness from 0.2 μm to 14 μm . This is a non-destructive process and allows for the thickness to be obtained for each electrode before electrochemical measurements.

Scanning electron microscopy

SEM images were obtained using a ZEISS Ultra Plus (Carl Zeiss Group), 2 kV accelerating voltage, 30 μm aperture and a working distance of approximately 1-2 mm. The samples were loaded onto the SEM stub using sticky carbon tape.

5.2.3 Electrochemical measurements

Electrochemical measurements were then carried out to evaluate the performance of the MoS₂ catalysts for the HER. Films were cut to an area of approximately 0.64 cm² and transferred onto a PyC substrate. Electrochemical measurements were performed in a three-electrode electrochemical cell in 0.5 M H₂SO₄ acidic electrolyte, with a large graphite counter electrode and a reversible hydrogen electrode (RHE)

as the reference electrode (Gaskatel Hydroflex). Catalytic activity was measured by performing linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) with a Gamry Reference 3000 potentiostat. Samples were conditioned at a given voltage for 100 s before each test. Linear voltage sweeps were performed at a scan rate of 5 mV s^{-1} in a window from 0 to -0.6 V (vs RHE). AC impedance was conducted in the frequency range of 0.1 to 10^5 Hz with perturbation voltage amplitude of 10 mV and DC bias of 0 mV. The uncompensated solution (R_u) of the system was determined from the high frequency plateau of the Bode plot. All the data was corrected for the electrolyte resistance by iR compensation.

5.3 Results and Discussion

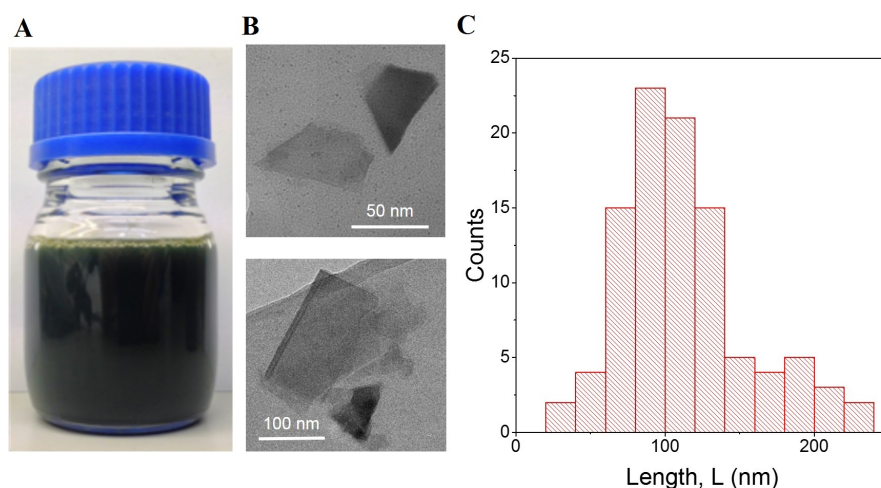


Figure 5.1: *Characterization of MoS_2 nanosheets (A) Stable dispersion of $\sim 0.6 \text{ mg mL}^{-1}$ MoS_2 nanosheets in aqueous-sodium cholate surfactant solution. (B) TEM images of exfoliated MoS_2 nanoflakes. (C) Histogram of flake length distribution. Average exfoliated flake size was $L = 114 \pm 4 \text{ nm}$*

5.3.1 Dispersion characterization

MoS_2 nanosheets were prepared by LPE in aqueous surfactant solution using a combined process of sonication and centrifugation.⁸³ This process resulted in dark green dispersions of MoS_2 nanosheets in water, stabilized by the surfactant sodium

cholate (figure 5.1A). TEM imaging (figure 5.1B) confirmed the dispersed material to be in the form of thin nanosheets with statistical analysis (figure 5.1C) giving a mean flake length of $L=114 \pm 4$ nm. The average length/width aspect ratio was also measured to be $k=1.98 \pm 0.09$.

The UV-vis extinction spectrum of such a dispersion is shown in figure 5.2 and is as expected for suspended few-layer MoS_2 nanosheets.⁸² Using the measured extinction coefficient of $\epsilon_{345} \text{ nm}=69 \text{ mL mg}^{-1} \text{ cm}^{-1}$,²⁴⁷ we found the MoS_2 concentration to be 0.6 mg mL^{-1} . The ratio of extinction at the B-exciton to that at 345 nm is sensitive to the mean nanosheet length (equation 4.3) while the wavelength associated with the A-exciton is determined by the mean nanosheet thickness (equation 4.4). We analyze the extinction spectrum, finding the average flake length to be $\langle L \rangle = 122 \pm 6$ nm, in good agreement with the TEM data. In addition, we found the mean nanosheet thickness, expressed as the average number of layers per flake to be $\langle N \rangle = 3.4 \pm 0.5$.

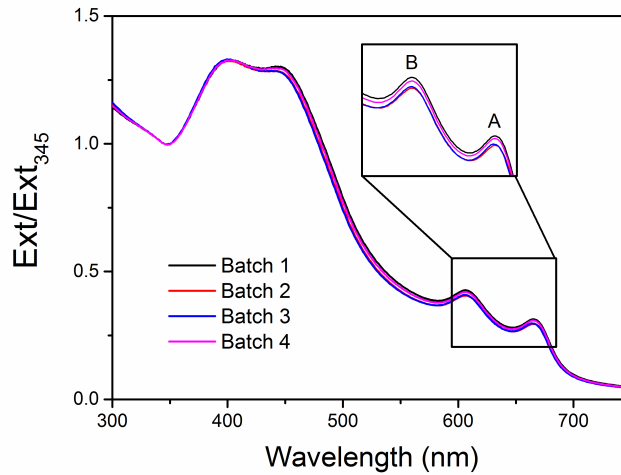


Figure 5.2: *UV-vis optical extinction spectrum of multiple MoS_2 nanosheet dispersions. The A- and B-excitations are indicated. Good agreement between spectra demonstrates the reproducibility of the LPE and LCC process*

5.3.2 Film preparation and characterisation

The nanosheet dispersion was used to prepare thin films by vacuum filtration. This method has the advantage that the deposited mass and resultant film thickness can be controlled relatively accurately. The films were prepared with mass per area (M/A) ranging from $0.06 - 4 \text{ mg cm}^{-2}$, a considerably broader range than used in previously published works.^{45,123,124,130,139} A section of each film was then transferred onto conductive pyrolytic carbon (PyC) (figure 5.3A). SEM images were taken of the thick films, shown in figure 5.3B and C, revealing a highly porous structure consisting of a disordered array of MoS_2 nanosheets.

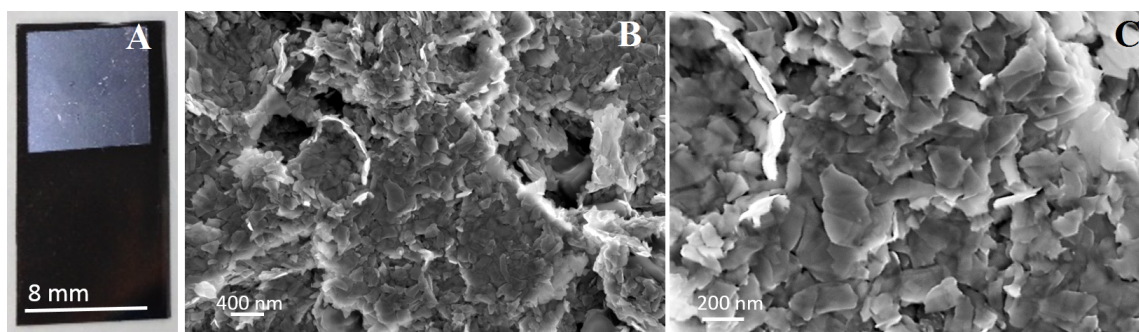


Figure 5.3: *Characterization of MoS_2 nanosheet films (A) Catalyst electrode fabricated from deposited MoS_2 flakes on a pyrolytic carbon substrate. (B, C) SEM images of (B) a $9.5 \mu\text{m}$ thick MoS_2 film and (C) magnified image of the same film, showing the porous structure of the film*

Step profiles of each film were taken using a profilometer, giving a thickness range of $0.21 \mu\text{m}$ to $14 \mu\text{m}$. An example of a profile is shown in figure 5.4A. The film density was found by plotting M/A *versus* the thickness, t (figure 5.4B), for films with a well-known mass. This shows a linear relationship, and the film density (ρ_{film}) was found from the slope using $M/A = \rho_{\text{film}} \times t$, to be $\rho_{\text{film}} \sim 2880 \text{ kg m}^{-3}$, invariant with thickness. The porosity (P) was then calculated using $P = 1 - \rho_{\text{film}}/\rho_{\text{NS}}$, where ρ_{NS} is the density of an MoS_2 nanosheet, taken as $\rho_{\text{NS}} = 5060 \text{ kg m}^{-3}$. This gives film porosity of $P \sim 43\%$, typical of that found for vacuum filtered nanosheet films.³¹⁶ This porous-network type morphology is advantageous for applications in electrocatalysis as it should enable free access of the electrolyte to the internal surface

of the electrode.

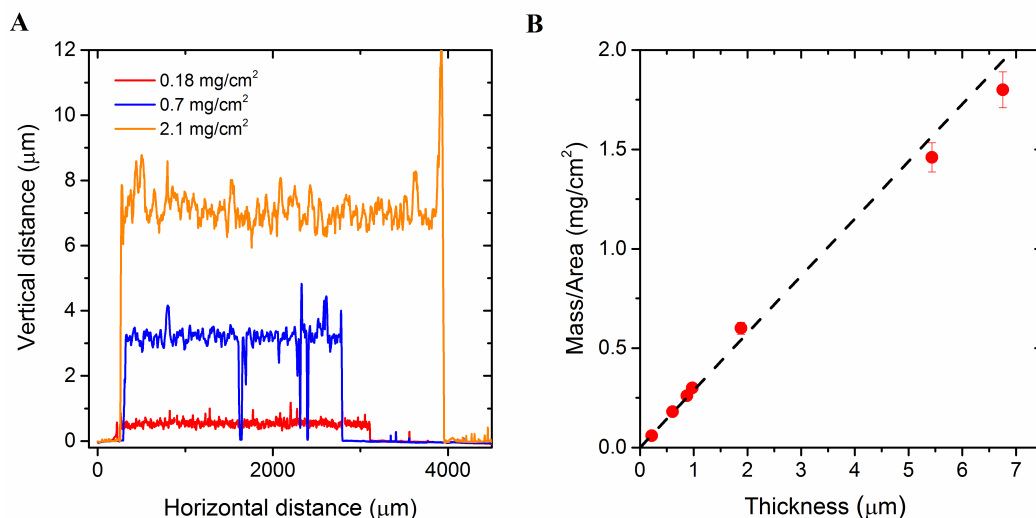


Figure 5.4: (A) Sample of a profilometer step height profiles for measuring film thickness. (B) Graph of film mass per unit area as a function of film thickness as measured by profilometry. The dashed line is a linear fit.

5.3.3 HER performance: Electrode thickness dependence

To test the electrocatalytic properties of such MoS_2 films with respect to the hydrogen evolution reaction, linear voltage sweeps (scan rate 5 mV s^{-1}) were performed on MoS_2 films with thickness ranging from $0.21 \mu\text{m}$ to $14 \mu\text{m}$ ($0.06 - 4 \text{ mg cm}^{-2}$). Typical polarization curves are presented in Figure 5.5A. It is immediately apparent that the thicker MoS_2 films have a dramatically increased current density and so greater HER activity compared to the thinner films. Much higher current densities were achieved for a given potential, as high as 44 mA cm^{-2} for an $11.8 \mu\text{m}$ film compared to 3 mA cm^{-2} for a $0.2 \mu\text{m}$ film, each measured at -400 mV vs RHE. The onset potential (see figure 5.5A inset), defined here as the potential required to achieve $J = 1 \text{ mA cm}^{-2}$, for a $0.2 \mu\text{m}$ thin film was observed to be -340 mV vs RHE while an $11.8 \mu\text{m}$ film displayed the lowest onset potential of -116 mV vs RHE, one of the lowest onset potentials achieved in literature (at the time) and comparable, if not superior to many similar and higher mass MoS_2 catalysts.^{131,139,143} The origins of

this improved HER activity can be attributed to the higher quantity of active MoS₂ edge sites available in the thicker films.

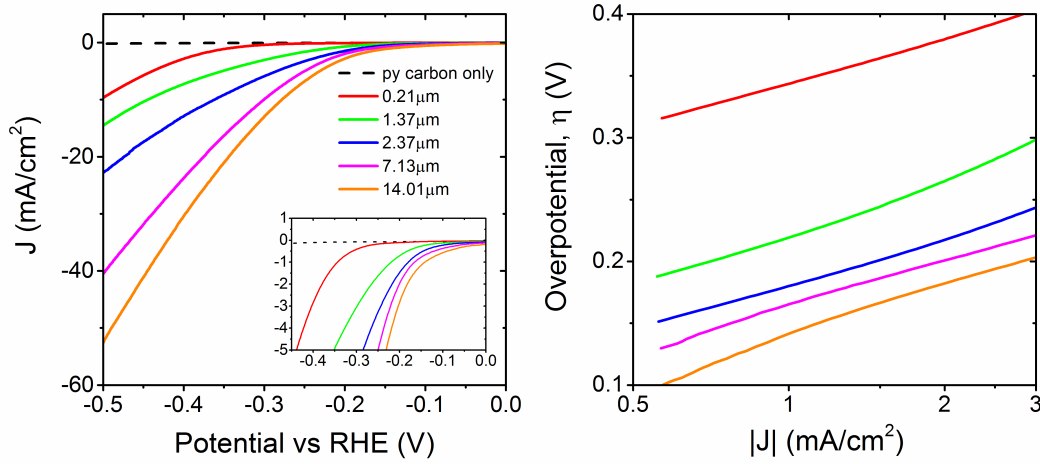


Figure 5.5: (A) Polarization curves (inset: lower potential regime) measured for MoS₂ films ranging in thickness from 0.21 to 14 μm. Thicker films show much higher current densities for the same potential values and much lower onset potentials. (B) Corresponding Tafel plots

For a HER electrocatalyst, the relationship between the overpotential and the current density is described by the cathodic term of the Butler-Volmer equation, known as the Tafel equation, which can be written as:

$$J = -J_0 \times 10^{\eta/b} \quad (5.1)$$

where J is the measured current density, J_0 is the exchange current density, η is the overpotential, and b is the Tafel slope. Shown in figure 5.5B is our data for MoS₂ electrodes of different thicknesses plotted as η versus $|J|$ on a Tafel plot. Values for b and J_0 can be found by fitting the linear portion (i.e. at currents low enough to make mass transport limitations unimportant) of the Tafel plots to equation 5.1. We found the Tafel slopes of virtually all electrodes to be in the range 100-150 mV dec⁻¹ with a mean of 125 ± 17 mV dec⁻¹ (see below for more detail).

Tafel slope *versus* film thickness

The Tafel slope is a useful parameter and is a measure of the potential increase required to improve the current density by one order of magnitude. More fundamentally, analysis of the Tafel slope is used to evaluate the dominant HER mechanism at the electrode/electrolyte interface. As previously discussed it is generally accepted that the HER in acidic media follows one of two possible reaction pathways;^{53,54} the Volmer-Heyrovsky or the Volmer-Tafel mechanism (see chapter 2 for reaction pathways), where either the Volmer or the Heyrovsky/Tafel step can be the r.d.s of the reaction (at a given potential). A Tafel slope of 40 mV dec⁻¹ or 30 mV dec⁻¹ suggests the Heyrovsky or Tafel reaction dominates while slope of 120 mV dec⁻¹ indicates it is the Volmer reaction.⁵³ While the measured value of 125±17 mV dec⁻¹ implies the rate limiting step to be the Volmer reaction in our case, it is worth exploring if this is the case independent of electrode thickness.

To do this, we found the Tafel slope for each film which we plotted against film thickness, as shown in figure 5.6A. The Tafel slope remains relatively constant with film thickness, ($\langle b \rangle = 125 \pm 17$ mV dec⁻¹), indicating the Volmer reaction to be the r.d.s of our MoS₂ catalyst for all film thicknesses studied. This agrees with many papers in the literature which give Tafel slopes between 100 – 145 mV dec⁻¹ for 2H MoS₂.^{118,123,127,139,157,337,338} Interestingly Vrubel et al¹³⁰ reported an increase in Tafel slope with higher mass loading of amorphous MoS₃ dropcast onto glassy carbon electrodes (from 41 mV dec⁻¹ for 8 µg cm⁻² to 63 mV dec⁻¹ for 128 µg cm⁻²). They attribute the increase to decreased efficiency in electron and proton transfer with the higher loading films. It is worth noting that, when considering all types of nanostructured MoS₂ an even larger spread of Tafel slopes is found, ranging from as low as 40 mV dec⁻¹ (often 1T MoS₂) up to 185 mV dec⁻¹.^{42,47,118,119,123–125,127,130,139,143,145,157,337–341} It appears the Tafel slope can vary greatly for different preparations of the same material. In addition, Kong et al¹¹⁹ noted that substrate morphology significantly affects the Tafel slope. The same MoS₂ made on smooth glassy carbon, rough glassy carbon or Mo foil gave Tafel slopes of 105-120, 86 and 75 mV dec⁻¹ respectfully. It seems there is a lack of sufficient understanding of the critical factors influencing the Tafel slope of MoS₂

electrocatalysts,⁴⁷ making materials comparison difficult.

Exchange current density *versus* film thickness

Increasing the film thickness increases the number of available catalytic sites within the interior of the film. This implies that both the exchange current density, J_0 , and the current at a given potential, $J(V)$ should scale directly with film thickness. Figure 5.6B shows J_0 to increase with film thickness from $\sim 0.003 \text{ mA cm}^{-2}$ for a $0.76 \text{ }\mu\text{m}$ film to an impressive $\sim 0.13 \text{ mA cm}^{-2}$ at a thickness of $11.4 \text{ }\mu\text{m}$. This is one of the highest values of exchange current density in literature for 2H MoS_2 -only films, with only a few examples such as 1T MoS_2 or MoS_2 /graphene composites, achieving higher current values^{123,139,154}. Although, as is often the case for J_0 , the data is scattered, it is clearly linear (dashed line) with a slope of $dJ_0/dt = 0.018 \pm 0.003 \text{ mA cm}^{-2} \mu\text{m}^{-1}$ (equivalent to a current per electrode volume of $180 \pm 30 \text{ kA m}^{-3}$).

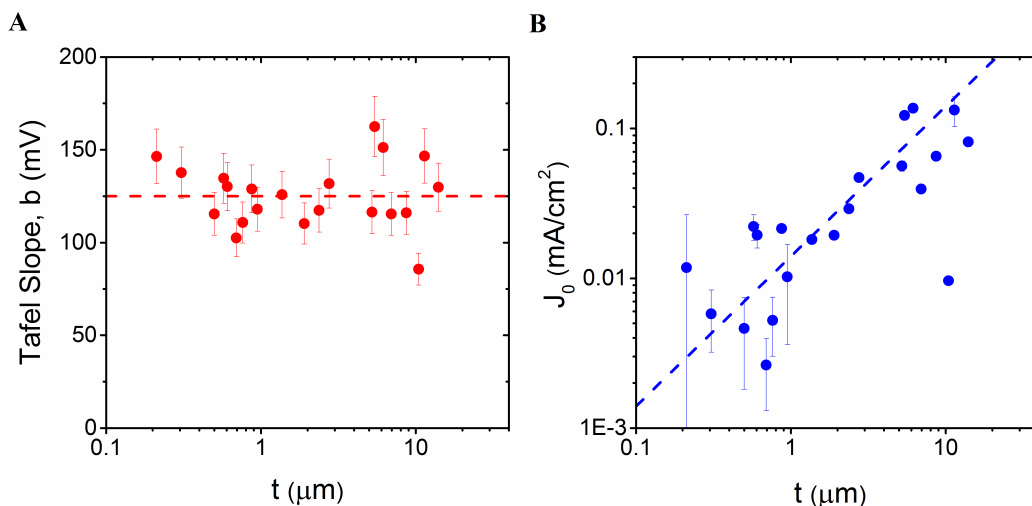


Figure 5.6: Relationship between electrocatalytic performance and thickness of MoS_2 films. (A) Tafel slope versus MoS_2 film thickness. There is no significant change in Tafel slope with increasing film thickness, with an average slope $b \sim 125 \pm 17 \text{ mV dec}^{-1}$. (B) Exchange current density versus MoS_2 film thickness showing linear increase of J_0 with rising thickness.

Current density *versus* film thickness

It is also useful to consider the current at a given potential as a measure of the effectiveness of the electrode as a HER catalyst. Figure 5.7 shows the positive value of the current density at $V = -250$ mV vs RHE, $-J_{-250\text{mV}}$, plotted *versus* electrode thickness. Here the data is much less scattered and clearly scales linearly with electrode thickness ($d(-J_{-250\text{mV}})/dt = 1.2 \text{ mA cm}^{-2}\mu\text{m}^{-1}$) as far as $t \sim 5 \mu\text{m}$, after which the current saturates. As long as the electrode morphology is thickness independent, the number (per unit area) of active sites will increase linearly with electrode thicknesses. Then, assuming the electrolyte is free to permeate throughout the entire film and there is nothing limiting the transport of charge from the current collector to the active sites, a linear increase in current with thickness implies that hydrogen generation is occurring throughout the internal free volume of the electrode. This is an important result as it shows that in porous electrodes such as these, the gas production rate can be increased simply by increasing the electrode mass.

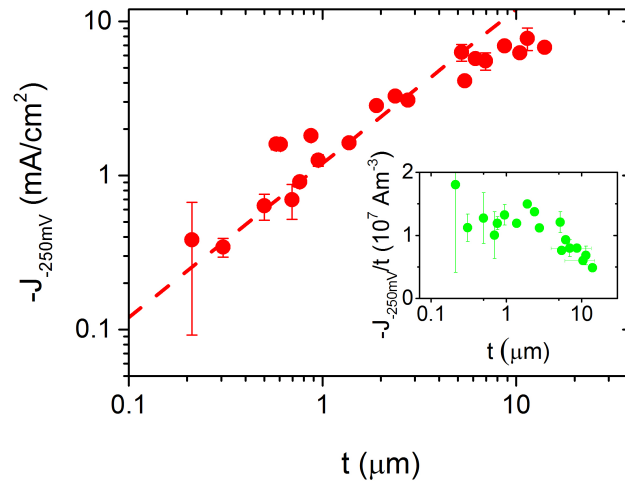


Figure 5.7: Current density measured at a potential of -250 mV vs RHE plotted versus MoS_2 film thickness. Current increases linearly (dashed line) with film thickness up to $\sim 5 \mu\text{m}$ then begins to saturate. Inset: Current density normalized to electrode thickness which shows a steady fall off with thickness for $t > 5 \mu\text{m}$

Edge site model - extracting a figure of merit

We can understand the thickness dependence of the current density quantitatively by developing a simple model which is based on the linear relationship between the current and the hydrogen production rate (i.e. the number of number of H_2 molecules produced per second, R_{H_2}).¹³ Assuming all active sites on the internal surface of the electrode are in contact with the electrolyte and nothing limits current flow between the external circuit and the catalytic sites, we can write the current density as

$$J = \frac{-neR_{H_2}}{A} = \frac{-neN_sR}{A} \quad (5.2)$$

Where, N_s is the total number of active sites, R is the number of H_2 molecules produced per site per second (the turnover frequency), A is the geometric area of the electrode and n is the number of electrons supplied per molecule produced (N.B. $n=2$ for HER but this equation can be adapted for other reactions by changing n).

For 2H MoS₂, the catalytic sites are associated with edge sulphurs.^{42,112,333} However, only a fraction of these may be active, perhaps due to functionalization with impurity species.^{42,112} Thus we characterise the active sites solely via their position on the nanosheet edge and through their separation, which we express via the number of catalytic active sites per unit monolayer edge length, B . Thus, in a few-layer nanosheet, the number of active sites is B times the perimeter length (p) times the number of monomers per nanosheet. The perimeter of a nanosheet of mean length L and aspect ratio k can be represented as: $p = 2L(1 + k)/k$ and the number of monolayers can be calculated as the total mass divided by the mass of a monolayer (M_T/M_{NS}). Thus we can work out the total number of active sites as the number of active sites per monomer edge length (B) multiplied by the monomer edge length per nanosheet (p) times the number of nanosheets per unit mass times the electrode mass, M_T . Then we find:

$$N_s = B \times \frac{2L(1 + k)}{k} \times \frac{M_T}{M_{NS}} = B \times \frac{2L(1 + k)}{k} \times \frac{M_T}{\rho_{NS}L^2d_o/k} \quad (5.3)$$

$$N_s = \frac{2B(1+k)}{\rho_{NS}Ld_0}M_T \quad (5.4)$$

where $d_0=0.6$ nm is the monomer thickness and ρ_{NS} is the nanosheet density (5060 kg m⁻³ for MoS₂). Combining equations 5.2 and 5.4, we find

$$J = -neR \frac{2B(1+k)}{\rho_{NS}Ld_0} \frac{M_T}{A} \quad (5.5)$$

Alternatively, this can be written as a function of electrode thickness, t :

$$J = -2ne [RB] \left[\frac{(1+k)(1-P)}{Ld_0} \right] t \quad (5.6)$$

where P is the porosity.

Based on the Butler-Volmer equation, the turnover frequency (R) should depend on overpotential as $R = R_0 \times 10^{\eta/b}$, where R_0 is the turnover frequency at zero overpotential, allowing us to write

$$J = -2ne [R_0B] \times 10^{\eta/b} \times \left[\frac{(1+k)(1-P)}{Ld_0} \right] t \quad (5.7)$$

This equation completely describes the thickness dependence observed in figure 5.7. By comparison with equation 5.1, this means we can write the exchange current density as

$$J_0 = -2ne [R_0B] \left[\frac{(1+k)(1-P)}{Ld_0} \right] t \quad (5.8)$$

We note that the first square bracketed quantity is a measure of the catalytic properties of the nanosheets while the second square bracketed property depends on the nanosheet dimensions and film morphology. As these second set of properties are known, we can use the fit from figure 5.6B to find $R_0B \approx 11 \pm 2.5$ H₂ molecules s⁻¹ μm⁻¹ of monolayer edge length. We propose that this number is a figure of merit which can be used to compare the catalytic performance of different 2D materials.

In general, most papers quote R_0 or $R(\eta)$ as a figure of merit for the nanosheet catalytic activity. However, this is not strictly correct as these parameters describe the activity of the catalytic site. The overall activity of the nanosheet is better

described by R_0B as it describes both the site activity and the site density. In fact, disentangling these parameters is always problematic as it can be hard to accurately measure B (or more generally the site density). In fact, many papers quote values of R_0 or $R(\eta)$ which are calculated using values of B which are based on dubious assumptions or approximations. Here we take a different approach. The catalytically active sites are edge disulphides^{42,112,333} which are 0.32 nm apart³⁴² and only exist on the S-rich edge which accounts for half the total edge length on average. Not all of these sites will be active as some may have become functionalised during the exfoliation process. Using this information, we find that $B_{\max}=1.56 \text{ nm}^{-1}$ is the maximum possible number of active sites per edge length. Given that we have measured $11 \pm 2.5 \text{ H}_2 \text{ molecules s}^{-1} \mu\text{m}^{-1}$, this means that $R_{0,\min} \sim (64 \pm 15) \times 10^{-3} \text{ s}^{-1}$ is the minimum zero-overpotential turnover frequency consistent with our data. This is certainly in line with most of the data in the literature for 2H MoS₂.^{34,41,45,119,150} If we take the zero-overpotential turnover frequency of $R_0=0.02 \text{ s}^{-1}$, quoted for perfect MoS₂ edges by Jaramillo,⁴² this means our MoS₂ is consistent with $B=0.55 \pm 0.013 \text{ nm}^{-1}$. Comparing this value to $B_{\max}$ implies that approximately two out of every three disulphides in our LPE MoS₂ are inactive. This in turn implies that the performance of LPE MoS₂ quoted here could possibly be tripled by chemically treating the edges to activate all disulphides. This is of course in addition, to more obvious strategies such as reducing nanosheet length^{128,153,337} or increasing the aspect ratio¹³⁴ implied by equation 5.8.

It is worth considering what could possibly be achieved by optimising the performance of LPE MoS₂ electrodes. Assuming chemical treatment could render all edge disulphide groups active (i.e. yielding $B=1.56 \text{ nm}^{-1}$), and that the exfoliation could be modified to give nanosheets with aspect ratio of 4 and then performing size selection²⁴⁷ to reduce the nanosheet length to 5 nm on average¹²⁸ would give a value of $dJ_0/dt = 19 \text{ MA m}^{-3}$, almost two orders of magnitude greater than achieved here.

Overpotential *versus* electrode thickness

We can also plot the potential required to generate a given current density (here 3 mA cm⁻²) *versus* electrode thickness as shown in figure 5.8 (plotted as $-V_{3\text{mA cm}^2}$). Note 3 mA cm⁻² is used here instead of the standard 10 mA cm⁻² as it is more consistent with the linear region of our Tafel plots. This is important as our treatment of the catalytic data is more for quantitative analysis rather than comparison to state-of-the art industry catalysts. We find a logarithmic decrease from ~ 400 mV at $t \sim 200$ nm to ~ 200 mV for $t \sim 5\text{-}6$ μm , after which the potential saturates. We can understand this via the linearity of J_0 with t embodied in equation 5.8. With this in mind, we can rewrite equation 5.1 as $|J| = dJ_0/dt \times t \times 10^{\eta/b}$. Then, the overpotential for a given current is given by

$$\eta(J) = -b \log t + b \log \left(\frac{|J|}{dJ_0/dt} \right) \quad (5.9)$$

This equation implies that the slope of an $\eta(J)$ *versus* $\log(t)$ graph should be equal to the Tafel slope of the nanosheets. This is supported by the fact that the slope of the dashed fit line in figure 5.8 is 129 mV dec⁻¹, very close to the mean Tafel slope of 125 mV dec⁻¹ found above.

It is worth considering how the material optimisation described above would affect the potential required to achieve a given current, say -30 mA cm⁻². Using equation 5.9 and assuming a Tafel slope of $b = 125$ mV dec⁻¹, a thickness of 5 μm and an optimised value of $dJ_0/dt = 19$ MA m⁻³ we find that $\eta(J=-30 \text{ mA cm}^{-2})=63$ mV. This would be an extremely low potential and would render LPE MoS₂ extremely attractive as a HER catalyst.

The improvements in both $|J|$ and $\eta(J)$ with thickness shown in figures 5.7 and 5.8 begin to saturate at thicknesses above $t \sim 5$ μm ($M/A=1.44$ mg cm⁻²). This can be seen more clearly in the inset in figure 5.7 which shows the current density divided by electrode thickness ($-J_{-250\text{mV}}/t$) plotted *versus* electrode thickness. While $-J_{-250\text{mV}}/t$ is roughly constant at $\sim 1.2 \times 10^7$ A m⁻³ for low electrode thicknesses, it clearly falls off for larger thicknesses. Others in the literature have also

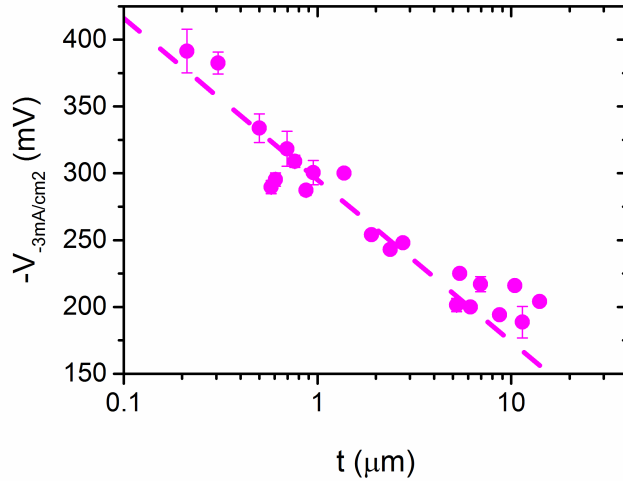


Figure 5.8: Potential required to achieve a current density of -3 mA cm^{-2} plotted versus MoS_2 film thickness. The dashed line represents a logarithmic decrease.

reported a degradation in performance when increasing the mass loading of their films.^{45,118,130,141,142} However, it should be noted that all of these M/A limits are far lower than for our electrodes.

5.4 Conclusion

We have demonstrated that dispersions of liquid exfoliated nanosheets are a versatile starting material for the production of electrodes for catalysing the hydrogen evolution reaction. Such electrodes can easily be fabricated at controlled thicknesses up to $\sim 14 \mu\text{m}$. We found the Tafel slope to be independent of electrode thickness, consistent with the hydrogen production rate being limited by the Volmer reaction. The exchange current density and the current density at fixed potential scaled linearly with electrode thickness while the potential required to generate a given current fell logarithmically with thickness. These behaviours imply that the electrolyte penetrates throughout the porous internal surface of the electrode resulting in hydrogen production at all available active sites. However, this behaviour only persists up to thicknesses of $\sim 5 \mu\text{m}$. For thicker electrodes, the current and potential saturates with no further gains achievable by increasing electrode thickness.

With no obvious mechanical instabilities in our system (films remained intact

and on the electrode during bubbling) this saturation is likely due to either limitations in the rates of transporting ions and gas bubbles to and from the electrode, as well as due to the difficulties of transporting charge through a thick insulating film. Electrical limitations have been previously reported to limit thick nanosheet catalysts^{130,136,141} and other electrochemical devices such as supercapacitors and batteries.^{288,293} We addressed these limitations in chapter 7 by adding carbon nanotubes to the electrode, increasing both its electrical and mechanical properties.

While we have used MoS₂ as an electrocatalyst for the HER to study the effect of electrode thickness, these learnings are general and could be applied to other systems such as Co(OH)₂ for catalysing the oxygen evolution reaction. We believe that the strategies outlined here will aid in pushing such a system across the boundary from promising to state-of-the-art.

Chapter 6

Liquid Exfoliated $\text{Co}(\text{OH})_2$ Nanosheets as Effective, Low-Cost, Catalysts for the Oxygen Evolution Reaction

6.1 Introduction

Due to the large associated overpotential it is widely accepted that the most energetically inefficient part of the electrolysis process is the oxygen evolution reaction (OER) at the anode:^{13,222} $4\text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$. To avoid expensive platinum group metals,³⁴³ much work has focused on developing low-cost catalysts which generate reasonable oxygen production rates at relatively low overpotentials.^{3,56,191} For alkaline electrolysis, oxides/hydroxides typically made of combinations of Ni, Co or Fe have proven to be the most effective catalysts.^{92,177,184,201} Of these, 2D layered double hydroxides (LDH),^{92,191,207} have attracted much focus, achieving high current densities of 50 mA cm^{-2} at overpotentials as low as $\sim 210 \text{ mV}$.¹⁸⁴ However, the best performing materials tend to require complex synthesis such that a material which combines high-performance with low cost has yet to be demonstrated.

Hindering development further is a lack of sufficient evidence for the active sites of

the LDHs catalysts, which was key to the strategic improvements of TMD catalysts for the HER. While believed to be the edge sites of LDH crystals this has never been experimentally verified.^{92,184,191} Nanostructuring materials to increase the surface area, for example by exfoliation,⁹² is common, but without direction as to the active sites this can often be a guessing game of what aspect of the crystal structure warrants focus.

We believe these traditional approaches can be complemented by material science methodologies, taking a more systematic approach to optimising the catalyst. This begins firstly with proper identification of the active sites in the material. Following this, optimising the catalytic electrode, rather than the catalyst material is an importance yet oft-overlooked aspect in OER. The O₂ production rate is represented by the current density, J , which must be maximised for a given overpotential. Because J is the product of an intrinsic activity and the electrode mass loading or thickness ($J = (I/M) \times M/A = (I/V) \times t$, where I is the current generated and M , V , A and t are the electrode mass, volume, area and thickness), both of these parameters must be simultaneously increased to achieve global performance maximisation. The traditional approach typically only addresses the intrinsic activity (I/M or I/V). Effectively, the electrode thickness is usually ignored with only a very few papers examining the dependence of activity on thickness.^{202,204,205} Where electrode thickness was varied, the maximum thickness was always less than a few microns, not enough to maximise OER performance.

As is usually the case thickness dependent studies are avoided due to diffusion, electrical and mechanical constraints.^{204,288,289} Because of these difficulties with thick electrodes, many researchers avoid them by using 3D supports^{92,183,193,199} to increase the catalyst mass per geometric area, while retaining low electrode thickness. Indeed often in the literature the crux of an analysis is performed on one, generally low mass loading electrode and occasionally a higher mass is loaded on a Ni foam or carbon fibre paper at the end to achieve an impressive result.^{183,207,208} There is rarely information on how the choice of this higher loading transpired, often seeming arbitrary.¹⁸⁵ As results from chapter 5 revealed, thicker electrodes can dramatically increase the performance of catalyst film, and without a systematic analysis optimum

thickness may not be chosen. On top of this, using 3D supports such as Ni foams should not be relied upon for achieving maximum performance as these reduce flexibility in electrode design, increase electrode mass with non-active material and may not be economically viable in real electrolyzers.

The aim of this chapter is to demonstrate that a cheap, easily produced material can be transformed from a relatively poor OER catalyst to a highly active one simply using systematic material science methodology. We use layered cobalt hydroxide ($\text{Co}(\text{OH})_2$, cost 41 cent g^{-1}) as a model OER catalyst to study electrode optimisation. Recently LDHs have been exfoliated into 2D nanosheets using LPE. This enables relatively large quantities of high quality few layer $\text{Co}(\text{OH})_2$ nanosheets²³⁸ to be produced. This combined with size selection via LCC^{91,248} allows us to prepare nanoflakes of a specific size with well-defined dimensions. Analysing the dependence of OER activity on nanosheet size and electrode thickness confirmed nanosheet edges to be catalytically active and allowed us to select the smallest nanosheets as the best catalysts. Optimising parameters such as these is a vital step in the roadmap to catalytic improvement.

6.2 Experimental Procedure

This project was a collaborative effort between many colleagues. While all data analysis was performed by this author not all experimental methods presented here were and appropriate acknowledgments will be made in the relevant sections. For this work layered cobalt hydroxide ($\text{Co}(\text{OH})_2$) was exfoliated into 2D nanosheets for the first time, following a similar procedure to previous work exfoliating $\text{Ni}(\text{OH})_2$. This was primarily carried out by Dr Andrew Harvey, including exfoliation, centrifugation, UV-vis and TEM analysis. A detailed breakdown of the experimental methods involved, including some material characterisation such as UV-vis and XPS can be found elsewhere and in published work and for the most part will not be reprinted here.⁹¹ AFM analysis was performed by Beata Szydłowska, Raman spectroscopy by Dr Victor Vega-Mayoral and electrochemical measurements between Dr Ian Godwin and myself.

6.2.1 $\text{Co}(\text{OH})_2$ dispersion preparation and characterisation

Exfoliation and size selection

Cobalt hydroxide ($\text{Co}(\text{OH})_2$) nanosheets were prepared as outlined previously. Detailed surfactant concentration and initial $\text{Co}(\text{OH})_2$ concentration studies were performed, described in detail elsewhere. In short, $\text{Co}(\text{OH})_2$ powder (>95% Sigma Aldrich item no. 342440) was pre-treated by sonication using a flathead sonic tip (Sonics VCX-750 processor) in 80 mL deionised water for 2 hrs. The dispersion was then centrifuged (Hettich Mikro 220R) for 1 hour at 4.5 krpm and the supernatant decanted with the sediment being retained. This pre-treated powder was then made into a 20 mg mL^{-1} dispersion by adding 80 mL of a sodium cholate, SC, de-ionized water solution (9 mg mL^{-1} SC) and exfoliated for 4 hrs using a sonic tip at 60% amplitude with a 6 s on 2 s off pulse rate and kept cool using an ice bath. Once sonicated, the dispersion was centrifuged for 120 min at 1.5 krpm to remove larger, unexfoliated material. The sediment was discarded and the supernatant kept. This dispersion is known as the standard sample and contains nanosheets with average flake length, $\langle L \rangle = 90 \text{ nm}$.

Liquid cascade centrifugation was used to separate out dispersions of $\text{Co}(\text{OH})_2$ nanosheets into different size ranges, as previously reported.²⁴⁸ These nanosheets were used to examine the activity of the edge sites for the OER. Later, film thickness investigations used s- $\text{Co}(\text{OH})_2$ nanosheets which had an average flake length, $\langle L \rangle = 50 \text{ nm}$. These were prepared by combining dispersions of the three smallest flake sizes obtained using LCC as a compromise between nanosheet size and produced mass.

UV-vis analysis

Optical absorption and extinction measurements were performed in a 4 mm path length cuvette using a PerkinElmer Lambda 650 spectrometer with an integrating sphere attachment. Spectroscopic metrics were developed to characterise mean nanosheet length and number of layers.

Transmission electron microscopy

Low-resolution bright field TEM imaging was performed using a JEOL 2100, operated at 200 kV. Holey carbon grids (400 mesh) were purchased from Agar Scientific and prepared by diluting a dispersion to a low concentration and drop casting onto a grid placed on a filter membrane to wick away excess solvent. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as “length”, L .

Raman spectroscopy

Raman spectra were acquired using a Horiba Jobin Yvon LabRam HR800. A He-Ne laser (632 nm) was chosen as excitation laser line. Signal was collected using a 100x objective (0.8 N.A.). 600 grooves per mm grating has been chosen in order to obtain $\sim 1.2 \text{ cm}^{-1}$ spectral resolution. Measurements were done in air at room temperature. Beam size on sample is approximately 2 μm diameter and the laser power was kept at 0.2 mW. No degradation or heating effects were observed at the chosen fluence. Each plotted spectra is the result of acquiring signal for 60 seconds and the average of 15 spectra is displayed.

Dispersion concentration

All $\text{Co}(\text{OH})_2$ dispersion concentrations were found by vacuum filtering known volumes onto a Whatman® Anodisc inorganic filter membrane of a known weight, removing surfactant by filtering through 200 mL of deionized water, and left to dry. Once dry, the membrane was weighed and $\text{Co}(\text{OH})_2$ dispersion concentration calculated.

6.2.2 Film formation and device characterization

Dispersions of $\text{Co}(\text{OH})_2$ in SC of a known concentration and volume were vacuum filtered through porous mixed cellulose ester filter membranes (MF-Milipore membrane, hydrophilic, 0.025 μm pore size, 47 mm diameter) resulting in spatially uniform films in a range of well-defined mass/areas (M/A). Films were “washed” to remove remaining surfactant and left dry overnight. Once dry, the films were cut

to desired dimensions using a hole puncher and transferred onto glassy carbon (GC, CH Instruments, CHI104) electrodes for electrochemical testing, glass substrates for profilometry thickness measurements and electrical measurements, and ITO glass for SEM imaging. The cellulose membrane was removed by a series of acetone baths. To help with adhesion and stability during the gas bubbling Nafion (Nafion® 117 solution, Sigam-Aldrich) was added to all films transferred onto GC electrodes. A 5% Nafion solution was prepared in isopropyl alcohol (IPA) and 10 μL was dropcast onto the $\text{Co}(\text{OH})_2$ films and allowed to dry in air.

Film Thickness

Film thickness was measured using a Dektak 6M profilometer from Veeco Instruments. Step height profiles were taken at five different locations to get an average film thickness. Films ranged in thickness from 0.22 – 8.3 μm .

Scanning electron microscopy

SEM images were obtained using a ZEISS Ultra Plus (Carl Zeiss Group), 2 kV accelerating voltage, 30 μm aperture, and a working distance of approximately 1–2 mm.

6.2.3 Electrochemical measurements

Electrochemical measurements were performed on a Gamry model 600 potentiostat. All experiments were conducted in a conventional three electrode cell, with an aqueous 1 M NaOH (pH 14) electrolyte. This solution was prepared from sodium hydroxide pellets (Sigma-Aldrich, minimum 99% purity). For all films, a glassy carbon electrode as a working electrode with a diameter of 3 mm. Prior to use, the glassy carbon electrode was polished with 0.3 μm alumina powder until a mirror finish was achieved. A spiral platinum rod was employed as the counter electrode and a mercury-mercuric oxide (Hg/HgO) reference electrode with a 1 M NaOH filling solution (CH Instruments, CHI 152) was utilised as the reference standard. For this study all potentials are expressed in terms of the oxygen evolution overpotential,

η , and are calculated as outlined in chapter 5. Linear sweep measurements were carried out at 1 mV s^{-1} . Electrochemical impedance spectroscopy was conducted at 0 mV vs Hg/HgO DC bias, 10 mV perturbation and in a frequency range of $0.1 - 10^6$ Hz. Solution resistance was corrected using electrochemical impedance spectroscopy taking the resistance at the high frequency ($>0.1 \text{ MHz}$) plateau of the Bode plot.

6.3 Results and Discussion

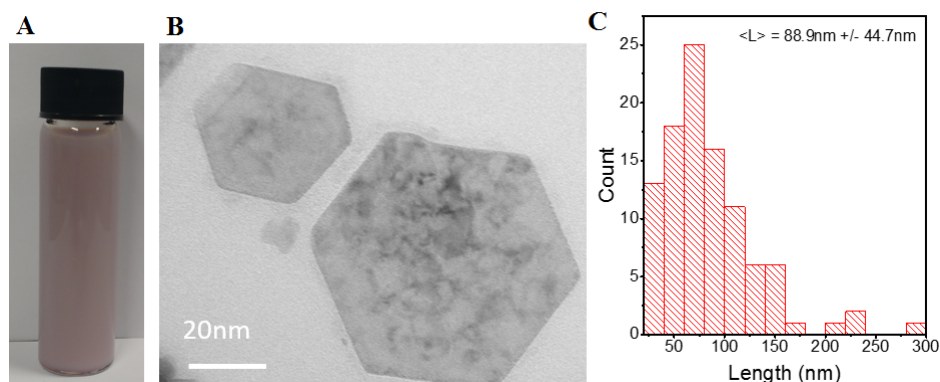


Figure 6.1: *Characterisation of a standard sample of Co(OH)_2 nanosheets. (A) Photograph of typical Co(OH)_2 dispersion in surfactant solution (concentration of Co(OH)_2 was 7 mg mL^{-1}). (B) Representative low resolution TEM image of exfoliated Co(OH)_2 nanosheets. (C) Nanosheet length distribution as measured by TEM*

6.3.1 Exfoliation of Co(OH)_2 nanosheets

Empirically, it has been shown that, like many other layered materials the electrochemical performance of cobalt hydroxide improves when exfoliated into thin 2D nanosheets.^{194,196,217,344} However in the past, LDH nanosheets have been produced by relatively complex methods such as hydrothermal synthesis coupled with exfoliation by ion exchange.^{92,150,184,193} Here we take a simpler approach, demonstrating that Co(OH)_2 nanosheets can be produced directly from the parent crystal using LPE.

Layered Co(OH)_2 , was purchased in powder form from Sigma Aldrich and washed to remove impurities.⁹¹ The simplest, most reliable form of LPE involves high in-

tensity ultrasonication of the layered powder in a water surfactant solution. The ultrasound breaks up the layered crystals to give nanosheets which are rapidly coated with surfactant molecules, stabilising them against aggregation. Surfactant exfoliation has been applied to both uncharged (e.g. graphene and WS_2)^{237,345} and charged (e.g. silicates)³⁴⁶ layered materials and has been used to produce $\text{Ni}(\text{OH})_2$ nanosheets.⁹¹

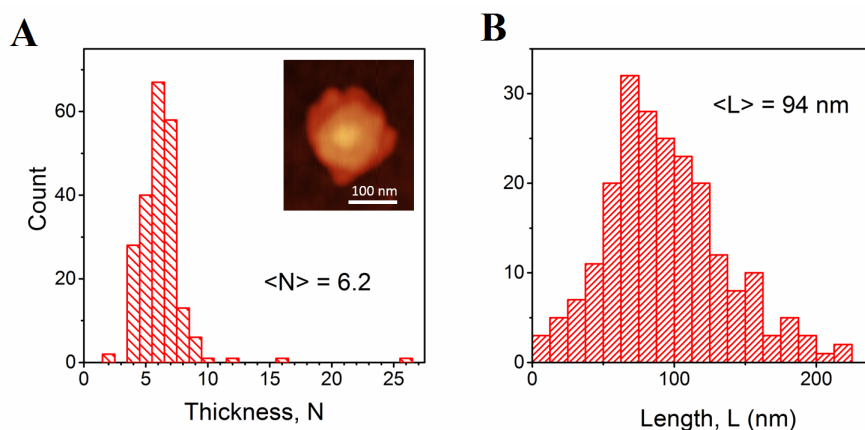


Figure 6.2: *AFM characterisation of standard sample. (A) Nanosheet thickness (layer number) distributions, with sample image in the inset, and (B) nanosheet length distribution.*

To exfoliate $\text{Co}(\text{OH})_2$, the washed powder was added to an aqueous surfactant solution (sodium cholate), tip sonicated, and the dispersion centrifused to remove large aggregates. This resulted in a stable dispersion (figure 6.1A) with the pale pink colour expected for $\beta\text{-Co}(\text{OH})_2$,¹⁶⁹ which we refer to as the standard sample (concentration $\sim 7 \text{ mg mL}^{-1}$).

The success of the exfoliation procedure was confirmed by transmission electron microscopy (TEM) which showed the dispersion to contain large quantities of well-exfoliated, electron transparent nanosheets with well-defined edges as seen in figure 6.1B. Statistical analysis of TEM images shows the nanosheets in the standard sample to be quite small, with lateral sizes (length, L , defined as maximum dimension) between ~ 20 and $\sim 300 \text{ nm}$ ($\langle L \rangle = 88 \pm 5 \text{ nm}$, figure 6.1C). Not all nanosheets were perfectly hexagonal yielding a mean length/width aspect ratio of 1.3 ± 0.1 .

AFM analysis (figure 6.2A and B) showed the nanosheet thickness (presented as number of monolayers per nanosheet, N) to vary between 2 and ~ 10 and gave an L-distribution similar to TEM ($\langle N \rangle = 6.2 \pm 0.2$, also $\langle L \rangle = 94 \pm 4$ nm).

Raman spectroscopy was used to characterise both the purchased $\text{Co}(\text{OH})_2$, as received, and the deposited film of exfoliated nanosheets, both a standard dispersion and one containing mostly 50 nm length flakes (named s- $\text{Co}(\text{OH})_2$, see below). Measured spectra (figures 6.3A) nicely match with those reported in the literature.^{210,347,348} The main spectral difference between the as purchased material and exfoliated nanosheets is a change in the relative intensity of the different peaks as shown in figure 6.3B. This relative intensity thickness dependence has been reported in other layered materials such as WS_2 .³⁴⁹ A final assignment however between Raman peak intensity ratios and nanosheet thickness would require a systematic study beyond the scope of this work. Further Raman analysis can be found in the appendix .

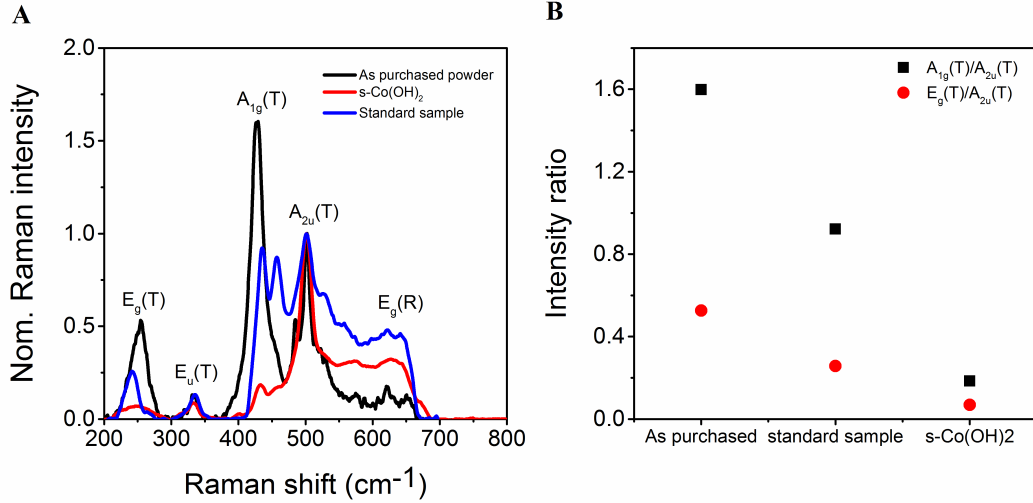


Figure 6.3: Raman characterisation of different sized nanosheets. (A) Raman spectra of as purchased, small flakes and standard sample of $\text{Co}(\text{OH})_2$ in the 200-800 cm^{-1} spectral window. (B) Thickness-dependent intensity ratio of $A_{1g}(\text{T})/A_{2u}(\text{T})$ and $E_g(\text{T})/A_{2u}(\text{T})$

6.3.2 Standard sample electrocatalytic analysis

Nanosheet dispersions can be easily formed into networked structures using vacuum filtration. Figure 6.4A shows an SEM image of a $\sim 0.1 \text{ mg cm}^{-2}$ $\text{Co}(\text{OH})_2$ film which clearly consists of a disordered, porous nanosheet network. The measured density of such films is $\sim 2300 \text{ kg m}^{-3}$ implying a fractional pore volume of $\sim 35\%$. This high porosity will allow electrolyte infiltration and makes such networks ideal for electrochemical applications.¹⁰⁰ To test the electrocatalytic performance of our exfoliated $\text{Co}(\text{OH})_2$ nanosheets, we measured linear sweep voltammograms (LSVs) for a 0.1 mg cm^{-2} film of standard sample nanosheets deposited on glassy carbon (GC) as shown in figure 6.4B (1 M NaOH). This curve shows the expected exponential increase and reaches a current density of 10 mA cm^{-2} at an overpotential of 440 mV. This performance is not exceptional: $\text{Co}(\text{OH})_2$ electrocatalysts reach 10 mA cm^{-2} at overpotentials in the range 300 – 450 mV.^{194,210,217} However, LPE-based samples have a significant advantage in that production and processing is very simple. This will facilitate electrode optimisation leading to significant improvements in the OER performance.

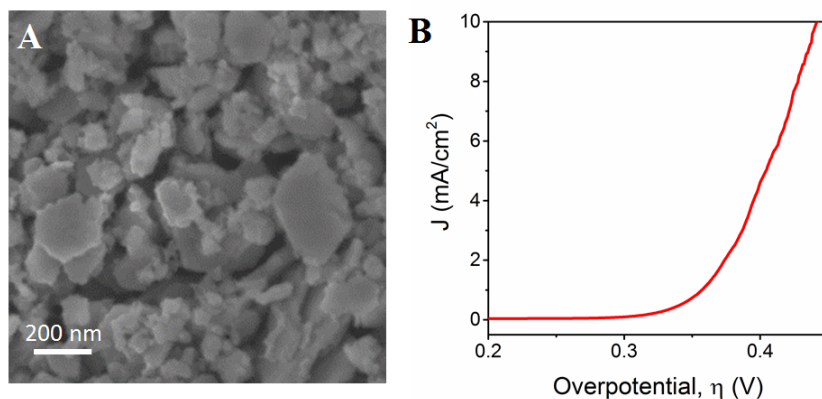


Figure 6.4: (A) SEM image of a vacuum filtered film of standard sample $\text{Co}(\text{OH})_2$ nanosheets. (B) Polarisation curve for an electrode consisting of vacuum filtered $\text{Co}(\text{OH})_2$ nanosheets on a glassy carbon electrode (1 M NaOH, scan rate 1 mV s^{-1}).

6.3.3 Optimisation of catalyst performance

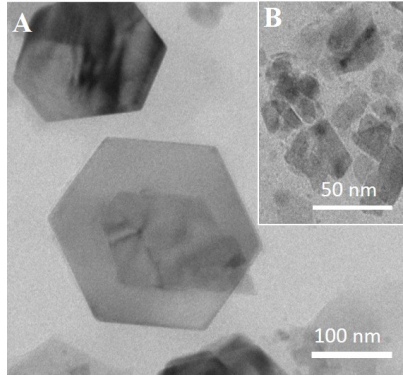


Figure 6.5: (A-B) Representative TEM images of size selected $\text{Co}(\text{OH})_2$ nanosheets from the largest (A) and smallest (B) fractions.

Length dependence and nanosheet edges

To maximise catalytic performance, it is necessary to identify the active sites for OER catalysis. Speculation and theoretical analysis^{92,184,188,189,191} implies edge sites, similar to TMDs for the HER⁴² however a fully characterised comparison between flake edges and OER activity is needed. Here, we attempt to show categorically that the active sites for $\text{Co}(\text{OH})_2$ OER catalysts lie on the nanosheet edges. In chapter 5 it was revealed that, for gas evolution reactions catalysed by nanosheets where the active sites are at the edges, the observed current density, J , is given by a specialised version of the Tafel equation^{289,350} (represented here in the anodic form)

$$J = 2ne [R_0 B] \times 10^{\eta/b} \times \left[\frac{(1+k)(1-P)}{\langle L \rangle d_0} \right] t \quad (6.1)$$

where η is the overpotential, b is the Tafel slope, n is the number of electrons supplied per gas molecule formed (here O_2 so $n=4$), R_0 is the zero-overpotential turnover frequency (per site), B is the number of catalytic active sites per unit nanosheet edge length, k is the nanosheet length/width aspect ratio, P is the electrode porosity, $\langle L \rangle$ is the mean nanosheet length, d_0 is the monolayer thickness and t is the electrode thickness. Here the product $R_0 B$ is the number of O_2 molecules produced per second

per unit edge length (including edges associated with all individual layers stacked in few-layer nanosheets) at zero overpotential and can be thought of as a figure of merit for the catalytic activity of a nanosheet.

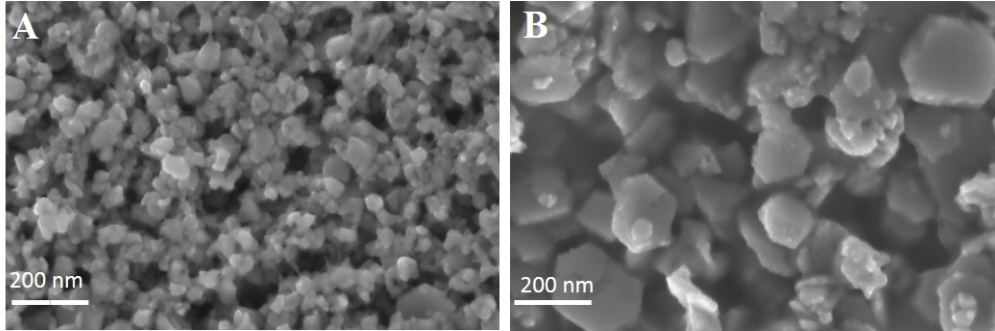


Figure 6.6: Representative SEM images of vacuum filtered film of Co(OH)_2 nanosheets from small (31 nm) (A) and large (115 nm) (B) fractions.

Clearly, this equation predicts that, if the edges are active, the current density at a given overpotential will scale inversely with $\langle L \rangle$. In addition, it predicts that the overpotential at a given current density, J , scales as

$$\eta_J = b \log \langle L \rangle + C(J) \quad (6.2)$$

where C is a combination of other parameters, including J . Thus, by analysing the dependence of catalytic performance on nanosheet length, one can determine whether or not edges are the active sites.

To perform such experiments, a stock dispersion produced by LPE was separated into fractions containing 14 different size nanosheets using liquid cascade centrifugation²⁴⁸. The optical properties of nanosheet dispersions can be very sensitive to nanosheet size thus the extinction, absorption and scattering coefficient spectra for five distinct sizes were measured and analysed. Details of this analysis is shown in the appendix. Combining UV-vis spectroscopy and statistical TEM analysis an empirical relationship between the scattering exponent, n , and average flake length, $\langle L \rangle$, can be found:

$$\langle L \rangle = 185 (n/4 - 1) \quad (6.3)$$

From this, flake lengths were determined, yielding values of $\langle L \rangle$ between 36 and 184 nm

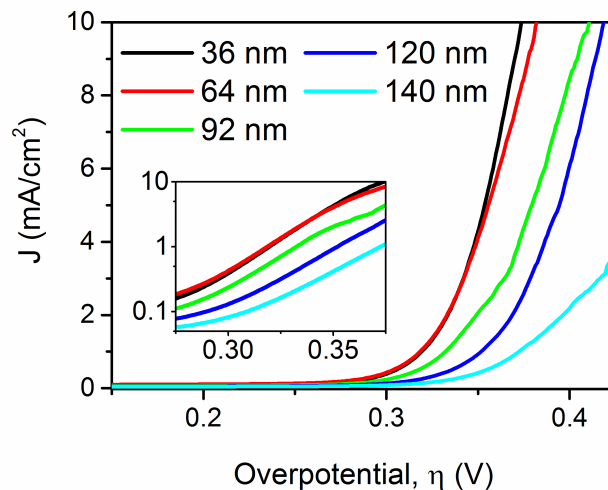


Figure 6.7: LSVs for $\text{Co}(\text{OH})_2$ electrodes with a fixed thickness of $\sim 0.43 \mu\text{m}$ (0.1 mg cm^{-2}) for a range of nanosheet lengths (1 M NaOH). Inset: corresponding Tafel plots.

Typical TEM images of the smallest and largest fractions are shown in figure 6.5A-B. These size-selected dispersions were used to prepare porous films of stacked nanosheets of approximately equal masses of $\sim 0.1 \text{ mg cm}^{-2}$ using vacuum filtration as shown in SEM images figure 6.6A and B. Electrode thickness was measured by profilometry giving an average value of $\sim 430 \pm 50 \text{ nm}$. The densities of these films were typically $2330 \pm 400 \text{ kg m}^{-3}$, leading to porosities of roughly $35 \pm 9\%$. A section of each film was then transferred onto glassy carbon (GC) electrodes for electrochemical testing (area 0.07 cm^2).

To test the electrocatalytic performance of such electrodes, LSVs (1 mV s^{-1} , 1 M NaOH) were performed in a three-electrode cell. Typical polarisation curves are shown in figure 6.7 and clearly show improved catalytic performance as $\langle L \rangle$ is decreased.

Tafel plots were then produced by plotting the log of current density (J) against overpotential, η , for each film as shown in the inset of figure 6.7. Fitting the linear portion of these to the Tafel equation ($\log(J) = \eta/b + \log(J_0)$) typically allows the extraction of the Tafel slope, b , and exchange current density, J_0 , for each film, as shown in figure 6.8A and B (J_0 is t normalised to remove any thickness effects on the activity, according to equation 6.1). While a trend appears to emerge, with J_0 decreasing with increasing nanosheet length and b increasing with increasing nanosheet length, we believe this trend to be spurious.

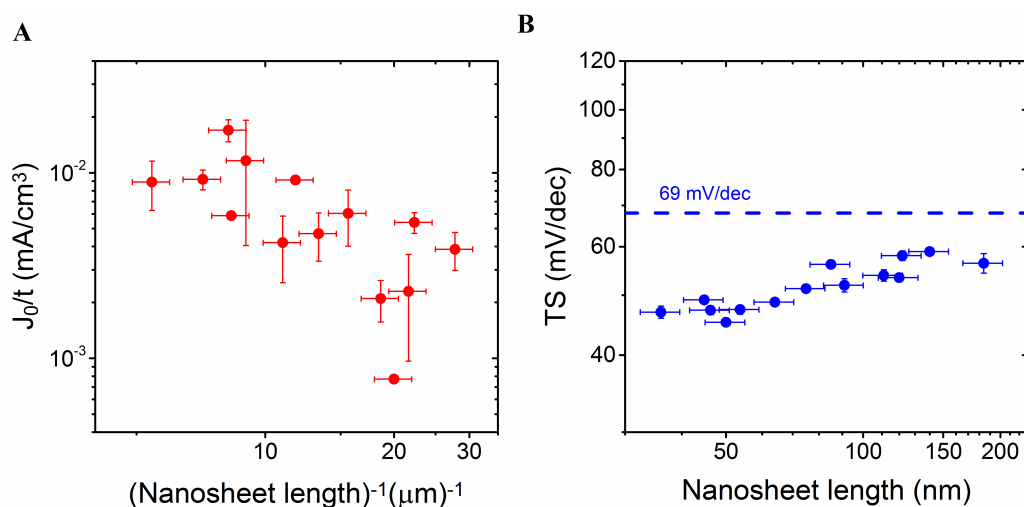


Figure 6.8: *Tafel plot analysis for $\text{Co}(\text{OH})_2$ films. (A) Thickness-normalised exchange current density, J_0 , and (B) Tafel slope plotted versus mean nanosheet length. Dashed line in (B) representing the calculated Tafel slope for $\text{Co}(\text{OH})_2$ based on equation 6.2.*

Taking the derivative of $\log(J)$ with respect to the overpotential gives $d(\log J)/d\eta = 1/b$. Thus, we would expect an LSV with a well-defined linear region to yield a graph of $d(\log J)/d\eta$ versus η which displays a clear plateau region with height $1/b$ which spans the full length of the linear Tafel region. A wide, well-defined plateau would indicate a well-defined linear Tafel region consistent with the Butler-Volmer equation. This would allow b and J_0 to be measured.

However, figure 6.9A shows that no such plateau region exists, rather a peak is found. This suggests that the linear region for $\text{Co}(\text{OH})_2$ has not had a chance

to fully develop in these samples. This leads us to conclude that both the Tafel slope, b , and J_0 cannot be reported with confidence. This lack of a fully-developed linear region may be due to oxidation of the material at low overpotential and diffusion limitations at higher overpotential. For example, at low potential, as η increases, more of the $\text{Co}(\text{OH})_2$ is oxidised into CoOOH . If both $\text{Co}(\text{OH})_2$ and CoOOH contribute to the OER, they will both have competing Tafel slopes for the reaction. Thus at any given potential the value measured for Tafel slope is a combination of these two Tafel slopes, and both change at each new value of potential. Conversely, at higher potential, when diffusion becomes rate limiting, $d(\log J)/d\eta$ will fall. If the overpotential ranges where oxidation and diffusion are important are too close together, a linear region will never develop and a plateau in $d(\log J)/d\eta$ vs η will not be observed.

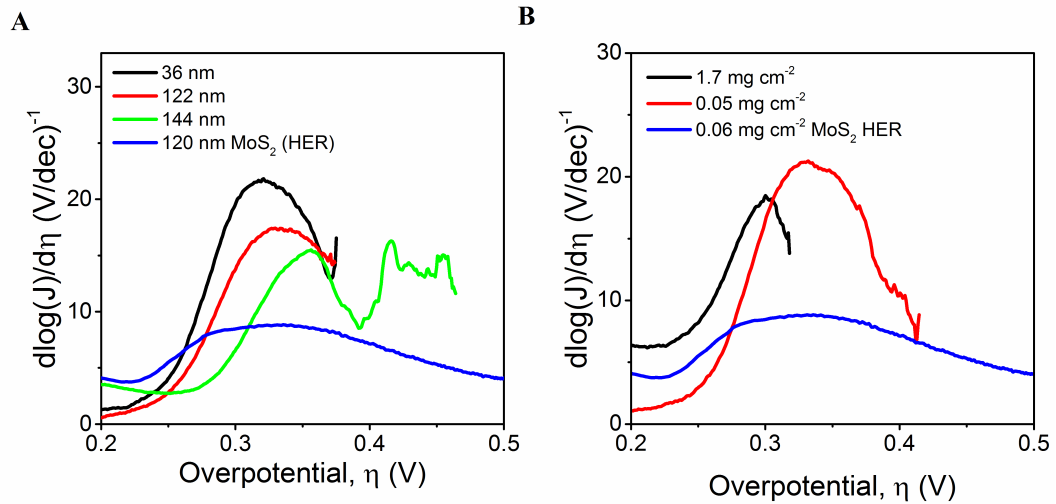


Figure 6.9: Plot of the derivative of $\log(J)$ with respect to overpotential, η , versus η for (A) 0.1 mg cm^{-2} film made of ranging nanosheet length and (B) for films made of ranging film thicknesses (including an MoS_2 film for the HER). The derivative is in units of inverse Tafel slope and shows a peak in place of a plateau region that would be expected if there was a well-defined Tafel region

If this is the case, we would expect the peak in the $d(\log J)/d\eta$ vs η curve to be narrower for thicker electrodes where diffusion becomes limiting at lower overpotential. As shown later in figure 6.9B, this is exactly what is observed. In addition,

for comparison we have plotted the results of $d(\log J)/d\eta$ vs η for data from the more stable cathodic hydrogen evolution reaction, HER, also shown in figure 6.9A and B (using an electrode made of MoS₂ nanosheets as an example catalyst). It can be seen that the peak for HER is much broader than in any of the OER data sets indicating that Co(OH)₂ OER reaction is indeed much less ideal.

In samples where the linear region does not develop, we would expect the peak in the $d(\log J)/d\eta$ vs η curve to be below the true plateau value (which represents $1/b$). This means that fitting the Tafel plot results in a measured value of b which is higher than the actual value. As a result, any values of b quoted here are effective values and do not represent the actual values. We could only conclude that the apparent Tafel slope was ~ 60 mV dec⁻¹ (or in-between 60 and 40) for all nanosheet lengths, consistent with literature reports.⁹² It should be noted however that the trend in figure 6.8B, where TS is increasing with increasing nanosheet flake length may have some semblance of truth behind it. Similar increases in measured Tafel slope as particle size decreases has been seen previously in literature.^{92,194}

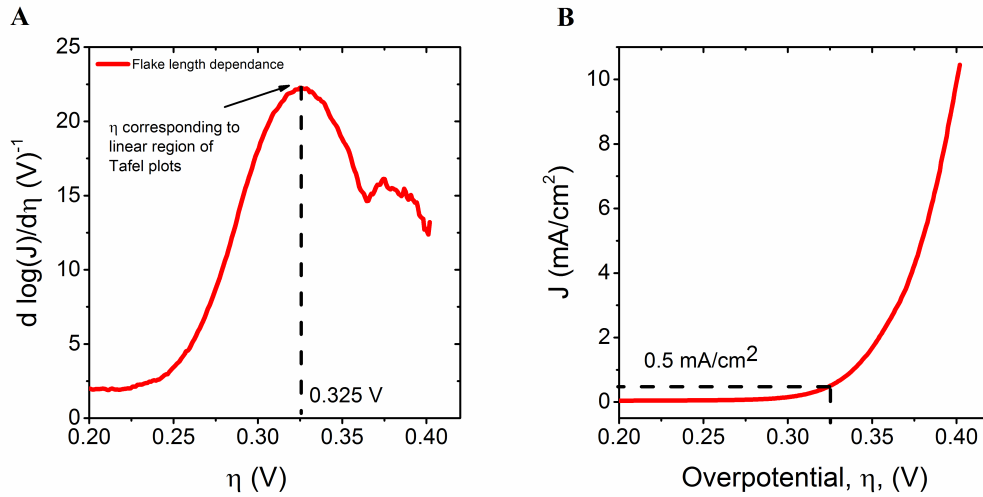


Figure 6.10: : (A) Plot of the derivative of $\log(J)$ with respect to overpotential, η , versus η for 0.1 mg cm^{-2} film made of nanosheets of length 50 nm and (B) the corresponding polarisation curve for that film.

Choice of metrics

To properly analyse the data, careful choice of metrics is important. To apply quantitative analysis based on the Tafel equation (equations 6.1 and 6.2), one must first identify regions of the Tafel plot which are as close to linearity as possible. The highest point in the $d(\log J)/d\eta$ *versus* η overpotential peaks of figure 6.9A corresponds to an overpotential region that is the most linear, or in other words is best described by the Butler-Volmer equation. This overpotential value in turn corresponds to a current density that is least affected by diffusion or other parameters that limit current (see figure 6.10A and B). And importantly, this ‘ideal’ value of current changes depending on parameters such as film thickness, flake length etc. In order to properly analyse our data and extract meaningful results we must choose metrics (η @ given J and J @ given η) that closely match the ‘ideal’ η and J values. Based on this, for each nanosheet length, we extracted from the LSVs the overpotential at 0.5 mA cm^{-2} ($\eta_{0.5 \text{ mA/cm}^2}$) and the current density at 0.3 V ($J_{0.3 \text{ V}}$) as metrics for catalytic performance as they best represented the linear region for each flake length while still allowing for consistency in comparing overpotentials throughout the results. In addition, to provide continuity and allow comparison with the literature, we extracted data for the overpotential at 10 mA cm^{-2} ($\eta_{10 \text{ mA/cm}^2}$).

In order to remove the effects of variations in film thickness on current density in the nanosheet dependence study, all measured current values were transformed into J , by $J = (J_{\text{measured}}/t_{\text{film}}) \times t_{\text{average}}$ where t_{film} is the thickness of the individual film (thus removing effects due to variations from electrode to electrode) and t_{average} is the average thickness across all measured films. These parameters are plotted *versus* $\langle L \rangle$ in figures 6.11A and B and show a logarithmic increase in $\eta_{0.5 \text{ mA/cm}^2}$ $\langle L \rangle$ and a linear scaling of $J_{0.3 \text{ V}}$ with $1/\langle L \rangle$, exactly as predicted by equations 6.2 and 6.1 respectively. Fitting the data in figure 6.11A to equation 6.2 yields an effective Tafel slope of $b=69 \pm 13 \text{ mV dec}^{-1}$, in reasonable agreement with the LSVs (figure 6.8B).

The length-dependent data described above clearly shows the smallest nanosheets to be the best OER catalysts because of their high edge content. Thus, for the rest of this work, we will use a size selection scheme (see Methods) designed to give the

smallest nanosheets which are attainable at a reasonable mass yield. We label this fraction s-Co(OH)₂, with AFM characterisation (figure 6.12A and B) showing it to contain nanosheets with $\langle N \rangle = 4.8 \pm 0.3$ and $\langle L \rangle = 57 \pm 4$ nm.

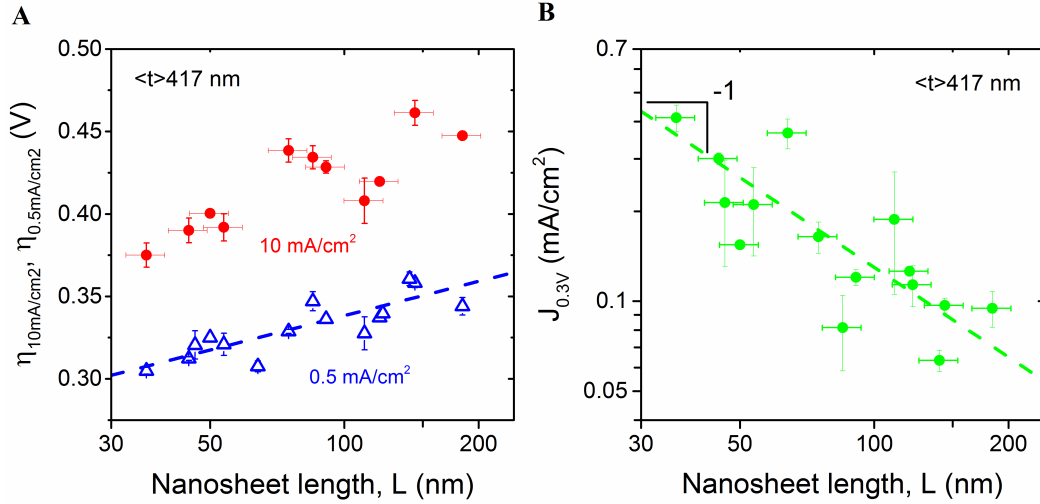


Figure 6.11: (A) Overpotential, η measured at current densities of 10 and 0.5 mA cm^{-2} and (B) current density, measured at $\eta = 0.3 \text{ V}$. Both (A) and (B) are plotted versus mean nanosheet length (on logarithmic scale). In (A) only the data measured at lower currents are fitted to equations 6.2 as the currents used represent the portions of the Tafel plots most closely approximating linearity.

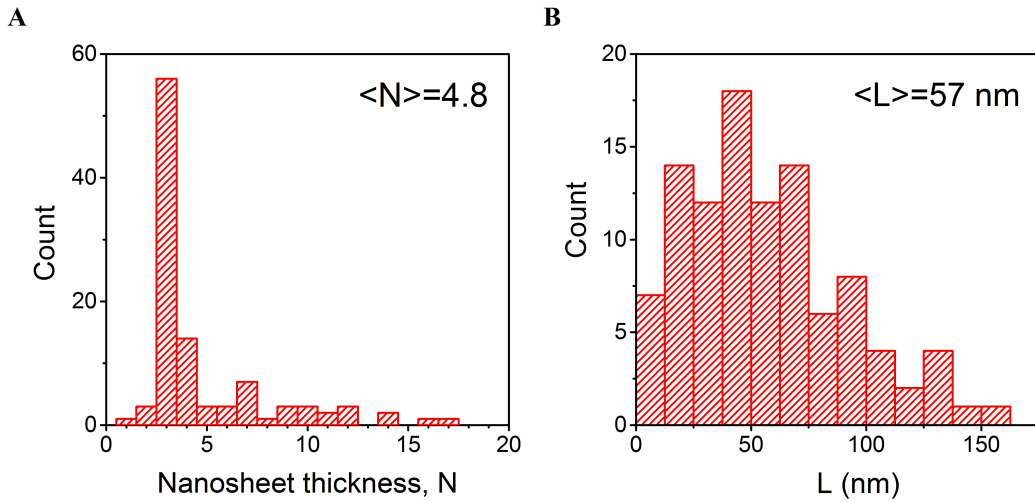


Figure 6.12: (A) AFM thickness distribution for s-Co(OH)₂ nanosheets and (B) corresponding length distribution.

Electrode thickness dependence

Improving catalyst design not only requires maximising the density of active sites (ie small nanosheets) but also maximising the total number of active sites in a given area. This can be achieved by increasing electrode thickness or mass/area (M/A) and enables the generation of high absolute currents necessary for practical industrial applications. This is illustrated by equation 6.1 which shows the current density to scale linearly with electrode thickness (t) and implies the overpotential at a given current density (J) to scale as

$$\eta_J = -b \log t + C'(J) \quad (6.4)$$

where C' is a combination of other parameters, including J.

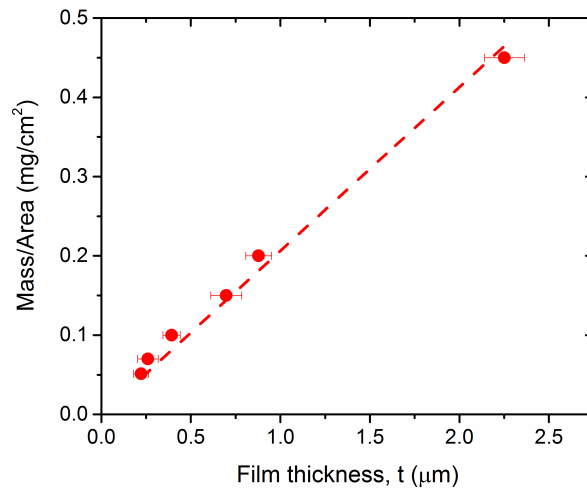


Figure 6.13: *Mass per unit area of s-Co(OH)₂ films plotted against measured film thickness.*

To examine the thickness dependence, we used s-Co(OH)₂ nanosheets to produce a range of electrodes (on glassy carbon) with M/A ranging from 0.042 to 1.7 mg cm⁻² (0.22 ≤ t ≤ 8.3 μm), a considerably broader range than tested previously in the literature.^{92,184,194,199,201,202,206,226}

To measure the average density and porosity of the films, firstly an accurate M/A of each film was measured by filtering a precisely known volume of dispersion, of known concentration onto a membrane, with known area. Once film thickness was measured the average film density was easily found by plotting M/A *versus* t , as shown in figure 6.13, and fitting to a linear relationship $M/A = \rho_{film} \times t$ to give $\rho_{film} = 2060 \pm 60 \text{ kg m}^{-3}$. The film porosity was then calculated using $P = 1 - \rho_{film}/\rho_{NS}$, taking density of $\text{Co}(\text{OH})_2$ nanosheets, $\rho_{NS} = 3597 \text{ kg m}^{-3}$, leading to an average porosity of $P = 43 \pm 2\%$.

LSVs were obtained for each film thickness, with representative curves shown in figure 6.14. As expected, we see a significant performance increase as the thickness is increased which we associate with the greater in the number of active sites. Again a trend emerges showing an increase of both b and J_0 with rising t (figure 6.15A and B). Yet as before, the linear region was not extensive enough to generate reliable data (figure 6.9B). Thus while an increasing J_0 with t is as seen previously for MoS_2 electrodes, the exact shape of this plot is unreliable. The same is true for Tafel slope, conclusions cannot be made beyond the fact that b is in the range of $\sim 45 - 60 \text{ mV dec}^{-1}$ for all electrodes (figure 6.15B).

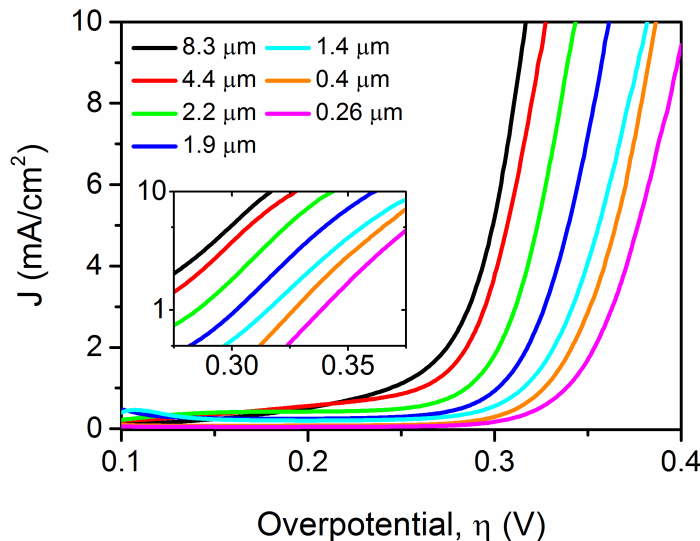


Figure 6.14: LSVs for electrodes of various thicknesses fabricated from $s\text{-Co}(\text{OH})_2$ (1M NaOH). Inset: corresponding Tafel plots

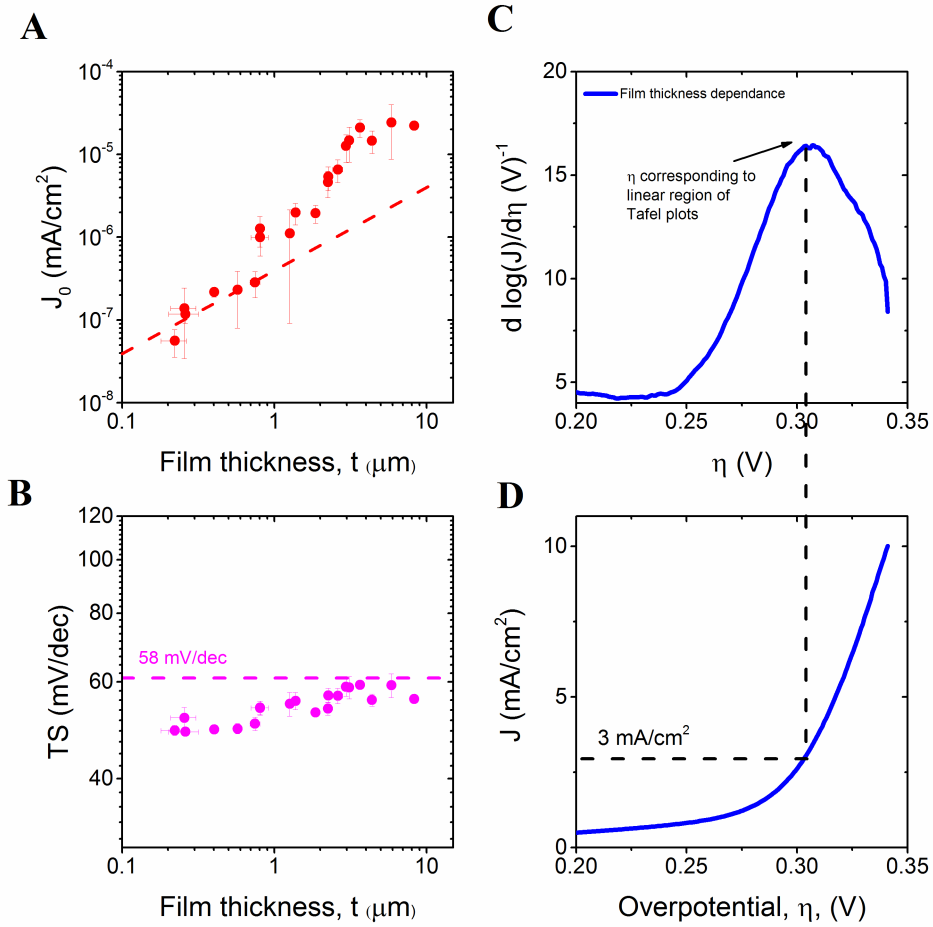


Figure 6.15: (A) J_0 and (B) Tafel slope plotted versus film thickness, with the dashed line in (B) representing the calculated Tafel slope for $\text{Co}(\text{OH})_2$ based on equation 6.4. (C) Plot of the derivative of $\log(J)$ with respect to overpotential, η , versus η for a thick $5.8 \mu\text{m}$ (1.2 mg cm^{-2}) film made of $s\text{-Co}(\text{OH})_2$ nanosheets and (D) corresponding LSV.

Using the same procedure as before, we identified metrics which best represent the linear portion of the Tafel plot (see figure 6.15C and D) as $\eta_{3\text{mA/cm}^2}$ and $J_{0.3\text{V}}$. Along with $\eta_{10\text{mA/cm}^2}$, these parameters are plotted *versus* film thickness in figures 6.16A and B. This data shows a logarithmic decrease of $\eta_{3\text{mA/cm}^2}$ with t and a linear scaling of $J_{0.3\text{V}}$ with t exactly as predicted by equations 6.4 and 6.1 respectively. Fitting the data in figure 6.16A to equation 6.4 yields an effective Tafel slope of $b = 58 \pm 5 \text{ mV dec}^{-1}$, in good agreement with the LSV data (6.15B).

6.3.4 Edges are active sites throughout the film (Active edge site discussion)

It is clear that the outputs of fitting the L- and t-dependent data using the edge-active site model represented by equations 6.1, 6.2 and 6.4 are in good agreement. The obtained Tafel slopes (69 ± 13 vs. 58 ± 5 mV dec⁻¹ respectively) agree within error and are in line with the values of ~ 60 mV dec⁻¹ implied by the LSVs and with literature values.⁹² However, a better way to compare the L- and t-dependent data is to note that equation 6.1 predicts the ratio of $t^{-1}dJ_{0.3V}/d(1/L)|_{\text{constant } t}$ to $dJ_{0.3V}/dt|_{\text{constant } L}$ should equal the mean nanosheet length for the experiments performed while varying film thickness. Thus taking $t^{-1}dJ_{0.3V}/d(1/L)|_{\text{constant } t} = X$, and $dJ_{0.3V}/dt|_{\text{constant } L} = Y$, we get;

$$X = t^{-1}dJ_{0.3V}/d(1/L) = 2ne [R_0B] \times 10^{\eta_X/b} \times \left[\frac{(1+k)(1-P)}{d_0} \right] \quad (6.5)$$

$$Y = dJ_{0.3V}/dt = 2ne [R_0B] \times 10^{\eta_Y/b} \times \left[\frac{(1+k)(1-P)}{\langle L \rangle d_0} \right] \quad (6.6)$$

$$X/Y = 10^{(\eta_X - \eta_Y)/b} \times \langle L \rangle \quad (6.7)$$

Using the values of experimental slopes for X and Y, where $\eta_X = \eta_Y = 0.3V$ and taking $\langle t \rangle = 430$ nm, this gives a mean nanosheet length of $\langle L \rangle = 62$ nm which can be compared with the value of $\langle L \rangle = 57$ nm measured by AFM. This agreement is excellent and is very strong evidence that the data is consistent with the edge-active site model represented by equations 6.1, 6.2 and 6.4. This of course strongly suggests the active sites to reside on the nanosheet edges.

Calculating the figure of merit, R_0B accurately is difficult due to the uncertainty in the Tafel slope. However, we found the data fits in figure 6.16A to give the lowest error: $R_0B \approx 685.34 \pm 100$ s⁻¹ m⁻¹. Using the data in figure 6.16B, we can more accurately estimate the oxygen production rate at $\eta = 0.3$ V ($R_\eta B = R_0B \times 10^{\eta/b}$) as 108 ± 25 molecules s⁻¹ μm^{-1} of edge length

It can be of interest to compare this value to typical calculated TOF of $\text{Co}(\text{OH})_2$ in the literature to measure active site density. Although it should be noted that most TOF calculations for $\text{Co}(\text{OH})_2$ are based on non-ideal assumptions about number of active sites (usually calculated from the voltammetric charge) and thus can generally be considered conservative estimates. Taking $R_{\eta=0.3V} = 0.09 \text{ s}^{-1}$ from reference¹⁹⁴ we can find a value for $B = 1.2 \text{ nm}^{-1}$ or in other words there is an active site every 0.83 nm along the nanosheet edge. Compared to the unit cell of $\text{Co}(\text{OH})_2$ which has a Co atom roughly every 0.317 nm we can approximately say one in every 2.6 Co edge atoms are active.

Thickness limitations

The observed linear scaling of $J_{0.3V}$ with t suggests O_2 is being generated throughout the porous film even up to film thicknesses as high as 8 μm . This lack of current saturation at high electrode thickness is in contrast to most of the literature^{92,185,201} and may be related to the relatively high porosity. Despite the linear scaling however, this work is indeed limited by problems at high electrode thickness. We found $t=8 \mu\text{m}$ to be the highest thickness where we could make $\text{Co}(\text{OH})_2$ nanosheet films reliably without spontaneous cracking during film drying or transfer to GC. This is a manifestation of the so-called critical cracking thickness (CCT), which is the maximum achievable thickness of granular films before the onset of mechanical instabilities.^{351,352} This is a significant issue as the only way to continue to improve performance of our electrodes is to further increase the thickness. What is required is a method to increase the CCT while at the same time removing the charge transport limitations which are expected for very thick electrodes.³⁵³ Achieving this would leave only mass transport (diffusion) effects to limit the performance of very thick films.

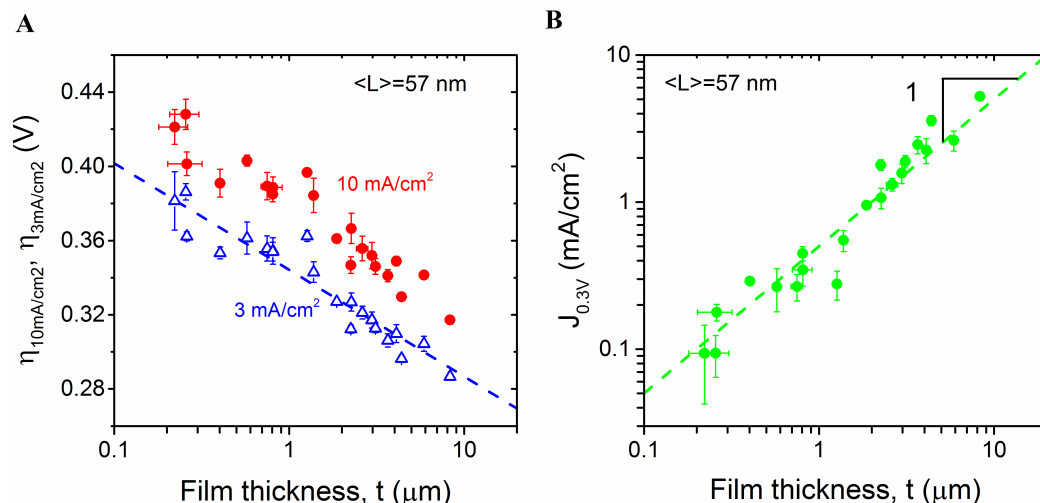


Figure 6.16: (A) Overpotential, measured at current densities of 10 and 3 mA cm^{-2} and (B) current density, measured at $\eta=0.3\text{ V}$, both plotted versus film thickness. In (A) only the data measured at lower currents are fitted to equations 6.4 as the currents used represent the portions of the Tafel plots most closely approximating linearity.

6.4 Conclusion

In this work, we have demonstrated that low-cost $\text{Co}(\text{OH})_2$ crystals can be exfoliated in surfactant solutions to give a dispersion of relatively thin $\text{Co}(\text{OH})_2$ nanosheets. Thin films of these nanosheets act as average OER electrocatalysts, requiring 440 mV to generate 10 mA cm^{-2} . However, the advantage of liquid phase exfoliation is that it gives large quantities of nanosheets in a very processable form. This allowed us to size select dispersions into varying nanosheet lengths using centrifugation, and ultimately link nanosheet activity to the edge sites of the catalyst through application of an edge site active model, developed in the chapter 5. We then increased the performance through optimising the electrode thickness and perfecting nanosheet size. This resulted in a reduction in overpotential of 123 mV to reach 10mA cm^{-2} . This is a total reduction of 30% using just systematic electrode optimisation techniques. This performance increase eventually reached a limit as higher thickness resulted in mechanical instability.

Chapter 7

1D:2D Composite Electrocatalysts for HER and OER

7.1 Introduction

To improve the performance of electrocatalysts made of exfoliated 2D nanosheets for the HER and OER maximising electrode thickness has proven to be a successful strategy. In chapters 4 and 5 we demonstrated how systematically increasing the electrode thickness (or mass per area) can result in higher rates of gas production and reduced overpotentials. Importantly, this increase in rate (current density) was shown to be directly proportional to the film thickness, thus providing a straightforward model to increase electrode performance.

However this improvement was not infinite, and performance gains ceased to continue beyond a threshold thickness. After $\sim 5\text{ }\mu\text{m}$ for MoS_2 nanosheet films and $\sim 8.3\text{ }\mu\text{m}$ for $\text{Co}(\text{OH})_2$ nanosheet films limitations arose, saturating performance or hindering film formation. This is a common phenomenon for thick electrodes and others in the literature similarly have experienced failure at high electrode thickness or mass loadings for both HER^{45,118,130,141,142} and OER²⁰⁴ electrocatalysts. It should be noted however that these limits are typically reached at far lower M/A than our catalyst electrodes.

There are a number of reasons why further increasing the thickness of nanosheet films may not result in significant performance increases. Perhaps the most well-

known are diffusion limitations arising due to slow mass transport rates of ions, and gas shielding effects by trapped bubbles. These effects can then lead to a limiting current. However, it is perhaps less appreciated that thick electrodes can be electrically and mechanically limited. Many catalytically active nanomaterials are low conductivity semi-conductors such as MoS_2 or Co(OH)_2 , meaning the high intrinsic activity of the material can be undermined by poor electrical transport kinetics.^{204,289}

Alternatively the mechanical integrity of the film may be a problem. It is not trivial to make arbitrarily thick electrodes from solution processed nanoparticles, as above a critical thickness mechanical instabilities can arise.^{351,352} These can then lead to cracking and electrode failure – especially during gas evolution. As discussed in chapter 6 for our Co(OH)_2 nanosheet films, above $8.3\text{ }\mu\text{m}$ a critical cracking thickness (CCT) was reached, after which mechanical instabilities inhibited film formation. Because the CCT scales with the fracture toughness of the film,^{351,352} the simplest approach to increasing it is to improve the mechanical properties of the electrode material.

One solution to address both electrical and mechanical shortcomings of nanosheet catalysts is to create hybrid films with conductive carbon additives,^{124,132,145–148,153,221–223,226} in particular 1D carbon nanotubes (CNTs).^{149–152,185,201,213,224,225} This has been approached in literature for both HER and OER catalysts however these generally involve complex synthesis methods with CNTs used as anchoring sites for catalytic particles.²⁹⁰ Producing composites in this manner reduces flexibility in controlling the fraction of filler to active material, making it more difficult to tune electrical properties.

A simpler and perhaps more versatile approach to is to use liquid exfoliation coupled with solution mixing⁸² to create dispersions of nanosheets mixed with carbon nanotubes (CNTs). Such dispersions can then be formed into robust composite films⁸² of a mixed nanosheet/nanotube network, using the same processing techniques as before. These composite films can be up to 10^9 times more conductive than a nanosheet networks alone¹⁴⁴ and display vastly improved mechanical properties.^{96,288} This approach has been explored in detail for supercapacitor electrodes²⁸⁸

however has only been touched upon for HER electrodes^{130,150,158} and even less so for OER.

By embedding conductive pathways throughout the film electrons can bypass the poorly conducting material, facilitating charge transport from the current collecting substrate to the nanosheet edges. Demonstrated recently for MnO₂ nanosheet supercapacitors,²⁸⁸ mixing single-walled carbon nanotubes (SWNTs) to form hybrid films, showed that just a few volume percent nanotubes could lead to dramatic enhancements in both the conductivity and capacitance. Notably, these enhancements were both fully consistent with percolation theory. Nanotubes also improve mechanical properties as the high aspect ratio makes them ideal as a binder material.²⁹³ Adding as little as 5wt% SWNTs to a network of MoS₂ nanosheets has been shown to improve both tensile toughness and electrical conductivity by $\times 100$ and $\times 10^8$ respectively.²⁹³

Lacking is a systematic investigation on the effects of CNTs on the catalyst activity. Such a detailed study would be important both from the perspective of basic science and for practical reasons: e.g. to identify the minimum nanoconductor mass fraction required.

In this chapter we aim to address the limitations associated with producing high-performance, thick catalytic electrodes by using composite nanosheet/nanotube films. Using LPE for both nanosheets and nanotubes facilitates the fabrication of composites by simple solution mixing. Initially MoS₂/SWNT hybrid catalysts are examined. Electrical conductivity improvements are seen which lead to catalytic improvements for the HER in acid. Subsequently Co(OH)₂/SWNT films are investigated, revealing both electrical and mechanical enhancements, leading to vast catalytic improvements for the OER in alkaline. We demonstrate improvements in all aspects can be described by percolation theory, meaning just a few weight percent of nanotubes can dramatically improve the mechanical, electrical and the catalytic performance.

Finally composite films allowed for the formation of freestanding films (FS) of Co(OH)₂ which were not mechanically or electrically limited. Removing the substrate allows issues with physical adhesion to be avoided. This is particularly rel-

evant when operating at large current densities required in industrial electrolyzers, typically $\sim 300 \text{ mA cm}^{-2}$.^{354,355} Using an optimised electrode thickness of $70 \text{ }\mu\text{m}$ and tuning the electrolyte concentration and temperature, we were able to achieve current densities of 50 mA cm^{-2} at overpotentials as low as 235 mV , only 25 mV above the state-of-the-art (50 mA cm^{-2} @ 210 mV).¹⁸⁴

7.2 Experimental procedure

Exfoliation and flake size selection of $\text{Co}(\text{OH})_2$ nanosheets were performed by Dr Andrew Harvey, $\text{Co}(\text{OH})_2/\text{SWNT}$ composite electrochemical measurements were performed by Dr Ian Godwin and myself, and mechanical measurements of $\text{Co}(\text{OH})_2/\text{SWNT}$ FS films were carried out by Dr Conor Boland.

7.2.1 Material dispersion preparation and characterisation

MoS_2 and $\text{Co}(\text{OH})_2$ nanosheets

A detailed description of the preparation of nanosheet dispersions of MoS_2 and $\text{Co}(\text{OH})_2$ can be found in the Methods of chapter 5 and 6 respectively and are as the same here. Bulk powder (MoS_2 or $\text{Co}(\text{OH})_2$) was tip sonicated in aqueous SC solution to give a stable dispersion of exfoliated nanosheets. Nanosheets were separated by flake size using LCC and a dispersion containing $\langle L \rangle = 120 \text{ nm}$ (MoS_2) or 50 nm ($\text{s-Co}(\text{OH})_2$) was obtained. Average flake length and number of layers per flake were found using UV-visible absorption spectroscopy measurements and TEM image analysis, as outlined previously.

Single-walled carbon nanotube (SWNT)

A stock solution of 10 mg mL^{-1} SC in deionised water was prepared. SWNT powder (Hanwah Nanotech) was added to the solution such that the SC/SWNT mass ratio in the resulting dispersion was 10:1 (SWNT concentration 1 mg mL^{-1}). The dispersion was divided into separate vials of 8-10 mL and each received 5 min of high power tip sonication using a tapered-tip at 25% amplitude, pulse rate 2 s on 2 s off, then

30 mins in a sonic bath (Branson 1510-MT sonic bath, 20kHz), followed by another 5 min of tip sonication.

The dispersions were then centrifuged at 5500 rpm for 90 min and the supernatant of each was retrieved. The concentration of the resulting SWNT dispersion was found by measuring the UV-vis extinction at 660 nm using a Varian Cary 6000i. From the Beer-Lambert relation: $Ext/\epsilon d$, the dispersion concentration, C , was found using the extinction coefficient of SWNT, $= 3389 \text{ mL mg}^{-1} \text{ m}^{-1}$,³²² and cell length $d=1 \text{ cm}$. Typically SWNT concentration was between $0.5 - 0.4 \text{ mg mL}^{-1}$.

7.2.2 Film formation and device characterisation

Composite films of nanosheet/SWNTs were made by first mixing a desired amount of the SWNT dispersion, based on the mass ratio needed, with the dispersion of MoS_2 or Co(OH)_2 and bath sonicating for 30 mins until the two were well mixed. Films were then made by vacuum filtration and washing methods as outlined previously.

Filtering smaller volumes (preferably $<5 \text{ mL}$) was found to give better results as it reduced filtering time and resulted in a more even distribution of SWNTs throughout the nanosheet network. This was particularly pertinent for MoS_2 dispersions, where the concentrations were typically $\sim 6\times$ lower than Co(OH)_2 dispersions (0.6 vs 4 mg mL^{-1}). Thus to achieve higher concentrations select volumes of known mass were centrifuged at 16000 rpm for 2.5 hours. This resulted in the MoS_2 being sedimented out of solution. The excess liquid was removed and the sediment was redispersed in a smaller volume of $3 \text{ mg mL}^{-1} \text{ SC}$, creating a high concentration dispersion.

The prepared films were then cut and transferred onto various substrates. MoS_2 was transferred onto pyrolytic carbon (PyC) for electrochemical, profilometry and SEM analysts and onto glass slides for electrical testing. Co(OH)_2 was transferred to glassy carbon (GC, CH Instruments, Inc) for electrochemical testing, ITO for SEM and glass slides for thickness and electrical measurements. The cellulose membranes (MF-Milipore membrane, hydrophilic, 0.025 um pore size, 47 mm diameter) were removed by acetone bath washing. 10 uL of 5% Nafion (Nafion® 117) solution was then dropcast onto the Co(OH)_2 films and allowed to air dry.

Free standing films

Co(OH)_2 free-standing films were produced by first mixing the required amounts of Co(OH)_2 and SWNT dispersions (for mechanical testing, TUBAL™ SWNTs were used instead as they were available in larger quantities at a much lower cost and their higher impurity content should not hinder the mechanical analysis) and bath sonicating for 1 hr. The dispersions were then filtered through a polyester (PETE, Sterlitech) membrane. For the free-standing films where larger volume are concerned, dispersions were filtered 5 mL at a time, adding the next 5 mL when the previous was settled on the surface. Filtering in layers resulted in a more even distribution of SWNTs throughout the Co(OH)_2 matrix. The films were then washed with 300 mL of deionized water and left to dry overnight. Once dry, the thick film could be peeled off the PETE membrane to give a free-standing film.

The free standing films were then mounted onto a stainless steel support and sandwiched between two PTFE sheets. The freestanding film has an exposed surface area of approximately 0.1 cm^2 . An inert epoxy (Araldite®) was used to ensure complete isolation of the support from the electrolyte.

Film thickness and SEM

Thickness measurements and SEM image collection are as outlined in the Methods sections of chapter 5 and 6.

Mass fraction and volume fraction

For composites, the SWNT mass fraction, $M_f = M_{NT}/(M_{NT} + M_{NS})$ was converted to volume fraction, $\phi = V_{NT}/V_T = V_{NT}/(V_{NT} + V_{NS}) = M_f (\rho_{film}/\rho_{NT})$, where M_{NT} and M_{NS} are the mass of the nanotubes and nanosheets, V_{NT} , V_{NS} and V_T are the volumes occupied by nanotubes, nanosheets and total film, and ρ_{film} and ρ_{NT} are the densities of the film and the nanotubes, respectively ($\rho_{NT} = 1500 \text{ kg m}^{-3}$).

Mechanical measurements

For mechanical testing, free-standing films of $\text{Co(OH)}_2/\text{SWNT}$ composites were cut into stripes 2.25 mm wide and 15 mm in length. The mechanical measurements were performed using a Zwick Z0.5 ProLine Tensile Tester (100 N Load Cell). For the tests, a gauge length of 5 mm and a strain rate of 1 mm/min was used. Each data point is an average of five measurements.

Electrical measurements

Electrical conductivity measurements were made with a Keithley 2400 source meter (Keithley Instruments, Inc) using a four-probe technique. Silver wire contacts were bonded to the film using Agar Scientific silver paint and electrode spacing was carefully recorded using ImageJ software.

7.2.3 Electrochemical measurements

Electrochemical measurements were conducted to evaluate the performance of the MoS_2/SWNT composites as catalysts for the HER and $\text{Co(OH)}_2/\text{SWNT}$ composites as OER catalysts. Both systems used a typical three-electrode electrochemical cell setup. As before all data was iR compensated unless otherwise stated.

HER: LSV and EIS measurements were carried out as described in chapter 5 using a 0.5 M H_2SO_4 electrolyte, a graphite counter electrode and a RHE reference electrode.

OER: LSV and EIS measurements were carried out as described in chapter 6 using a GC working electrode, a spiral platinum rod as a counter electrode and a Hg/HgO reference electrode. Aqueous 1 M NaOH was used as the electrolyte and reference electrode filling solution at a constant temperature of 20 °C unless clearly indicated otherwise.

7.3 Results and Discussion

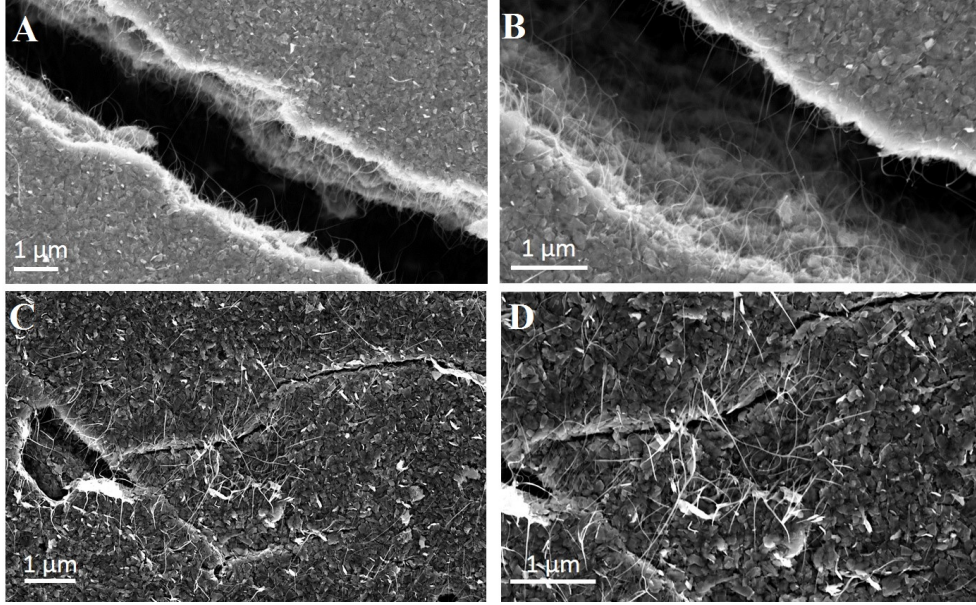


Figure 7.1: SEM image of MoS₂/SWNT composite film with (A-B) 3 wt% and (C-D) 13 wt% loading of SWNTs. The images suggest effective mixing of the two components.

7.3.1 MoS₂ nanosheet / SWNT composite films

7.3.1.1 Film preparation and characterisation

To test the effect of nanotubes on MoS₂ films for the HER we prepared a range of mixed dispersions of SWNT/MoS₂ by solution mixing. These were filtered to form composite films which were then transferred onto various substrates as before. To facilitate analysis, the composite films had a fixed MoS₂ mass of $\sim 1.45 \text{ mg cm}^{-2}$ ($\sim 5.05 \text{ } \mu\text{m}$) while the SWNT mass fraction, M_f , was varied from 0.03 – 13 wt% ($M_f = M_{NT}/(M_{NT} + M_{MoS_2})$). Typically M_f was converted to volume fraction, $\phi = V_{NT}/V_T = V_{NT}/(V_{NT} + V_{MoS_2}) = M_f (\rho_{film}/\rho_{NT})$ for quantitative analysis ($\sim 0.06 - 22 \text{ vol\%}$)

We performed SEM analysis of the composite films with a typical examples shown in figure 7.1A-D. The SWNTs are clearly visible throughout the films, suggesting effective mixing of the nanotubes within the MoS₂ matrix. The density was

calculated for each composite film from an individual measurement of M/A and t . This gave density values as shown in figure 7.2A, with mean composite density of 2660 kg m^{-3} . These values were then used to calculate the porosity of each film via the equation:

$$P = \frac{V_{Pore}}{V_{Total}} = 1 - \left[\frac{\rho_{film}}{\rho_{NS}} M_f + \frac{\rho_{film}}{\rho_{NS}} (1 - M_f) \right] \quad (7.1)$$

using values of $\rho_{NS}=5060 \text{ kg m}^{-3}$ for MoS_2 and $\rho_{NT}=1500 \text{ kg m}^{-3}$ for nanotubes. The resultant values are shown in figure 7.2B. The composite films were found to maintain their high porosity, with free volume of $\sim 45 \pm 5\%$, unchanged with addition of SWNT. This is important as it shows that any improvements associated with addition of SWNTs are not due to increasing porosity or morphological changes.

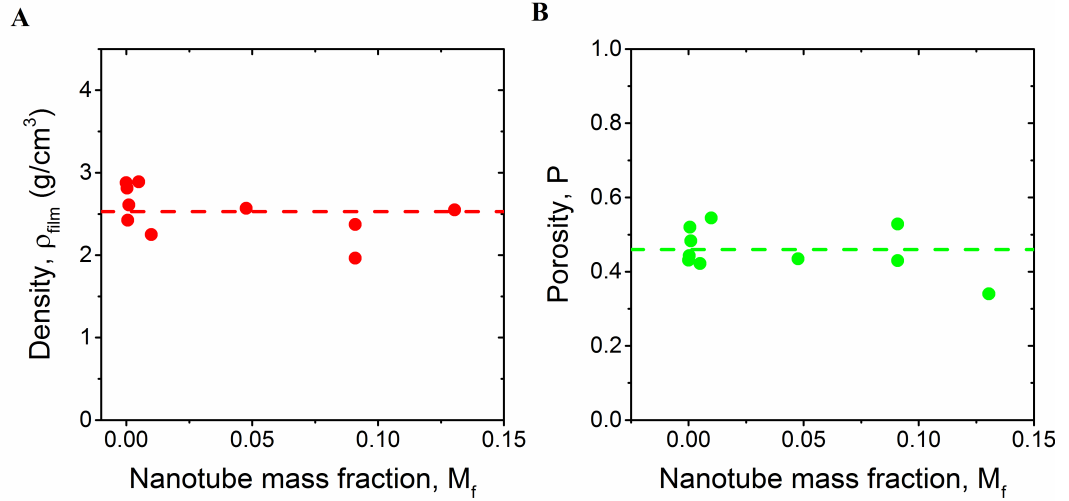


Figure 7.2: (A) Density and (B) porosity of MoS_2/SWNT composite films as a function of nanotube mass fraction.

7.3.1.2 Electrical measurements

We propose that addition of nanotubes will facilitate the transport of electrons from the current collector to the catalytically active sites within the electrode. This will require the enhancement of the out-of-plane conductivity of the electrode. However for reasons of practicality, we assess the effect of the nanotubes by measuring the

in-plane conductivities, σ , for a range of MoS_2/SWNT composites. Firstly, we note due to limitations in the measuring software values of σ for MoS_2 -only films could not be obtained, however we can compare to the known in-plane conductivity of an LPE MoS_2 nanosheet network ($\sim 10^{-6} \text{ S m}^{-1}$, ref^{144,356}) showing the composites dramatically increased conductivity. As shown in figure 7.3A, σ increases rapidly with M_f , reaching $\sim 275 \text{ S m}^{-1}$ for $M_f = 1 \text{ wt}\%$ and $\sim 1.2 \times 10^4 \text{ S m}^{-1}$ for the $M_f = 13 \text{ wt}\%$. This behaviour is consistent with previously reported composites of carbon nanotubes mixed with MoS_2 nanosheets,¹⁴⁴ as well as the broader field of nanotube-filled polymers.³⁵⁷

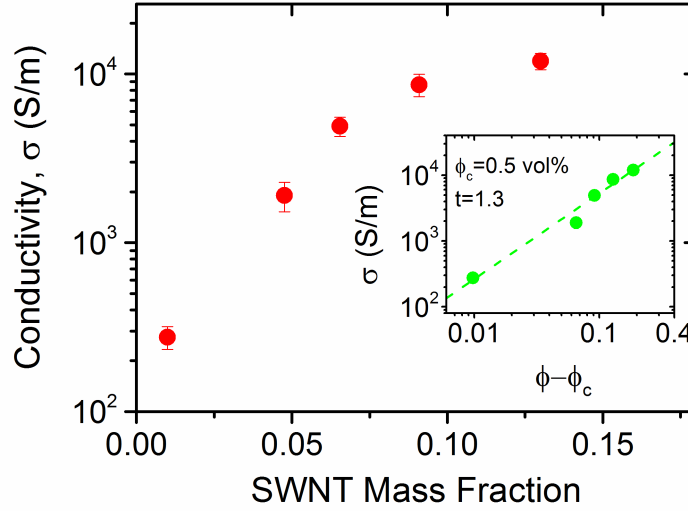


Figure 7.3: *In-plane electrical conductivity, σ , of composite films ($\text{MoS}_2/\text{SWNTs}$) plotted versus SWNT mass fraction. Inset: percolation analysis of composite films, σ plotted versus SWNT volume fraction, ϕ minus the percolation threshold, $\phi_{c,e}$. The volume fraction was estimated used a mean film density of 2660 kg m^{-3} . The line is fit to percolation theory equation 7.2.*

The electrical properties of insulating matrices filled with conducting particles is usually described using percolation theory.³¹² Within this framework, as the filler volume fraction (ϕ) is increased, the film conductivity remains similar to that of the matrix until a critical filler volume fraction, the percolation threshold, $\phi_{c,e}$, is reached. At this point the first conducting path across the film is formed and current

begins to flow. Above percolation threshold, the conductivity is described by the percolation scaling law:^{144,312,357}

$$\sigma = \sigma_0 (\phi - \phi_{c,e})^n \quad (7.2)$$

where n is the percolation exponent and σ_0 approximates the conductivity of film prepared from filler particles alone. As shown in the inset of figure 7.3A, our data is consistent with percolation theory, with fitting giving values of $\sigma_0 = 1 \times 10^5 \text{ S m}^{-1}$, $\phi_{c,e} = 0.5 \text{ vol\%}$ and $n = 1.3$. This value of σ_0 is consistent with other percolation studies,^{144,288} but also with measurements on nanotubes films showing conductivities of $\sim 10^5 \text{ S m}^{-1}$ are generally achieved.³³⁵ The percolation threshold is also as expected,^{144,288} and is consistent with theory which predicts $\phi_{c,e}$ to be approximately given by the ratio of mean nanotube diameter to length.³⁵⁷ Such a small percolation threshold for conductivity is advantageous as only a very small amount of SWNT filler is required for a large increase in conductivity. This means very little catalytic material has to be sacrificed to introduce the conductive paths. Finally, the exponent is identical to the universal percolation exponent ($n = 1.3$) for transport in two dimensions and similar to measured percolation exponents ($n = 1.2$ and $n = 1.8$) in other nanotube-nanosheet networks.^{144,288}

It is important to point out that the paragraphs above describe in-plane conductivity whereas it is the out-of-plane conductivity that is relevant in HER (as well as OER). This distinction is important as MoS_2 films are known to be electrically anisotropic with out-of-plane conductivity ~ 1000 times lower than in-plane conductivity.^{101,356} To our knowledge the out-of-plane conductivity has never been measured for nanosheet-nanotube composites partly due to the difficulty in avoiding pinholes. However, it is reasonable to assume that addition of nanotubes will result in out-of-plane conductivity increases which are in proportion to the measured in-plane increases described above. This hypothesis is supported by the large increases in supercapacitance of MnO_2 nanosheet films recently observed on addition of nanotubes.²⁸⁸ Such increases could not occur if addition of nanotubes did not enhance the out-of-plane conductivity.

7.3.1.3 HER electrocatalytic measurements

We have shown that small amounts of added SWNTs can dramatically improve the DC conductivity of thick MoS_2 films. The next step is to examine whether this added conductive value plays a role in improving the actual catalytic performance of the thick electrodes. To do this we performed linear voltage sweep measurements on a series of composites (MoS_2 M/A = 1.45 mg cm^{-2} , $t \sim 5\text{-}6.5 \text{ }\mu\text{m}$, $8 \times 8 \text{ mm}$) and plotted polarisation curves shown in figure 7.4. A considerable increase in current density is measured with the addition of just a few wt% SWNTs. This strongly supports the idea that the introduction of conductive paths facilitates charge transport to active sites of the MoS_2 . The onset potential (potential to reach 1 mA cm^{-2}) is also reduced by 20%, from -140 mV vs RHE to -112 mV vs RHE for a film of just 10 wt% SWNTs. The addition of SWNTs clearly has a positive impact on the HER catalytic activity

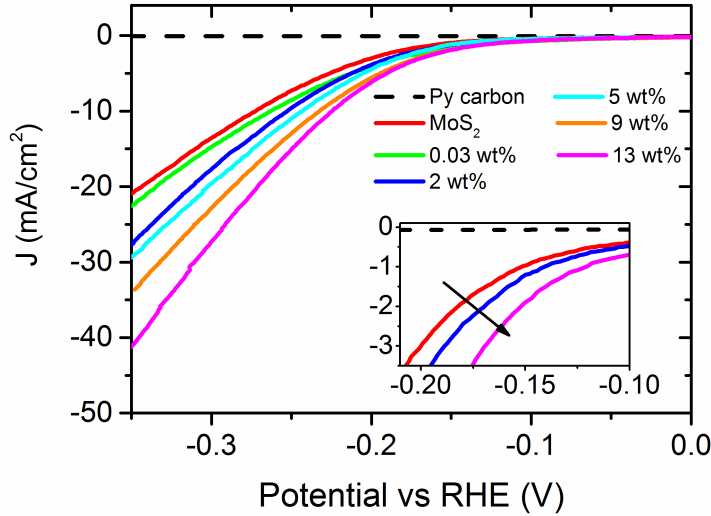


Figure 7.4: Polarization curves of MoS_2 /SWNT composites ($\sim 1.45 \text{ mg cm}^{-2}$ MoS_2) with SWNT weight percent ranging from 0 wt% to 13 wt%. Higher current densities are obtained with the addition of a few wt% SWNT. Inset: lower potential region.

Tafel slope *versus* SWNT vol%: Tafel plots were then generated for each composite film (figure 7.5 inset) and the Tafel slopes extracted. Figure 7.5 shows

the Tafel slope remains roughly constant, around $102 \pm 17 \text{ mV dec}^{-1}$, when plotted against SWNT volume fraction. The invariance of Tafel slope with the addition of SWNTs suggests that while the charge transport properties have improved the reaction is still somewhat limited by the inefficient adsorption of H^+ (Volmer step, $b = 120 \text{ mV dec}^{-1}$). From investigation of the literature there does not seem to be a consensus on the effect of adding carbon nanotubes to the Tafel slope for MoS_2 catalysts. Vruble et al¹³⁰ and Dai et al¹⁵⁰ noticed a decrease in Tafel slope with the addition of MWNTs, however Voiry et al¹⁵⁸ observed an increase when adding SWNTs.

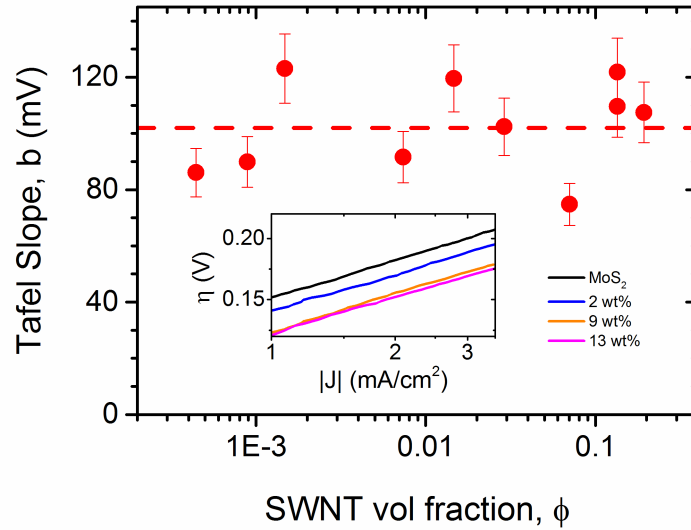


Figure 7.5: *Tafel slope versus SWNT volume fraction, ϕ , of MoS_2 /SWNT composite films with 1.45 mg cm^{-2} of MoS_2 ($t \sim 5 \text{ }\mu\text{m}$). Inset: corresponding Tafel plots. There is no significant change in Tafel slope with increasing ϕ , with average slope of $b \sim 102 \pm 17 \text{ mV dec}^{-1}$.*

J_0 and $J(\eta)$ versus SWNT vol%: In order to further characterise the impact of adding nanotubes to the MoS_2 electrode, we have plotted J_0 and $-J_{-250\text{mV}}$ versus SWNT volume fraction in figures 7.6 and 7.7A and B. Shown in figure 7.6 is data for exchange current density, J_0 , as a function of nanotube volume fraction. Here the data is somewhat scattered as is often the case for values of J_0 extracted from

Tafel plots. However, the dashed line is a guide to the eye and suggests the exchange current does indeed increase with nanotube content.

More reliable is data for current density read directly from polarisation curves. Shown in figure 7.7A is data for the current density, measured at $V = -250$ mV vs RHE, plotted *versus* ϕ . It is clear from this data that the current is constant at $7-8$ mA cm⁻² at low volume fractions but increases sharply when the volume fraction surpasses 0.5-1 vol%, reaching ~ 14 mA cm⁻² for nanotube contents of ~ 22 vol%. We interpret this behaviour as reflecting the improved charge transport through the film above the percolation threshold. This facilitates efficient delivery of electrons to the catalytically active sites and results in higher hydrogen production rates. Similar behaviour has been seen previously for MnO₂/SWNT supercapacitors²⁸⁸ and MoS₂/SWNT lithium ion battery electrodes.²⁹³ In the case of the composite supercapacitors, it was found that the excess capacitance, i.e. the capacitance increase relative to the matrix associated with the addition of the nanotubes followed a percolation scaling law.²⁸⁸

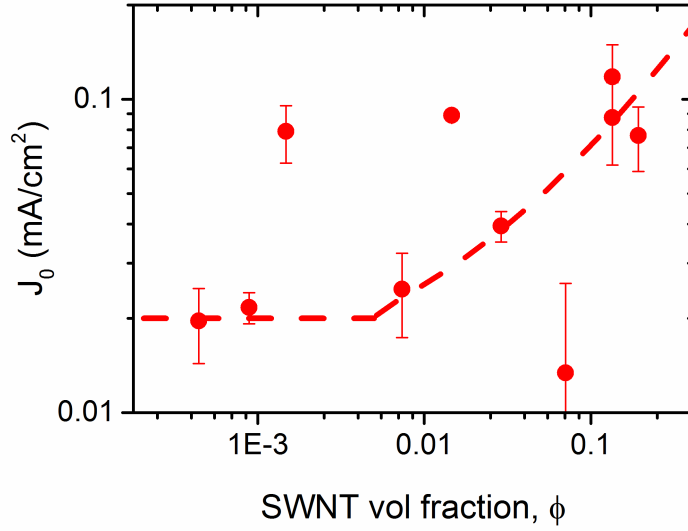


Figure 7.6: Exchange current density versus SWNT volume fraction, ϕ , of MoS₂/SWNT composite films with 1.45 mg cm⁻² of MoS₂ ($t \sim 5$ μ m).

Assuming the same behaviour is found here would imply the hydrogen production rate, and so the current density to scale as:

$$-J_{-250mV} = -J_{-250mV}^{MoS_2} + J_{Perc} (\phi - \phi_{c,c})^{n_c} \quad (7.3)$$

where $J_{-250mV}^{MoS_2}$ is the current density at -250 mV for an MoS₂ only film, J_{Perc} is a constant and $\phi_{c,c}$ and n_c are the percolation threshold and exponent associated with the percolation of catalysis. We have fit equation 7.3 to the current density *versus* data in figure 7.7A, finding very good agreement. Shown in figure 7.7B is the percolation plot where we fit the data to;

$$|\Delta J|_{-250mV} = J_{Perc} (\phi - \phi_{c,c})^{n_c} \quad (7.4)$$

where $|\Delta J|_{-250mV} = -(J_{-250mV} - J_{-250mV}^{MoS_2})$ and $(\phi - \phi_{c,c})$ is known as the reduced volume fraction. This graph shows particularly clearly that this data is consistent with percolation theory. From the fitting, we find values of $\phi_{c,c}=0.5$ vol% and $n_c=0.75$. Interestingly, the catalytic percolation threshold is identical to the electrical percolation threshold, strongly suggesting the performance increase to be associated with the conductivity increase. The catalytic percolation exponent is significantly smaller than the electrical percolation exponent similar to previous observations for MnO₂/SWNT composite supercapacitors²⁸⁸ and MoS₂/SWNT composite Li ion battery electrodes.²⁹³

While this is not fully understood, we suggest that the percolative nature of the hydrogen production rate is due to the scaling of the extent of the nanotube network with ϕ . When $\phi > \phi_c$, nanotubes can either belong to the network spanning the entire film or be isolated from it. The strength of the network is the probability that a given nanotube belongs to the network and is given by $P \propto (\phi - \phi_c)^\beta$.³¹² We propose that stronger networks are more able to deliver electrons to catalytic sites throughout the film. This results in the power law scaling of $-J_{-250mV}$ with $\phi - \phi_c$. That the exponent is relatively low may be a reflection of the fact that β is usually quite low; values as low as 0.14 have been proposed for certain lattices.³⁵⁸ However, we note that we would not expect the exponent n_c to be equal to β . It is likely that the exact value of n_c is specific to the details of the parameter being examined (i.e. here $-J_{-250mV}$).

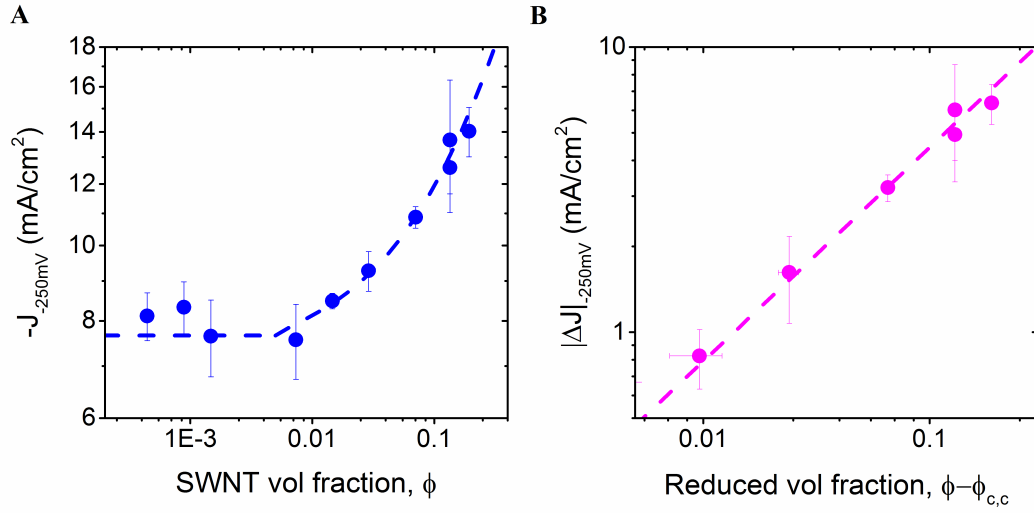


Figure 7.7: (A) Current density measured at a potential of -250 mV vs RHE plotted versus SWNT volume fraction, ϕ . (B) Percolation plot of $|\Delta J|_{-250\text{mV}} = -(J_{-250\text{mV}} - J_{-250\text{mV}}^{\text{MoS}_2})$ versus $\phi - \phi_{c,c}$ with $\phi_{c,c} = 0.5$ vol% and $J_{-250\text{mV}}^{\text{MoS}_2} = -7.7$ mA cm⁻².

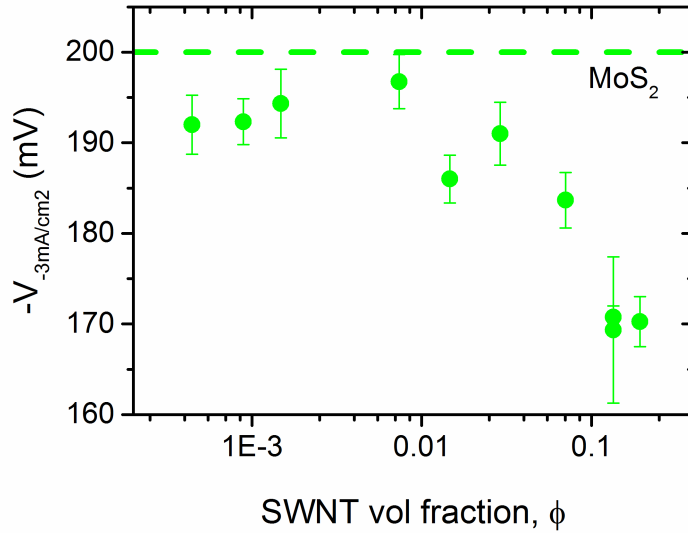


Figure 7.8: Potential required to achieve a current density of -3 mA cm⁻² plotted versus SWNT volume fraction, ϕ .

Overpotential *versus* SWNT vol%: Another important parameter is the potential required to achieve a given current density. When continuously producing

hydrogen at a constant rate, it is critical that the required potential is as low as possible to minimise power consumption. Shown in figure 7.8 is a graph of the potential required to generate a current density of -3 mA cm^{-2} plotted *versus* SWNT volume fraction. At low volume fractions, the potential is similar to but slightly lower than the equivalent potential in MoS_2 only films. However at $\sim 0.7 \text{ vol\%}$ the potential begins to fall sharply, reaching 170 mV for a nanotube content of 22 vol%. Because the power consumption in a hydrogen generator will scale as $P \propto JV$ and because the hydrogen production rate scales linearly with J , this reduction in $V_{-3\text{mA cm}^{-2}}$, is equivalent to a 15% reduction in the energy cost per H_2 molecule relative to a MoS_2 only electrode of equivalent thickness.

Impedance spectroscopy and charge transfer resistance: We performed impedance spectroscopy on a number of composite electrodes and data for a subset of them is plotted in figure 7.9A as Nyquist plots. These curves show the classic semi-circle shape expected for an electrocatalysts being described in some way by a resistor and capacitor in parallel. To extract meaning from the Nyquist plots the curves were fitted to a an equivalent circuit model³³² (figure 7.9B) which describes both the MoS_2/SWNT electrode and interfacial processes. A discussion of the equivalent circuit model and representative elements can be found in the appendix.

An important parameter to extract from this model for the description of the HER is the charge transfer resistance, R_{ct} . This resistance essentially describes the rate of charge-transfer across the electrode/electrolyte interface during the Volmer or Heyrovsky reactions. We found R_{ct} (N.B., we have normalized by multiplying by geometric electrode area) to be $130 \text{ } \Omega\text{cm}^2$ for the MoS_2 -only electrode. However, the charge-transfer resistance fell sharply on addition of carbon nanotubes, reaching $72 \text{ } \Omega\text{cm}^2$ for the 14 vol% sample, as shown in figure 7.10. We suggest that the presence of nanotubes increases the conductivity of the electrode and so enables a rapid supply of electrons from current collector to catalytic sites. This allows electron transfer to approach its intrinsic rate and results in a reduction of R_{ct} .

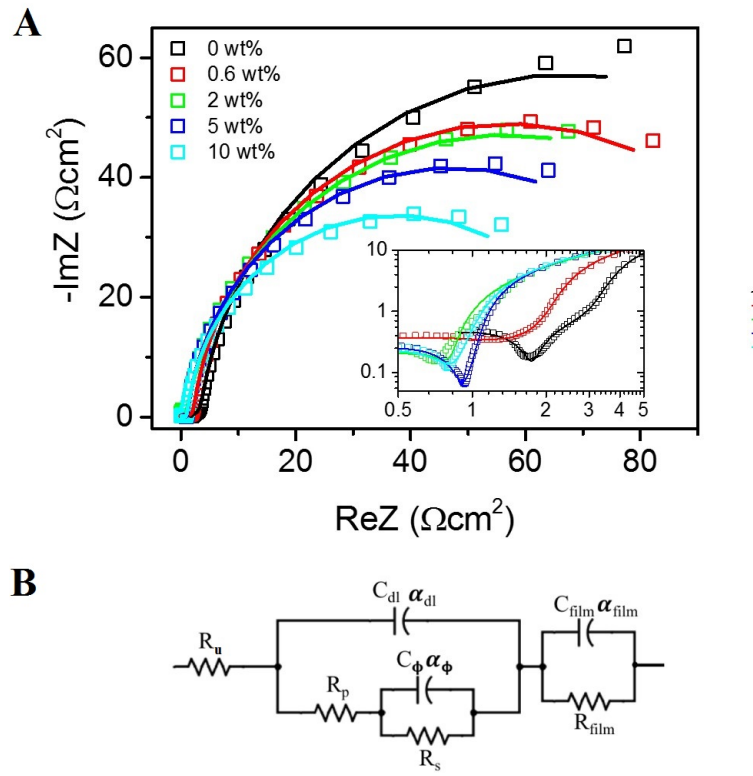


Figure 7.9: (A) Impedance spectroscopy data plotted as Nyquist plots for an MoS_2 -only electrode and composite electrodes. The lines are fits to the equivalent circuit model in (B). All impedance spectra were collected at an overpotential of 150 mV.

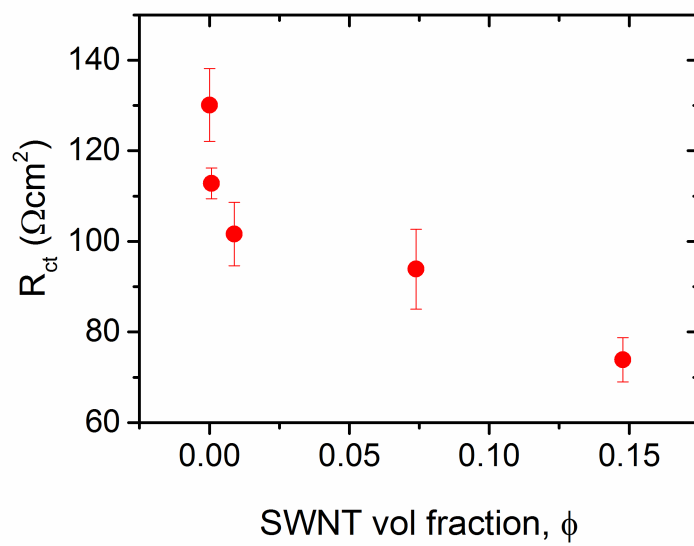


Figure 7.10: Charge transfer resistance, R_{ct} as measured by impedance, plotted versus SWNT volume fraction, ϕ .

Electrode stability: Finally, we have measured the stability of electrodes fabricated from both MoS₂ nanosheets and a 10 wt% MoS₂/SWNT composite ($t=5\text{ }\mu\text{m}$ in both cases). We performed chronoamperometry at a fixed overpotential of 300 mV for approximately 160 minutes on each electrode (figure 7.11). In both cases, we found a steady fall in current density over the first hour with subsequent stabilisation of current. We find a 48% fall off in current for the MoS₂-only sample over approximately two and a half hours. However, addition of 10% nanotubes significantly stabilized the electrode with a fall-off of only 27% over the same timescale. We suggest that the source of instability is the mechanical fragmentation of the electrode due to the stresses associated with bubble release. As observed previously,⁸² addition of nanotubes should significantly increase the robustness of the electrode resulting in the observed increase in stability.

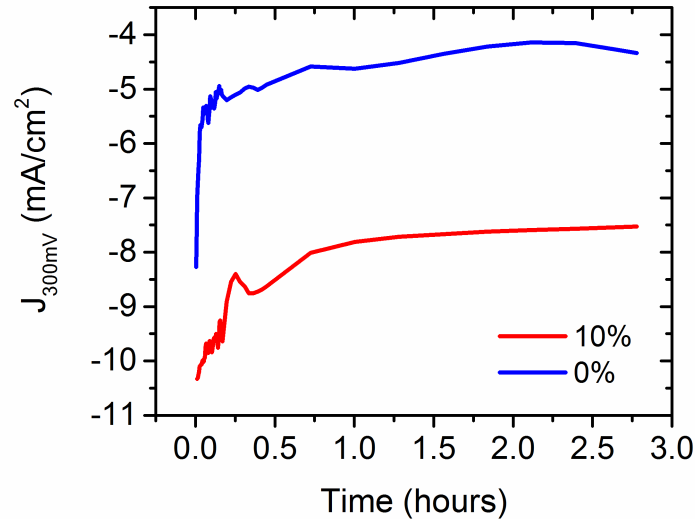


Figure 7.11: *Current density measured at fixed overpotential of 300 mV plotted versus time for $\sim 5\text{ }\mu\text{m}$ thick films of MoS₂ and MoS₂/10 wt% SWNT. .*

7.3.1.4 HER discussion

Adding carbon nanotubes has clearly addressed the saturation in performance of thick MoS_2 electrodes, increasing both its electrical properties and mechanical stability. While the Tafel slope was largely independent of nanotube content, we found the exchange current density, the current density at fixed potential and the potential required to generate a given current to improve with the increasing nanotube content. This increase in performance is associated with the introduction of conducting paths through the thick electrodes allowing for charge to better reach previously inaccessible sites. This activates more of the MoS_2 thus leading to a more active catalyst. The results present further supporting evidence to suggest that the saturation of electrode performance at higher thicknesses is majorly due to electrical and not mass transport limitations. We also found the current at a given potential to be well described by percolation theory. Finally, these learnings are general and so should also apply to our $\text{Co}(\text{OH})_2$ OER catalysts that have become mechanically unstable at high thickness.

7.3.2 $\text{Co}(\text{OH})_2$ nanosheet / SWNT composite films

As has been discussed in detail in chapter 6, thick electrodes made of stacked s- $\text{Co}(\text{OH})_2$ ($\langle L \rangle = 50$ nm) exfoliated nanosheets reach a critical cracking thickness (CCT) as the mass loading is increased beyond $\sim 1.7 \text{ mg cm}^{-2}$ ($8.3 \text{ }\mu\text{m}$). After this point, mechanical instabilities due to cracking make it no longer feasible to process and analyse a device. As was seen with MoS_2 , electrical conductivity through the semiconducting material should also become a problem, as thickness is increased beyond $8 \text{ }\mu\text{m}$. The addition of SWNTs to the device should alleviate these issues.

7.3.2.1 Film preparation and characterisation

To determine the effect of SWNTs on s- $\text{Co}(\text{OH})_2$ films, we prepared a range of SWNT/ $\text{Co}(\text{OH})_2$ composite films. For mechanical measurements, thick, free-standing composites were made while for electrical and electrochemical measurements, thinner films were prepared and transferred onto glass and GC respectively. The SWNT

mass fraction was varied between 0.01 – 20 wt% (0.016 – 28.3 vol%) while the active $\text{Co}(\text{OH})_2$ mass was kept constant. SEM imaging of a typical 0.9 mg cm^{-2} $\text{Co}(\text{OH})_2/\text{SWNT}$ composite films (figure 7.12A 1wt% and B 10wt%) shows again the nanotubes mixing well throughout the nanosheet stacks.

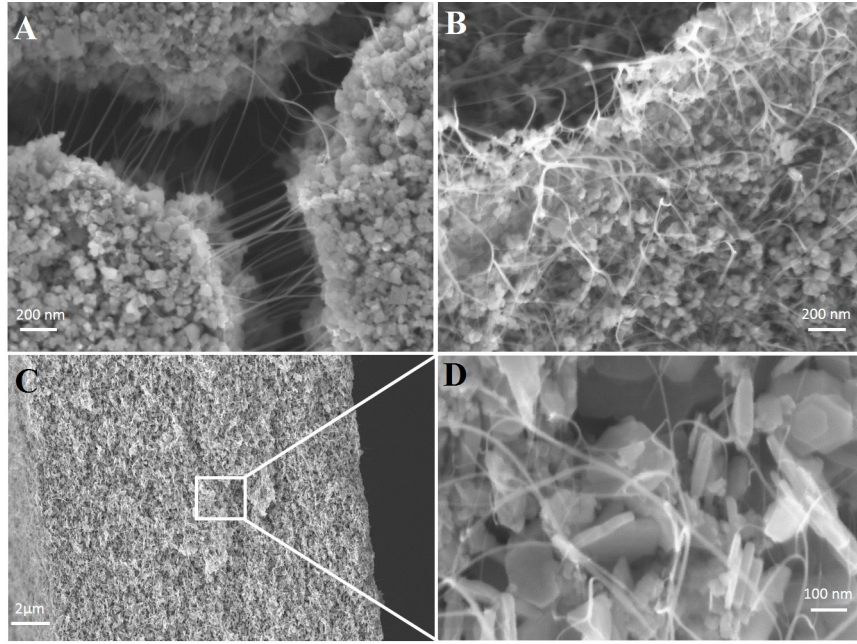


Figure 7.12: SEM image of $\text{Co}(\text{OH})_2/\text{SWNT}$ composite film (0.9 mg cm^{-2}) with (A) 1 wt% and (B) 10 wt% loading of SWNT, showing effective bridging of cracks by nanotubes. (C-D) SEM images of free-standing composite films (4 mg cm^{-2}) with 1 wt% SWNTs.

7.3.2.2 Mechanical optimisation

To determine the effect of adding SWNTs to the mechanical properties of $\text{Co}(\text{OH})_2$ -based films, we performed tensile stress-strain measurements on thick, free-standing composite films ($\sim 4 \text{ mg cm}^{-2}$, $t=18\text{--}28 \text{ }\mu\text{m}$). As shown in figure 7.12C and D these films were prepared using larger, $\langle L \rangle \sim 150 \text{ nm}$, $\text{Co}(\text{OH})_2$ nanosheets as the larger flake dispersions can be prepared to a much higher concentration, making it easier to produce larger quantities of thick FS films (see Methods).

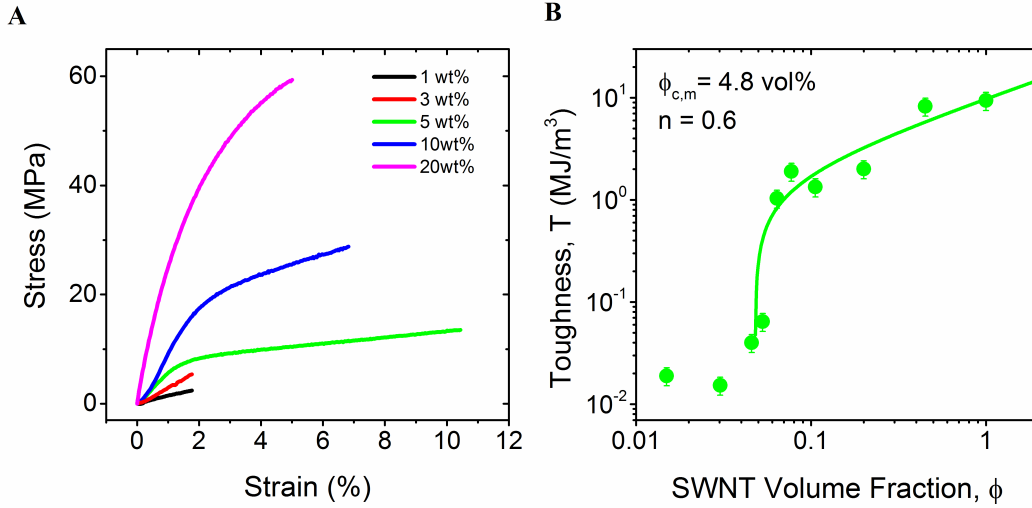


Figure 7.13: Mechanical data for free-standing composites of $4 \text{ mg cm}^{-2} \text{ Co(OH)}_2$. (A) Stress strain curves for a subset of composites. (B) Mechanical toughness (volumetric work to failure) as a function of volume fraction, ϕ . Toughness is shown to scale with ϕ , as per percolation theory.

Shown in figure 7.13A are a sample of typical stress-strain curves for composites with different SWNT content. Clearly the addition of nanotubes drastically improves the stiffness, strength and toughness (area under stress-strain curve) of the electrodes. Previously, the toughness, which is a measure of the volumetric fracture energy (it's equivalent to the energy absorbed up to fracture divided by sample volume), has been linked with the cycling stability of battery electrodes.²⁹³ The toughness, T , is plotted in figure 7.13B *versus* SWNT volume fraction and shows a 1000-fold improvement, characterised by a sharp increase at $\phi \sim 5 \text{ vol}\%$. It has been suggested²⁹³ that such an increase coincides with the formation of a fully-formed nanotube network with the toughness increase subsequently described by percolation theory: $T - T_0 \propto (\phi - \phi_{c,m})^{n_m}$, where T_0 is the toughness of a nanosheet-only electrode. Fitting gives the mechanical percolation threshold and exponent to be $\phi_{c,m} = 4.8 \text{ vol}\%$ and $n_m = 0.6$ respectively, similar to previous reports.²⁹³

Other parameters were also obtained from the stress strain curves such as the Young's modulus (defined as slope of stress-strain curve at low strain), mean values of the film strength (ultimate tensile strength, UTS, defined as maximum stress

observed) and strain-at-break. These are plotted *versus* nanotube loading in figure 7.14. In each case reinforcement is observed although the strain at break tends to fall off at loading levels above $\sim 8\text{wt}\%$. For a loading of $10\text{wt}\%$, the mechanical properties were as follows: modulus= 0.8 GPa , strength= 35 MPa and strain at break= 9% . For comparison purposes, such values are similar to those found for typical thermoplastics e.g. polyethylene. We note that the reinforcement mechanism is in-part associated with the fact that cracking is suppressed by bridging with nanotubes (figure 7.12A).

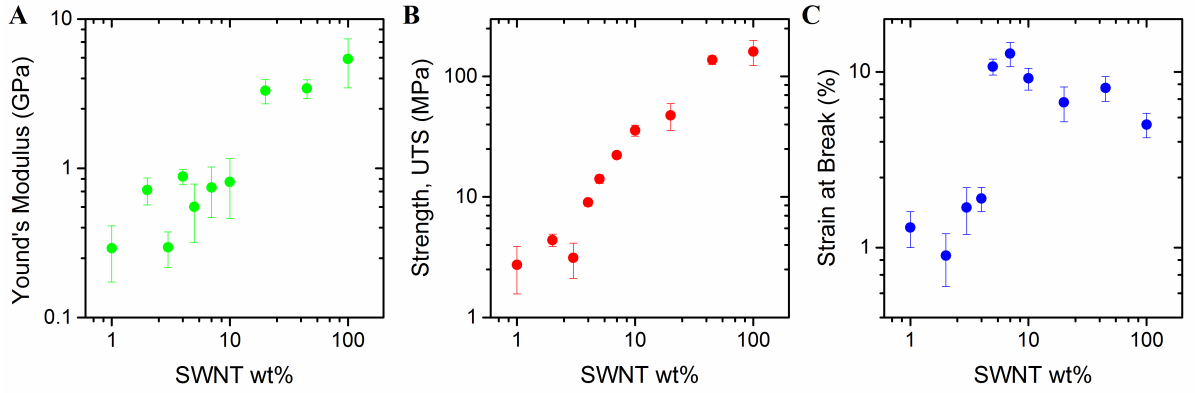


Figure 7.14: *Mechanical properties of 4 mg cm^{-2} free-standing $\text{Co}(\text{OH})_2$ -SWNT composites. (A) Young's modulus, (B) Ultimate tensile strength, UTS and (C) strain at break, plotted versus SWNT weight %.*

7.3.2.3 Electrical optimisation

While this significant toughness enhancement would be expected to increase the CCT and so stabilise thick composite films, as described above for MoS_2 , adding nanotubes yields further benefits. Adding SWNTs significantly increases the electrical conductivity, σ , as shown in figure 7.15 for s- $\text{Co}(\text{OH})_2$ /SWNT films of 0.9 mg cm^{-2} (thickness $3.5\text{--}5.3\text{ }\mu\text{m}$). The conductivity increased by $\times 10^{10}$, with a sharp increase at a nanotube volume fraction of $\sim 0.1\text{vol}\%$. Again, this can be described by percolation theory:^{144,312} $\sigma \propto (\phi - \phi_{c,e})^{n_e}$ with fitting giving the electrical percolation threshold and exponent to be $\phi_{c,e}=0.15\text{vol}\%$ and $n_e=2.2$, similar to the values of the MoS_2 /SWNT composites and previous 1D:2D composites.^{288,293}

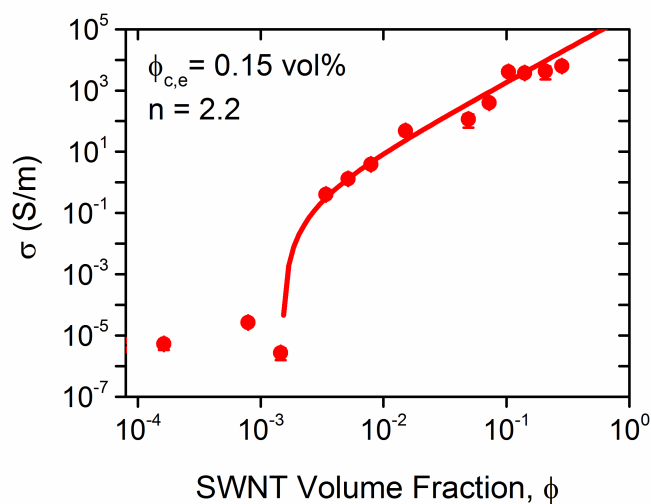


Figure 7.15: *In-plane electrical conductivity plotted against volume fraction of carbon nanotubes (SWNTs) in composite films of thickness $3.5\text{--}5.3\ \mu\text{m}$ ($\sim 0.9\ \text{mg cm}^{-2}$ Co(OH)_2). Electrical conductivity is shown to fit to percolation theory.*

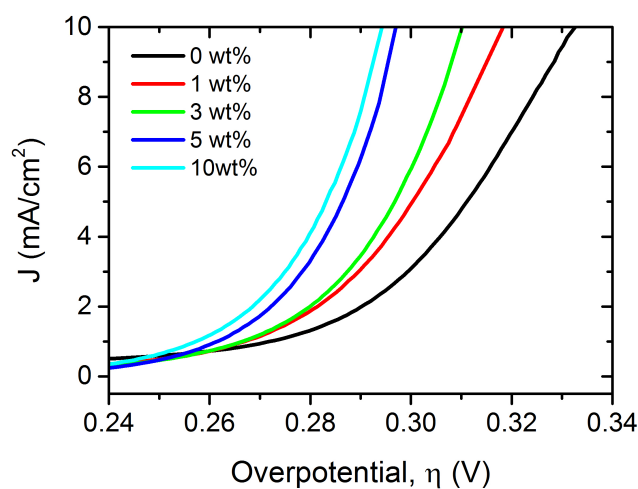


Figure 7.16: *Linear sweep voltammograms for composite electrodes with a fixed Co(OH)_2 loading of $0.9\ \text{mg cm}^{-2}$ for a range of nanotube contents*

7.3.2.4 OER measurements for $\text{Co(OH)}_2/\text{SWNT}$ films

As we saw with the HER above, because the conductivity increases with nanotube addition the OER catalytic performance is likely to also improve due to the more

efficient charge distribution. To examine this, we made a series of thick 0.9 mg cm^{-2} s-Co(OH)₂ composite films from 0 wt% to 10 wt% and performed linear voltage sweep measurements as shown in figure 7.16 (area 0.07 cm^2). The effect of the SWNTs is immediately apparent with higher current densities achieved and lower OER onset potentials.

For easy comparison to previous s-Co(OH)₂ only films we again, as metrics, plot $\eta_{10 \text{ mA/cm}^2}$ and $J_{0.3 \text{ V}}$ as a function of CNT volume fraction in figure 7.17A and B respectively. In all cases we found unambiguous improvements, with $\eta_{10 \text{ mA/cm}^2}$ falling roughly 12% from ~ 335 to ~ 295 mV for the thick composites. Currents also improved with $J_{0.3 \text{ V}}$ increasing from 3.1 to 14 mA cm^{-2} for thick composites (4.5X) as the SWNT content increased. Again, rise in J can be described by percolation theory giving, $\phi_{c,c}=1 \text{ vol\%}$ and $n_c=0.55$ These improvements are significant and highlight the utility of incorporating nanotubes in OER catalytic electrodes.

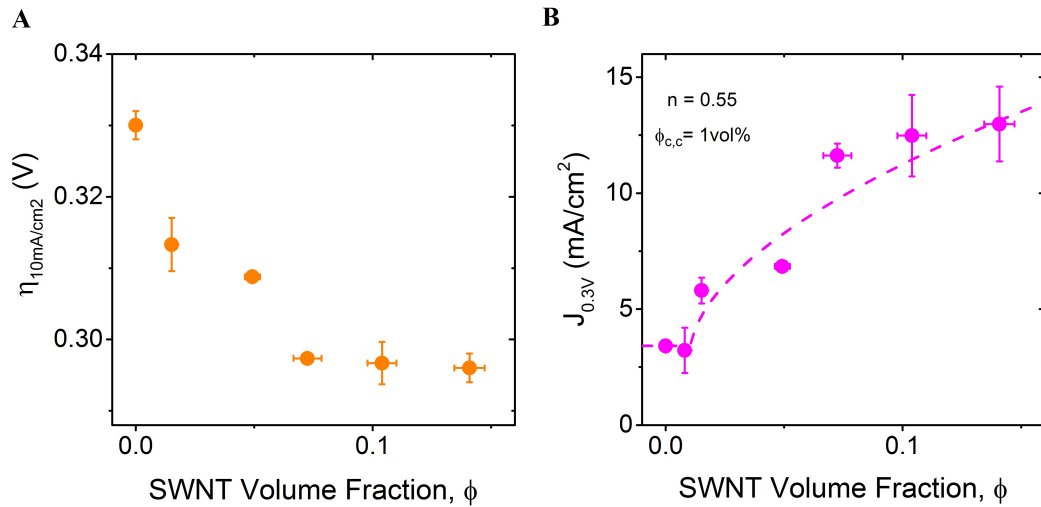


Figure 7.17: (A) Overpotential required to produce 10 mA cm^{-2} and (B) current density at overpotential of 0.3 V , both plotted as a function of SWNT volume fraction. All figures pertain to s-Co(OH)₂ using 1 M NaOH as an electrolyte where applicable.

Finally, EIS was carried out at 0.41 V which corresponds to a potential region where oxygen is evolved. We examined the charge transfer resistance, R_{ct} , as a function of SWNT content as shown in figure 7.18A and B. Creating a model circuit

to fit this data is complicated and time consuming. Here we take a shortcut, instead measuring the diameter of the semi-circle in the Nyquist plot as R_{ct} , which is a fair assumption when compared to the previous MoS_2 data and is often used in literature.³⁵⁹ One can see from figure 7.18B increasing the SWNT content up to 5 wt% decreases R_{ct} from 66 to 16 Ω , which can account for the increased OER activity with increasing nanotube content.

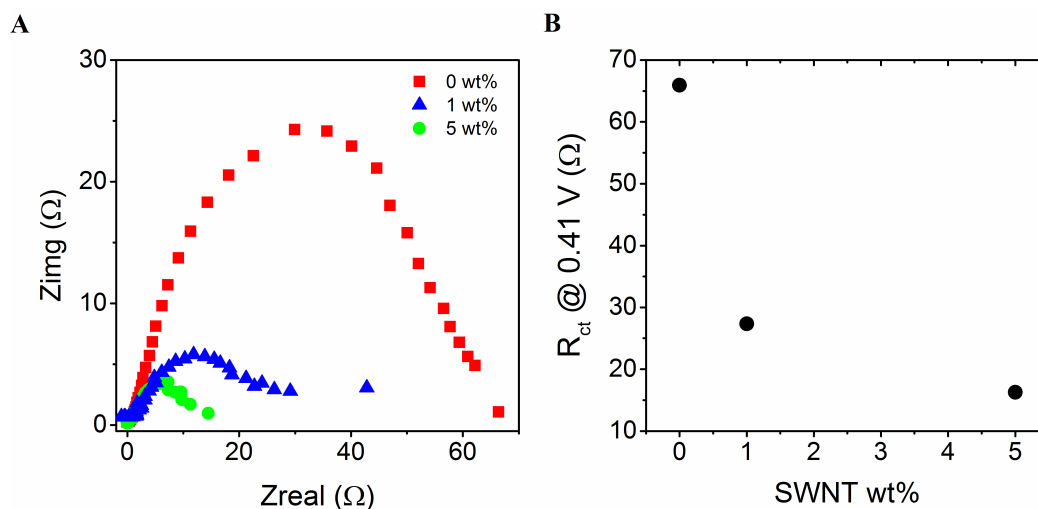


Figure 7.18: EIS data for thick 0.9 mg cm^{-2} Co(OH)_2 -SWNT films (A) Nyquist plots for Co(OH)_2 -SWNT composite films with increasing nanotube content. (B) Charge transfer resistance, R_{ct} , plotted versus SWNT wt% is shown to decrease as more nanotubes are added, reaching a saturation point around 5wt% SWNTs.

7.3.3 High performance free-standing composite electrodes

Although the increase in mechanical properties associated with the addition of nanotubes allows the production of composite films with thickness considerably greater than $8 \mu\text{m}$, we found it impossible to transfer films $>14 \mu\text{m}$ thick to the GC support due to adhesion problems (see figure 7.19). To avoid this issue, we decided to study thick free-standing (FS) films as OER catalysts. FS films will allow us to maximise the current i.e. maximise O_2 generation which is advantageous for industrial applications. Typically FS films would be difficult to make with just nanosheets

alone. They are too brittle to stand freely without support and would easily become hindered due to difficulties in transporting mass to the interior surfaces and transporting charge to the outer regions. Thankfully, as we have shown, mechanical stability, high electrical conductivity and catalytic improvements can all be achieved by mixing ~ 10 wt% carbon nanotubes into our nanosheet films. Therefore only diffusion limitations should be the cause of any degradation in performance as we now further maximise the electrode thickness.

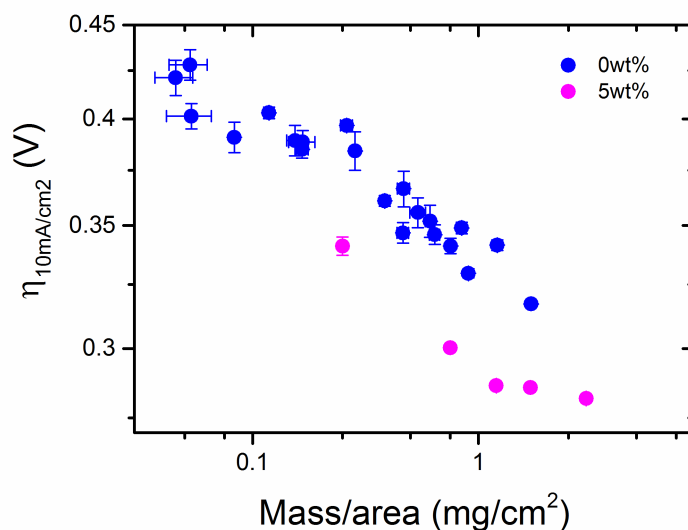


Figure 7.19: Overpotential at 10 mA cm^{-2} plotted versus Co(OH)_2 mass per area for Co(OH)_2 -only films and composites with 5wt% SWNTs (both on GC electrodes). The addition of nanotubes not only improves catalytic performance but also allows for the production of much thicker films as a result of much improved mechanical stability. However it was found impossible to create films greater than $14 \text{ }\mu\text{m}$ due to adhesion problems during the transferring of the film onto the GC substrate.

A series of free-standing films were prepared using s- Co(OH)_2 mixed with 10wt% SWNTs, with thicknesses in the range $19\text{--}120 \text{ }\mu\text{m}$ ($3\text{--}13 \text{ mg cm}^{-2}$). An example of such a film is shown in figure 7.20A. The FS films were supported between two thin PTFE sheets and electrically connected to the external circuit via a small strip of stainless steel as shown in figure 7.20B. This support prevented snapping of the film due to the surface tension of the electrolyte when placing the film into the cell. Cross-sectional SEM images in figure 7.20C - H show the SWNTs to be evenly distributed

throughout the film as suggested earlier where no flake is at an appreciable distance to an electrically conducting CNT.

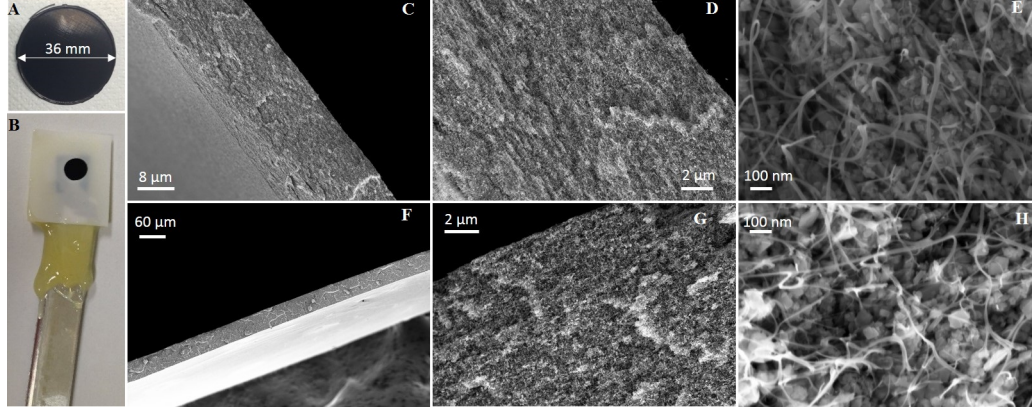


Figure 7.20: *Free-standing composite catalytic films with a range of $\text{Co}(\text{OH})_2$ loadings and 10 wt% SWNTs. (A) Picture of free-standing composite films as made by vacuum filtration. (B) Mounted free-standing composite electrode (exposed area of 0.1 cm^2). (C-H) Cross-sectional SEM of composite film with protruding nanotubes shown in magnified region for a 3 mg cm^{-2} (C-E) and 6.5 mg cm^{-2} $\text{Co}(\text{OH})_2$ film.*

Shown in figure 7.21A are LSVs for a number of free-standing s- $\text{Co}(\text{OH})_2$ /SWNT composite electrodes of different thicknesses. Note that unless otherwise stated, all potentials quoted for free-standing films have not been iR corrected. Due to the relatively large mass of $\text{Co}(\text{OH})_2$ used in the free-standing films, double layer capacitive currents contributed non-negligibly, introducing errors into measurements involving small currents (see appendix). As a result, for the free-standing films, we use the overpotential at 50 mA cm^{-2} (i.e. $\eta_{50 \text{ mA/cm}^2}$ rather than $\eta_{10 \text{ mA/cm}^2}$) as a performance metric.

For free-standing electrodes, the current density tended to increase sub-linearly at high overpotential due to diffusion limitations. As shown in figure 7.21B, $\eta_{50 \text{ mA/cm}^2}$ displays a well-defined minimum of around 420 mV, for a free-standing film thickness of between 50-70 μm . The increase in $\eta_{50 \text{ mA/cm}^2}$ above $t \sim 70 \mu\text{m}$ is most likely related to electrolyte diffusion limitations and gas shielding effects. For all subsequent experiments, we used an optimised 70 μm thick composite electrode containing s- $\text{Co}(\text{OH})_2$ mixed with 10wt% SWNTs.

Films prepared using this method were found to be extremely robust under vigorous oxygen evolution. This is illustrated in figure 7.22 which shows that, for an optimised composite electrode, currents of $>1 \text{ A cm}^{-2}$ can be achieved while the overpotential required to generate a fixed high current density of 200 mA cm^{-2} remained relatively constant over a period of 24 hours. It should be noted that this current density is 20 times higher than the 10 mA cm^{-2} commonly used in the stability testing of OER catalysts.^{10,360}

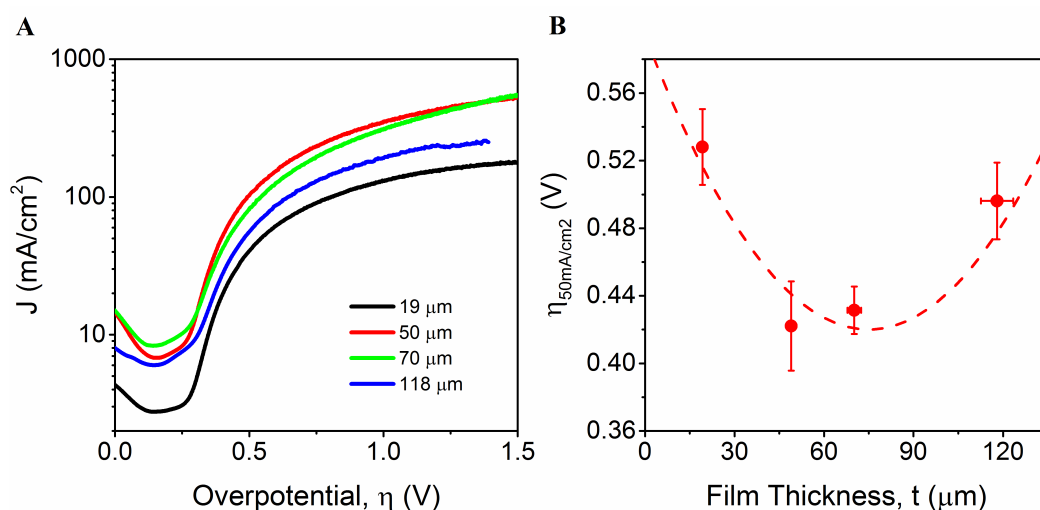


Figure 7.21: *Free-standing composite films 10 wt% SWNTs. (A) Representative linear sweep voltammograms as a function of film thickness. (B) OER overpotential (50 mA cm^{-2}) vs. film thickness. The line is a guide to the eye.*

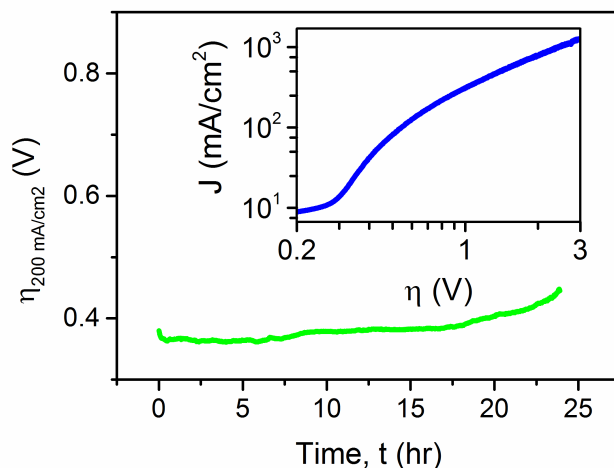


Figure 7.22: Overpotential at 200 mA cm^{-2} vs. time for a $70 \mu\text{m}$, $10\text{wt}\%$ SWNT, $s\text{-Co(OH)}_2$ free-standing film. Inset: Corresponding linear sweep voltammogram showing capability of free-standing films to achieve high currents

Electrolyte optimisation

Although electrolytes with concentrations of $0.1\text{-}1 \text{ M}$ KOH or NaOH are widely used to characterise potential OER catalysts in the literature,^{73,361} in industrial alkaline electrolyzers it is common to use $30\text{wt}\%$ or $\sim 7 \text{ M}$ KOH. Such high concentrations yield higher currents at a given overpotential,^{362–364} and result in lower Ohmic solution resistances. This is due to the measured OER current at a fixed overpotential being directly related to amount of OH^- species present in the electrolyte,^{362–364}. With this in mind, for the optimised composite electrode, we measured the overpotential required to achieve 50 mA cm^{-2} for a range of OH^- concentrations. As shown in figure 7.23A, we found $\eta_{50\text{mA/cm}^2}$ to fall by $\sim 160 \text{ mV}$ when increasing the concentration from 0.5 M to 5 M NaOH. Increasing the electrolyte concentration beyond this was shown to give no further decrease in overpotential.

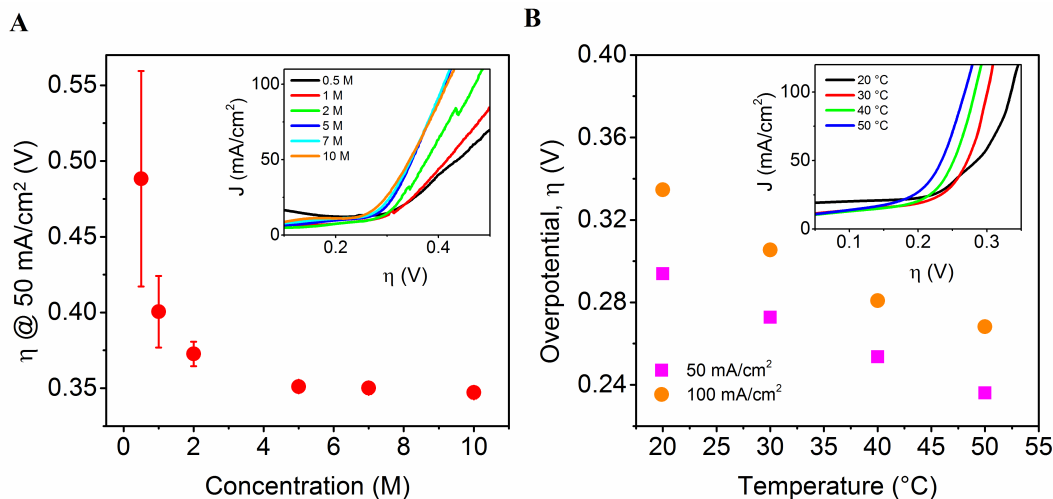


Figure 7.23: (A) Overpotential at 50 mA cm⁻² vs. electrolyte (NaOH) concentration. Inset: corresponding linear sweep voltammograms. (B) Overpotential at 50 and 100 mA cm⁻² as a function of electrolyte temperature (inset: corresponding linear voltage sweeps) measured in 5 M NaOH electrolyte. For temperature dependence data is IR corrected.

Temperature optimisation

Another parameter rarely examined or varied in the benchmarking of OER catalysts is the electrolyte temperature. While the bulk of OER data in the literature corresponds to room temperature (generally between 20-25 C°)³⁶⁵, we believe a temperature study is useful because, industrial alkaline electrolyzers operate at elevated temperatures of at least 80 C°.³⁶⁶ With this in mind we varied the temperature (electrolyte concentration 5 M NaOH), as shown in figure 7.23B from 20-50 C° and observed a 60 mV decrease in overpotentials required to achieve current densities of 50 and 100 mA cm⁻², reaching a global low of 236 mV and 268 mV respectively (iR corrected). This drop in overpotential at a fixed current with increasing temperature is consistent with the work of Miles and co-workers.³⁶⁷ It was not possible to increase the temperature further as the reference electrode used was not rated for higher temperatures. It is worth noting that even without these temperature and electrolyte optimisations, the activity of our free-standing electrodes far exceed comparable free-standing systems published recently in the literature.^{368,369}

7.3.4 Conclusion

We have demonstrated that by mixing CNTs with thick electrodes of stacked MoS₂ nanosheets we can eliminate electrical limitations associated with high mass loading films and these electrical improvements were fully described by percolation theory. Furthermore, such enhancements lead to improved catalytic performance, with current density doubling with the addition of a few wt% SWNTs, and also being described by percolation scaling.

These learnings could then be applied to Co(OH)₂/SWNT OER catalysts as well. With the addition of a few wt% carbon nanotubes we can enhance the mechanical, electrical and catalytic properties of our OER catalyst. Furthermore optimising the electrode thickness by producing free standing films, optimising electrolyte concentration and the electrolyser temperature yield an improved composite electrode which can yield a current density of 50 mA cm⁻² at an overpotential of 236 mV under realistic conditions.

In order to properly benchmark these optimisations and to put them into perspective, we have compared our results to the current state-of-the-art in OER catalysts. We have attempted to include a fair representation of the most active Co(OH)₂-based and other state-of-the-art materials tested at elevated temperatures and a higher base concentrations. These are quantified via the lowest reliable values of the overpotential required to generate 50 mA cm⁻² we could find in the literature with the state-of-the-art being 211 mV.¹⁸⁴ The comparison is shown pictorially in figure 7.24 with our lowest η_{50mA/cm^2} obtained in this work given by the black dashed line. It is clear that our best result is a mere 25 mV off the state-of-the-art. We emphasise that our result utilised a cheap starting material coupled with a scalable processing procedure. By contrast, the state-of-the-art employs a more complex NiFeSe material, synthesized on Ni foam.¹⁸⁴ These methods are not practically scalable as they often require several high temperature steps in their synthesis, combined with hazardous starting materials such as hydrazine and DMF. In addition, our result relied on the combination of an average material coupled with a processing-based optimisation protocol. We believe that combining our optimisation protocol with a more active material could yield a catalyst which far exceeds the

current state-of-the-art.

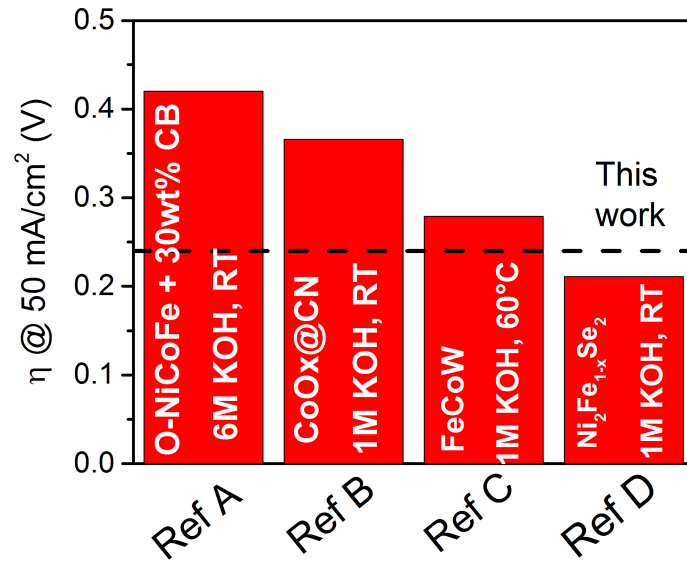


Figure 7.24: Comparison of lowest overpotential at 50 mA cm^{-2} obtained in this work to the state-of-the-art materials in the literature. All figures pertain to a free-standing $s\text{-Co(OH)}_2$ with 10 wt% carbon nanotubes. Ref A =²²⁶, Ref B =²⁰¹, Ref C =¹⁷⁷ and Ref D =¹⁸⁴.

Chapter 8

Summary and Future Work

8.1 Summary

In this thesis a comprehensive study into optimising the catalytic performance of nanosheet electrodes was presented. Nanosheet films of MoS_2 and $\text{Co}(\text{OH})_2$ were used as model systems for the HER and OER and were investigated using an holistic strategy which included studying the effects of film thickness, nanosheet size and nanotube content on the catalytic activity.

Bulk powders of layered MoS_2 and $\text{Co}(\text{OH})_2$ were successfully exfoliated into 2D nanosheets in liquid surfactant solutions using LPE. This facilitated straightforward nanosheet characterisation using UV-vis and TEM analysis and allowed for the control of flake sizes using centrifugation. These nanosheet dispersions could easily be produced into catalyst films by stacking nanosheets into a porous network morphology using vacuum filtration.

Films of MoS_2 nanosheets were initially investigated as HER catalysts in 0.5 M H_2SO_4 acidic media. Using centrifugation, dispersions of MoS_2 nanosheets of $\langle L \rangle = 120$ nm were consistently produced. Nanostructuring the MoS_2 into small nanosheets increases the edge to basal plane ratio, thus increasing the density of active sites. Following this, an investigation was carried out into the effects of increasing film thickness, t , on catalyst performance. Thick films up to ~ 14 μm were attainable which sustained a high porosity of 43%. The HER activity was then measured *versus* t , from 200 nm to 14 μm . Lower onset potentials and higher

currents were realized with increasing film thickness. In particular, the exchange current density rose from $\sim 0.003 \text{ mA cm}^{-2}$ to an impressively high $\sim 0.13 \text{ mA cm}^{-2}$. The Tafel slope however remained virtually unchanged at $\sim 125 \pm 17 \text{ mV dec}^{-1}$.

These improvements were analysed quantitatively and a simple model was developed to describe the relationship between thickness and activity. This model was based on the assumption that active sites of the catalyst resided on the flake edges and that nothing limits the access of electrolyte or charge to these sites. Fitting the experimental data revealed a linear relationship between thickness and current density (J_0 and $J(\eta)$), while $\eta(J)$ scaled with $\log(t)$. Extracted from this activity model was a figure of merit, R_0B or $R(\eta)B$, used to describe the activity of the MoS_2 nanosheets. This describes the number of H_2 molecules evolved per second per monolayer edge length and thus characterised the activity of the catalyst active sites, via their position on the nanosheet edge. For our LPE MoS_2 nanosheets we measured $R_0B = 11 \pm 2.5 \text{ H}_2 \text{ molecules s}^{-1} \mu\text{m}^{-1}$. From this we can estimate that approximately two thirds of every edge disulphide are inactive.

The linear behaviour of current with thickness implied hydrogen is produced at all available active sites. Thus, increasing film thickness proved to be a facile method of improving hydrogen production. Importantly, these results are general and should transfer to other nanosheet or nano-object systems. However, these behaviours only persisted up to thickness of $\sim 5 \mu\text{m}$, after which current and potential saturates with no further gains achievable by increasing electrode thickness. We proposed electrical limitations through the thick films to be the cause.

Films of Co(OH)_2 nanosheets were also investigated as active catalysts for the OER in 1M NaOH alkaline conditions. We demonstrate that Co(OH)_2 can be successfully exfoliated using LPE and stabilised in surfactant medium. Dispersions of 2D nanosheets are realised with a range of sizes from $\langle L \rangle = 36$ to 184 nm , and are used to prepare porous ($35 \pm 9\%$) films. The effect of flake size on catalyst activity was investigated to identify whether the active sites of LDHs reside on the nanosheet edges. A logarithmic increase in η with $\langle L \rangle$ and a linear scaling of $J(\eta)$ with $1/\langle L \rangle$, was observed, exactly as predicted by the edge-site active model. These results suggested that the active sites of the Co(OH)_2 crystal were indeed the

edges.

Following this, catalyst optimisation was pursued by developing thick films using small ~ 50 nm sized flakes. Porous films ($43 \pm 2\%$) were produced in a thickness range from 220 nm to $8.3 \mu\text{m}$ ($0.042 - 1.7 \text{ mg cm}^{-2}$) and activity was examined. As expected, the data matched the edge site model for t dependence of η and $J(\eta)$. Comparing the results from the size dependence and thickness study gave an experimentally determined value of 62 nm for the flake length used, extremely close to the AFM measured value of 57 nm. The close agreement gave further credence to the statement that the data is consistent with the edge site active model, thus strongly suggesting that the active sites of $\text{Co}(\text{OH})_2$ reside on the nanosheet edges. Interestingly, current saturation did not occur at $5 \mu\text{m}$, as for the MoS_2 system, however problems did arise beyond $\sim 8 \mu\text{m}$ as stable films were no longer attainable due to spontaneous cracking during film processing. This reflected the critical cracking thickness of the films.

Thus, it was shown that films of both MoS_2 and $\text{Co}(\text{OH})_2$ nanosheets achieve impressive results with increasing thickness, however at high thickness films were severely hindered by poor electrical and mechanical properties. These issues were addressed by blending dispersions of carbon nanotubes with nanosheets to create hybrid films. These 1D:2D composites combine the intrinsic catalytic properties of MoS_2 and $\text{Co}(\text{OH})_2$ with the conductivity and strength of the nanotube network. SEM analysis confirmed a high degree of mixture of the two phases, with nanotube bridging across cracks in the film structure.

A comprehensive investigation of MoS_2/SWNT and $\text{Co}(\text{OH})_2/\text{SWNT}$ composites films was carried out. In-plane conductivity increases of many orders of magnitude are realised in both films and this increase could be fully characterised using percolation theory. As little as 0.5 (MoS_2/SWNT) and 0.15 ($\text{Co}(\text{OH})_2/\text{SWNT}$) vol% SWNT were required to reach the electrical percolation threshold. Changes to the mechanical properties of $\text{Co}(\text{OH})_2/\text{SWNT}$ composites were also investigated, showing improvements to the toughness, strength, Young's modulus and strain at break. Additionally, toughness increase was shown to follow percolation scaling laws, with a larger percolation threshold of 4.8 vol%.

These enhancements to the fundamental properties of the networked films were reflected in substantial increases in the catalytic performance. Approximately 2x and 4x increases in current densities were observed for MoS_2 and $\text{Co}(\text{OH})_2$ systems respectfully and reductions of >30 mV in overpotential were attained. Interestingly, this increase in current density for both HER and OER also obeyed percolation theory, with low percolation thresholds of 0.5 and 1 vol% respectfully. These low threshold values mirrored the values for electrical and mechanical enhancements, providing further evidence that increasing the electrical and mechanical properties are responsible for the catalytic improvement. EIS analysis also confirmed a reduction in the charge transfer resistance for both HER and OER.

Finally, the collective learnings from these investigations could be compiled to fabricate an electrode with maximum performance. The benefits gained from the addition of nanotubes allowed for $\text{Co}(\text{OH})_2$ film thickness to be further increased, beyond the previous limit. Free-standing composite films could be produced with thickness up to $120\text{ }\mu\text{m}$, which were no longer mechanically or electrically limited. Optimum thickness was obtained at $70\text{ }\mu\text{m}$, after which diffusion became a limiting factor. Multiple enhancements were performed on this FS film of the electrolyte concentration and temperature resulting in an optimum performing catalyst. This catalyst compared favourably to a host of state-of-the-art catalysts materials in OER literature, generating 50 mA cm^{-2} at a low 236 mV, only 25 mV off the best NiFe catalyst.

It is worth quantifying this optimisation to see how far we have come. Starting with a standard $\text{Co}(\text{OH})_2$ sample which required 440 mV to generate 10 mA cm^{-2} , and applying systematic optimisation of the catalyst material through size selection, electrode thickness maximisation and nanotubes results in a $\Delta\eta$ of over 200 mV for $5\times$ greater current densities. The work presented in this thesis can be considered a road map for the future catalyst development. One can imagine that applying these techniques to a highly active material, such as $\text{NiFe}(\text{OH})_2$ could result in a beyond state-of-the-art catalyst. Furthermore, the methodologies developed here not restricted simple to catalytic or even electrochemical systems but should be applicable to many other technologies such as thermoelectric devices, further demonstrating

the usefulness and versatility of nanomaterials science.

8.2 Future Work

Improving the OER activity of $\text{Ni}(\text{OH})_2$ catalysts by incorporating Fe has been well reported^{370,371} and in general, $\text{Ni}_{1-x}\text{Fe}_x$ hydroxides are considered the most active OER catalysts in basic media.^{18,184} Often only a small amount of Fe is needed, typically less than 35 mol% for vast improvements to the Ni catalyst.¹⁸¹

It has also been reported that $\text{Ni}(\text{OH})_2$ electrodes are highly sensitive to Fe impurities in the electrolyte media (far more than $\text{Co}(\text{OH})_2$) to the extent that $\text{Ni}(\text{OH})_2$ can be used as an absorbent to remove trace Fe from KOH.^{181,205} These Fe impurities get incorporated into the $\text{Ni}(\text{OH})_2$ lattice and this can have a dramatic effect of the OER activity of Ni containing films. Previous work by Corrigan has shown that Fe impurities in KOH increase the performance of $\text{Ni}(\text{OH})_2$ OER catalysts,³⁷¹ and it has even been shown that $\text{Ni}(\text{OH})_2$ studied in highly pure KOH (with <40 ppb Fe) is a poor OER catalyst, suggesting Fe incorporation is key to the intrinsic activity of $\text{Ni}(\text{OH})_2$ catalysts.²⁰⁵

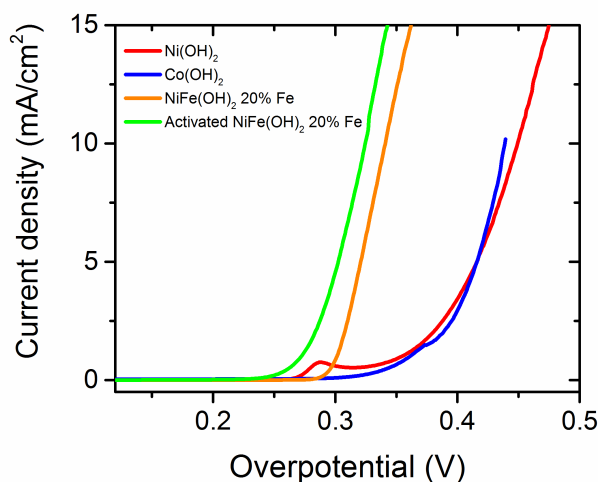


Figure 8.1: *Polarisation curve comparing the activity of $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$ and $\text{NiFe}(\text{OH})_2$ catalysts. All catalysts have a mass loading of 0.1 mg cm^{-2}*

Naturally this leads to the assumption that mixing a high Fe concentration solution with a dispersion of $\text{Ni}(\text{OH})_2$ could lead to a NiFe-like hydroxide with superior OER activity. Thus, inspired by this unique Ni-Fe relationship we proposed an alternative route to synthesising NiFe compounds using a cheap and scalable method. We have previously reported that layered $\text{Ni}(\text{OH})_2$ can be exfoliated in aqueous surfactant solutions, like $\text{Co}(\text{OH})_2$ outlined in this thesis.⁹¹ By simply mixing a dispersion of exfoliated $\text{Ni}(\text{OH})_2$ nanosheets with an aqueous iron salt solution (iron(III) nitrate, $(\text{Fe}(\text{NO}_3)_3)$) through a process of mild sonication should allow Fe incorporation into the $\text{Ni}(\text{OH})_2$ nanosheets. This could potentially form a $\text{NiFe}(\text{OH})_2$ compound with higher OER activities. If attainable this would result in a more straightforward method of preparing $\text{NiFe}(\text{OH})_2$ than commonly reported, especially if using LPE to exfoliate the $\text{Ni}(\text{OH})_2$ nanosheets. Additionally, the strategies developed in this thesis for improving catalyst activity should apply to such a system, which may lead to beyond state-of-the-art catalytic performance.

This was investigated by mixing dispersions of exfoliated $\text{Ni}(\text{OH})_2$ nanosheets in sodium cholate with iron(III) nitrate aqueous solutions. This resulted in an orange-yellow coloured dispersion. The precise nature of this mixture is unknown; however, we label it $\text{NiFe}(\text{OH})_2$ from herein for simplicity.

Nanosheet films were then made from both the $\text{Ni}(\text{OH})_2$ and $\text{NiFe}(\text{OH})_2$ with 20 mol% Fe, and examined as catalysts for the OER, the results of which are shown in figure 8.1. The loading of $\text{Ni}(\text{OH})_2$ was kept constant at 0.1 mg cm^{-2} , however $\text{NiFe}(\text{OH})_2$ showed a superior OER activity compared to the $\text{Ni}(\text{OH})_2$ only catalyst. These were also compared to a typical $\text{Co}(\text{OH})_2$ catalyst, showing $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ to be very similar. Activating the $\text{NiFe}(\text{OH})_2$ was also found to improve performance. This was achieved by applying a constant current density of 1 mA cm^{-2} for ~ 5 mins until a stable potential was reached. This increases the response perhaps due to surface roughening, or Fe further chemically bonding to the Ni. This result was promising, however only invites more questions such as; where is the Fe going, is the Fe chemically bonding to the $\text{Ni}(\text{OH})_2$ or simply decorating the nanosheet surface and what is the optimum Fe content to maximise performance. These studies are ongoing, however preliminary results are presented below.

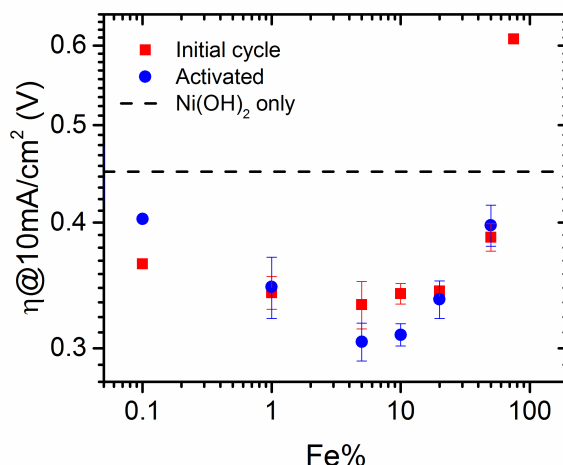


Figure 8.2: *Optimum mol% Fe shown typical U-shaped curve with performance peaking at 5% Fe*

We investigated the optimum Fe to Ni content by creating a series of $\text{Ni}(\text{OH})_2/\text{Fe}$ mixed dispersions with varying Fe content from 0.1 – 75 mol%. These were then fabricated into electrodes of 0.1 mg cm^{-2} $\text{Ni}(\text{OH})_2$ and tested for the OER. As shown in figure 8.2 a characteristic U-shaped trend emerged, revealing the optimum Fe was approximately 5 mol%. This is in line with similar NiFe synthesised from others in the literature.³⁷²

At the crux of this investigation lies the question of where in the $\text{Ni}(\text{OH})_2$ lattice is the Fe^{3+} incorporated and what is the bonding relationship between the two metals. Thus in depth characterisation of this newly formed NiFe compound is required. We performed standard TEM and SEM analysis on samples of NiFe with varying % Fe as shown in figure 8.3. Little information however is gained from these techniques, as the nanosheets were found to resemble standard $\text{Ni}(\text{OH})_2$ nanosheets.

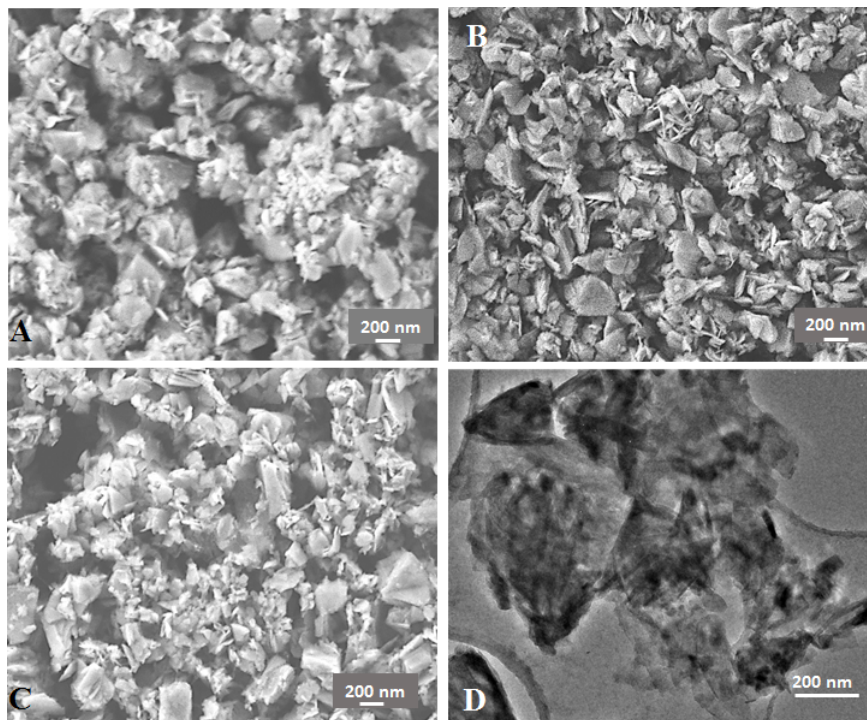


Figure 8.3: (A-C) SEM images of (A) $\text{Ni}(\text{OH})_2$, (B) $\text{NiFe}(\text{OH})_2\text{-5\%Fe}$ and (C) $\text{NiFe}(\text{OH})_2\text{-10\%Fe}$ nanosheet films. (D) TEM images of $\text{NiFe-5\%Fe}$ nanosheets

To gain further insights into the nature of this mixture high resolution TEM (HRTEM) was performed coupled with energy dispersive x-ray spectroscopy (EDX) (figure 8.4). This technique should allow for precise high-resolution elemental analysis of individual $\text{NiFe}(\text{OH})_2$ flakes, facilitating identification of the Fe on the nanosheet surface. Preliminary results from HRTEM show that the Fe is scattered over the entire nanosheet, with perhaps a slight preference for the nanosheet edges. This however does not indicate the bonding regime between materials or whether the Fe is incorporating within the lattice spacing of the $\text{Ni}(\text{OH})_2$ layers. Further analysis is required using x-ray photoelectron spectroscopy (XPS), x-ray diffraction techniques (XRD) etc. to probe deeper into the material properties.

Despite a large quantity of research there still remains much confusion over the precise role of Fe in improving the activity of Ni based OER catalysts. The activity gain has been attributed to anodic shifts in Ni redox peaks allowing sooner onset of OER,^{371,373} to changes in the physical and electronic structure of NiOOH ,²⁰⁵ and to claiming Fe is an active site.³⁷⁴ One often proposed hypothesis is that the

Fe enhances the electrical conductivity of the $\text{Ni}(\text{OH})_2$.³⁷¹ However, others have claimed this boost in electrical conductivity is insufficient to account for the high increase in OER activity.²⁰⁵ By creating composite films of $\text{Ni}(\text{OH})_2$ and $\text{NiFe}(\text{OH})_2$ with conductive carbon nanotubes we can investigate these claims by comparing the percentage improvement of both systems.

In summary, this project is very much in an early stage and further work is needed, however the preliminary results are extremely promising. Using the protocol developed to maximise the performance of $\text{Co}(\text{OH})_2$ catalysts, through thickness, mechanical, electrical and electrolyte optimisation creating free-standing films of $\text{NiFe}(\text{OH})_2$ may prove best-in-class particularly when considering the cheap and simple synthesis techniques

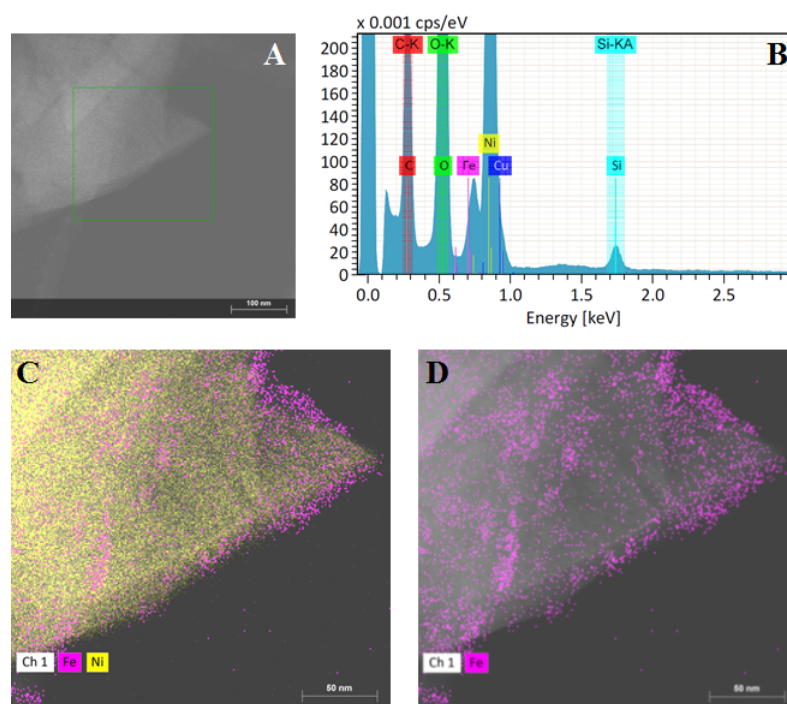


Figure 8.4: (A) Section of nanosheet probed with HRTEM and EDX. (B) EDX elemental spectrum. (C-D) HRTEM image showing Ni and Fe locations on the nanosheet.

Chapter 9

Appendix

9.1 Raman spectroscopy for $\text{Co}(\text{OH})_2$ nanosheets

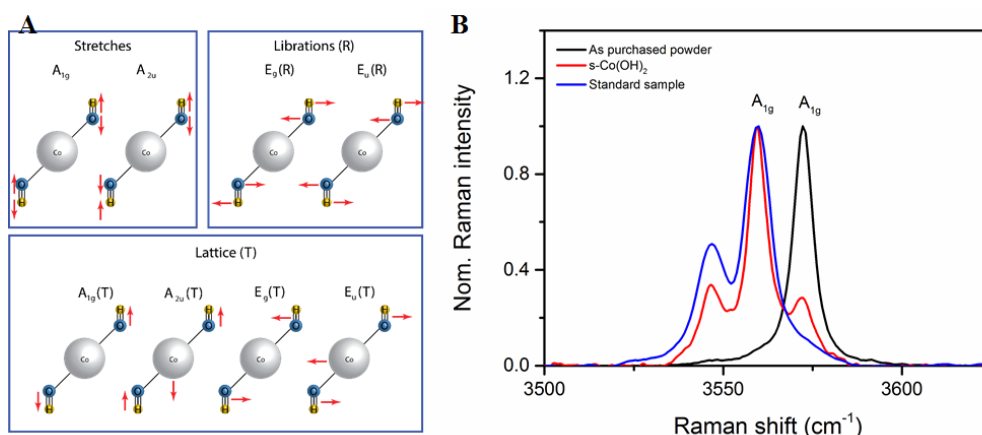


Figure 9.1: (A) *Vibrational modes of layered double hydroxides.*^{375,376}. (B) *$\text{Co}(\text{OH})_2$ Raman characterisation of A_{1g} O-H stretching mode of the three samples and its satellite peaks.*

Raman vibrational modes of LDHs can be assigned to lattice (T), stretching or libration (R) modes (figure 9.1A). In our spectra we can recognise $E_g(T)$, $E_u(T)$ and $A_{1g}(T)$, $A_{2u}(T)$. The broad tail observable at higher cm^{-1} of $A_{2u}(T)$ is typically assigned to $E_g(R)$. The presence of a more or less prominent peak (depending on the observed sample) at 456 cm^{-1} has previously been observed in different $\text{Co}(\text{OH})_2$ samples and was assigned to an OCoO vibrational mode.³⁷⁷

The A_{1g} O-H stretching mode is present at higher cm^{-1} (3570 cm^{-1}), shown in figure 9.1B. In similar materials, $\text{Ni}(\text{OH})_2$, the presence of satellite peaks in the vicinity of A_{1g} has been assigned to adsorbed water,³⁷⁸ but it may also originate from surface defects. Regardless, it is reasonable that those peaks will increase their relative intensity as the tested nanosheet reduce in size.

9.2 $\text{Co}(\text{OH})_2$ flake size selection UV-vis spectra and analysis

Flake size selection and UV-vis analysis was carrier out by Dr Andrew Harvey and is represented here for completeness. The optical properties of nanosheet dispersions can be very sensitive to nanosheet size thus the extinction, absorption and scattering coefficient spectra for five distinct sizes were measured and analysed. Details of this analysis is shown in figure 9.2A-C. The extinction, absorption and scattering are clearly sensitive to flake size, with ϵ increasing strongly with $\langle L \rangle$ at all wavelengths, similarly to previously shown $\text{Ni}(\text{OH})_2$.⁹¹ Additionally the scattering spectra (figure 9.2C) appear very similar to the extinction spectra for all nanosheet sizes confirming the optical properties to be dominated by scattering.⁹¹ In figure 9.2D and E the extinction coefficient, $\epsilon_{400\text{nm}}$ and absorption coefficient, $\alpha_{400\text{nm}}$ are plotted versus $\langle L \rangle$ respectively, both showing a general increase $\langle L \rangle$. The extinction coefficient increases strongly with nanosheet length in a manner which can be described empirically by:

$$\epsilon_{400\text{nm}} = 7.72 \langle L \rangle^2$$

Where $\langle L \rangle$ is in nm.

The scattering spectra in figure 9.2C are characterised by a power law decay, $\sigma \propto \lambda^{-n}$, which holds in the entire non-resonant regime (i.e. $\lambda > 300 \text{ nm}$). The scattering exponent, n , can be extracted from either the extinction or scattering spectra and is plotted versus $\langle L \rangle$ in figure 9.2F. This graph shows an increase from 2 for large nanosheets to 3.5 for smaller nanosheets, which is congruent with

Rayleigh theory, where for very small nanosheets with $\langle L \rangle \ll \lambda$ $n = 4$. For larger nanosheets, Mie scattering becomes predominant and there is a reduction in n . Therefore an empirical relationship between the scattering exponent, n , and average flake length, $\langle L \rangle$, can be found:

$$\langle L \rangle = 185 (n/4 - 1)$$

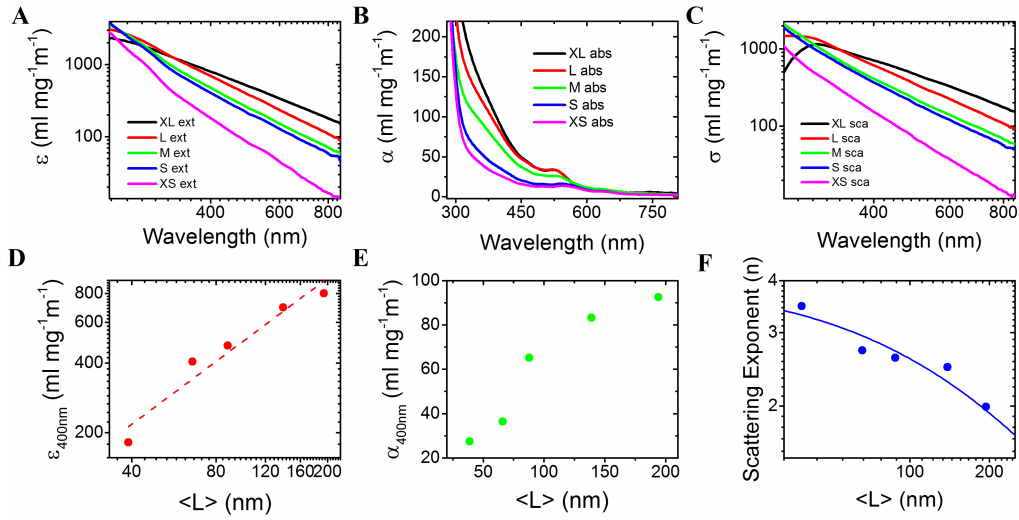


Figure 9.2: Normalised Extinction (A), absorption (B), scattering (C) for XL, L, M, S, XS sizes of Co(OH)_2 nanosheets respectively. The dispersions were prepared using $C_i = 20 \text{ g L}^{-1}$, $C_{\text{surf}} = 9 \text{ g L}^{-1}$ and $t_{\text{sonic}} = 4 \text{ h}$.

9.3 Fitting impedance spectra for MoS_2/SWNT films

For the MoS_2 and MoS_2/SWNT HER data shown in chapter 7, the electrochemical cell can be represented using an appropriate equivalent circuit model (figure 7.9B), where each element represents a feature in the reaction. The series resistance, R_u , represents the uncompensated electrolyte resistance and resistances in the supporting electrode, wiring etc. R_u is obtained from the real component of the impedance at high frequencies from either a Bode or Nyquist plot. This added potential is

removed from the recorded overpotential in the LVS through the application of IR correction:

$$\eta = \log(-J) b - \log(J_0) b + JR_u$$

$$\eta_{IR,corr} = \eta - JR_u$$

The $C_{\text{film}}R_{\text{film}}$ loop in figure 7.9B describes the catalyst electrode itself and in this case is controlled by the properties of the MoS_2 or MoS_2/SWNT film.³³² We note that because of the presence of the C_{film} capacitance in parallel with R_{film} , the resistance of the electrode is not included in the iR compensation.

The C_{dl} component in figure 7.9B models the double layer capacitance of the MoS_2 nanoflake-electrolyte interface. The R_p and R_s elements are related to the kinetics of the interfacial charge transfer reaction and the total faradaic resistance, which can be taken as the charge transfer resistance, is given by $R_{ct} = R_p + R_s$.³³² According to Harrington and Conway³⁷⁹ the capacitor C_ϕ , in parallel with R_s , is required to correctly model the relaxation of the charge associated with an adsorbed intermediate. Finally, constant phase elements (CPE) are used here instead of capacitors as they are necessary to simulate the frequency dispersion in the capacitive responses that arise due to surface roughness and inhomogeneity of the film. The impedance of a CPE has the form:

$$Z_{CPE} = \left(\frac{1}{Y_0} \right) (J\omega)^{-\alpha}$$

In the case of an ideal capacitor $Y_0 = C_{\alpha-1}$, however more often in reality $\alpha \leq 1$. Fit parameters for this model to our EIS data is found in table x

Table 9.1: *Fit parameters for impedance data. We note that the errors in C_{dl} are extremely large ($\sim 100\%$)*

CNT	R_u	C_{dl}	α_{dl}	R_s	C_ϕ	α_ϕ	R_p	C_{film}	α	R_{film}
Wt%	Ω	μF		Ωcm^2	$\mu F cm^{-2}$		Ωcm^2	$\mu F cm^{-2}$		Ωcm^2
		cm-2								
0	26	0.9	0.77	128	10	0.92	1.8	9.4	0.6	2.2
0.05	34	1.5	0.67	111	8.8	0.96	1.3	9.4	0.62	4.1
0.6	24	0.3	0.73	100	9.3	0.94	1.4	19	0.55	1.1
5	17	0.3	0.62	93	11	0.94	0.9	112	0.72	0.2
10	21	3.6	0.8	72	8.7	0.95	1.5	58	0.73	0.9

9.4 Composite free-standing films: capacitive current correction

The measured current when applying a potential to a solid electrode in a liquid electrolyte is usually a combination of a capacitive current I_C , due to ions accumulating at the solid/liquid interface, and the Faradaic current I_F which is associated with charge transfer reactions. Normally for reactions such as the OER, the usual case is $I_F \gg I_C$ and thus the measured current when quoting overpotentials is usually assumed to be I_F .³⁸⁰ However, when I_C is approaching a similar value as I_F , it is appropriate to correct for this as the quoted overpotential for the OER at a given measured current will not be a true value. In our case for the free standing (FS) films, as we used a relatively large mass of $Co(OH)_2$ the capacitive current contributed non-negligibly when quoting the often used benchmark of η at 10 mA cm^{-2} . Figures 9.3A and B show the effect of correcting for I_C on the η vs film thickness. Figure 9.3C shows the same trend is observed at both 10 and 50 mA cm^{-2} when corrected. However, it is clear to note that the η values quoted at 50 mA cm^{-2} vary insignificantly with and without this correction and thus we have chosen to use this current density for all benchmarking for our FS films to avoid any potential errors.

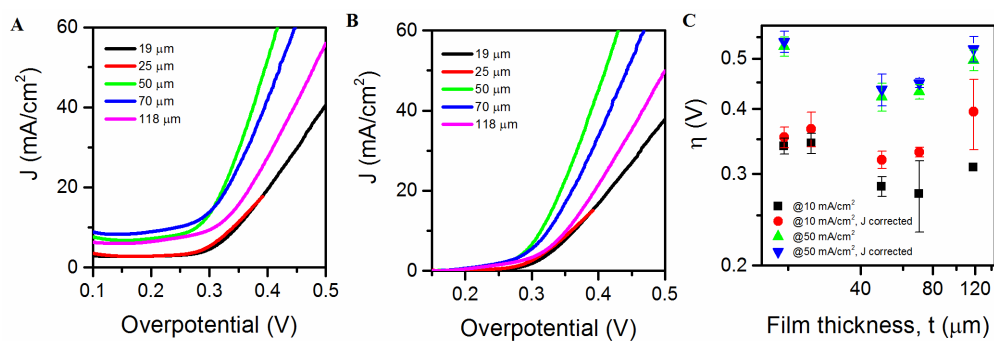


Figure 9.3: *Polarisation curves of thick free standing (FS) films. (A) As measured linear voltage sweeps of FS films showing high capacitive currents. (B) The same linear voltage sweeps with capacitive currents removed. (C) Overpotential measured at 10 and 50 mA cm⁻² versus FS film thickness, showing the effects of correcting for capacitive currents.*

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