

# **Post-Synthetic Treatment of Layered Nanomaterials for Optimized Performance in Energy Transfer & Storage Devices**



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By

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## Abstract

Controlled syntheses of PbO and NiFe LDH layered nanomaterials were carried out for this work, followed by comprehensive studies to determine the extent to which improvements can be made, in terms of performance in their respective energy applications, by way of post-synthesis processing steps. Namely, particle size control and composite optimization with carbon nanotubes were the principle approaches for enhancing the performance, along with some additional key cell design considerations.

NiFe LDH is studied for its electrocatalytic properties. Highly crystalline NiFe hexagonal platelets with high morphological regularity and sub-micrometre lateral dimensions were synthesized using a homogeneous precipitation technique. The hexagons exhibit exceptional electrocatalytic activity for the oxygen evolution reaction (OER), especially in alkaline media, and for this reason have potential applications in water electrolysis for H<sub>2</sub> gas extraction. Considering edge sites are the point of activity, efforts were made in this work to tailor the platelet dimensions within the synthesized dispersions. To this point, synthetic approaches for size control of NiFe LDH platelets have not been transferable based on published work for such processes with other LDH materials and for that reason we instead use post-synthetic treatment techniques to improve edge-site density. Namely, a combination of ultrasonication and centrifugation-driven size-selection steps were applied to the NiFe LDH and the electrocatalytic behaviour towards OER was characterized. Synthesized platelets of mean lateral size  $\langle L \rangle = 0.78 \pm 0.02 \mu\text{m}$  can be selectively reduced to values below  $0.2 \mu\text{m}$  with overpotential  $\eta = 245 \pm 7 \text{ mV}$ . Composite optimization allows for further reduction in this value with important long-term stabilizing effects on the system. In recognition of the complex, still-debated mechanism for NiFe LDH alkaline water electrolysis, additional efforts are presented here to determine the factors which govern the short and long term OER performance of the catalyst. It is suggested that a combination of subtle phase changes and gradual leaching of metal components from the LDH structure will govern the catalyst's stability and hence, performance.

PbO is another material with significant potential, this time in battery applications as a LIB anode, but requires a degree of processing in order to realise its full potential. Controlled thermal degradation of  $\text{PbCO}_3$  can be used to synthesize PbO in its phase-pure tetragonal ( $\alpha$ ) and orthorhombic ( $\beta$ ) symmetries. Similar particle size and composite preparation steps can act to reduce long range stress experienced by the material during lithiation, as well as improving the conductivity and ionic diffusion with the crystal. Composites of phase pure tetragonal  $\alpha$ -PbO with SWCNTs can outperform commercial polymorphic material, with  $670 \text{ mAh}\cdot\text{g}^{-1}$  at 0.1 C and 82% capacity retention through ten cycles.

In summary, this thesis aims to explore the utility of simple, transferable steps which can be applied to promising nanomaterials with novelty in energy devices, to greatly enhance their long-term performance and outlook in practical applications.

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## Abbreviations

0D/1D/2D/3D – zero/one/two/three dimensional

AAS – Atomic Absorption Spectroscopy

AFM – Atomic Force Microscopy

Ag/AgCl – Silver/Silver Chloride

CNT – Carbon Nanotube

CP – Chronopotentiometry

CV – Cyclic Voltammetry

DI – deionised

ECSA – Electrochemical Surface Area

EDX – Energy-Dispersive X-ray spectroscopy

EELS – Electron Energy Loss Spectroscopy

EIS – Electrochemical Impedance Spectroscopy

FT-IR – Fourier Transform Infrared spectroscopy

GCPL – Galvanostatic Cycling with Potential Limitation

HAADF – High Angle Annular Dark Field

HER – Hydrogen Evolution Reaction

HRTEM – High-Resolution Transmission Electron Microscopy

ICP-MS – Inductively Coupled Plasma – Mass Spectroscopy

ICP-OES – Inductively Coupled Plasma – Optical Emission Spectroscopy

IPA - Isopropanol

IR – Infrared

k – Spring Constant

LDH – Layered Double Hydroxide

LIB – Lithium Ion Battery

LV – Linear Sweep Voltammetry

<L> - mean lateral size

M<sup>2+</sup>/M<sup>3+</sup> - divalent/trivalent metal centres

NiFe – Nickel-Iron

NMP – N-Methyl-2-Pyrrolidone

OER – Oxygen Evolution Reaction

PbO – Lead(II) Oxide

PVDF – Polyvinylidene Fluoride

PVP - Polyvinylpyrrolidone

RHE – Reversible Hydrogen Electrode

SAED – Selected Area Electron Diffraction

SEM – Scanning Electron Microscopy

sr – Size-reduced

(S)TEM – (Scanning) Transmission Electron Microscopy

TEA – Triethanolamine

TGA – Thermogravimetric Analysis

UV-Vis – Ultraviolet-Visible

wt% - Weight %, Mass Fraction

XPS – X-ray Photoelectron Spectroscopy

XRD – X-Ray Diffraction

$\eta$  - Overpotential

$\lambda$  - Wavelength

$\sigma$  – Standard Deviation

## Publications

(Published)

- *Low-temperature synthesis and investigation into the formation mechanism of high quality Ni-Fe layered double hydroxides hexagonal platelets* - Sonia Jaśkaniec, Christopher Hobbs, Andrés Seral-Ascaso, João Coelho, Michelle P. Browne, **Daire Tyndall**, Takayoshi Sasaki and Valeria Nicolosi.

(Under review)

- *Post-Synthetic Treatment of Nickel-Iron Layered Double Hydroxides for Optimum Catalysis of the Oxygen Evolution Reaction* – **Daire Tyndall**, Sonia Jaskaniec, Brian Shortall, Ahin Roy, Michelle P. Browne, Joao Coelho, Valeria Nicolosi

## Communications

(Presentation)

- **Daire Tyndall**, Sonia Jaskaniec, Valeria Nicolosi; “*Synthesis and Investigation into the Formation Mechanism of Ni-Fe Layered Double Hydroxides for Oxygen Evolution Reaction*”; 256<sup>th</sup> ACS National Meeting 2018 (August 19 – 23), Division of Inorganic Chemistry Symposium, Boston, MA, USA
- **Daire Tyndall**, Sonia Jaskaniec, Valeria Nicolosi; “*Synthesis and Formation Mechanism of Ni-Fe Layered Double Hydroxides for Oxygen Evolution Reaction*”; Flatlands: Beyond Graphene 2018 (September 3 – 7), Leipzig, Germany
- **Daire Tyndall**, Valeria Nicolosi; “Tailored Ni-Fe Layered Double Hydroxide Platelet Size for Optimized OER Catalysis”; 2019 MRS Fall Meeting & Exhibit (December 1 – 6), Metal & Metal Oxide Catalysts Symposium, Boston, MA, USA

(Posters)

- **Daire Tyndall**, João Coelho, Sonia Jaśkaniec, Valeria Nicolosi; “*Post-Synthetic Treatment of  $Ni_xFe_y$  Layered Double Hydroxide for Enhanced Catalysis of the Oxygen Evolution Reaction*”; Graphene Study 2018 (February 5 – February 10), Obergurgl, Austria.
- **Daire Tyndall**, João Coelho, Sonia Jaśkaniec, Valeria Nicolosi; “*Post-Synthetic Treatment of  $Ni_xFe_y$  Layered Double Hydroxide for Enhanced Catalysis of the Oxygen Evolution Reaction*”; 2018 MRS Spring Meeting (April 2 – April 6), Nanomaterials of the Water and Energy Nexus symposium, Phoenix, AZ, USA
- **Daire Tyndall**, João Coelho, Sonia Jaśkaniec, Valeria Nicolosi; “*Tailored Nickel-Iron Layered Double Hydroxide Particle Size for Optimized O.E.R. Catalysis*”; AiMES and SMEQ Joint International Meeting 2018 (September 30 – October 4), Nanotechnology General Session, Cancun, Mexico

# 1 Introduction

One of the most significant generational concerns in today's society is the global energy crisis which we actively face. Fossil fuels are the energy source on which the worldwide economy largely relies, and they are running out. Soon fossil fuel-derived petroleum and other non-renewable resources will become precious commodities, too valuable to remain as the obtainable resources they are today. Scientists and engineers around the world face the prospect of not only devising a replacement strategy in terms of sustainable energy but also attempting to address the damage caused by the carbon output resulting from 150 years of burning fossil fuels.<sup>1, 2</sup> Since the first modern commercial oil well was drilled around 1859, as well as the subsequent invention of motorized vehicles and first internal combustion engine in the late 19<sup>th</sup> century, the energy demand from petroleum and similar fuels has seen an exponential rise. Peter Tertzakian equates the modern global oil consumption to about 1000 barrels a second, or an average of two litres of oil per day consumed by every single person on earth.<sup>3</sup>



**Figure 1.0.1: Graphical representation of the principle energy resources in use globally today.<sup>1</sup>**

Despite the near constant increase in energy consumption from oil, coal and natural gas, the global statistics for the year 2020 present an interesting change. In their annual global energy review, the International Energy Agency (IEA) report some major implications of the COVID-19 pandemic

on global economies, energy use and CO<sub>2</sub> emissions. In terms of energy, countries which went into lockdown experienced a 25% drop in energy consumption during that time.<sup>1</sup> In the first quarter of 2020, global road use was down almost 50%, culminating in a 5% drop in oil use for the quarter and a 3.8% drop in energy demand entirely. Figure 1.0.2 presents how this looks in the worldwide energy data projected for 2020 against the steady climb of the last 100 years or so. Without context, this data set may be misleading. The truth is that the trending growth of supply and demand for unsustainable resources will return to normal and likely continue to grow until collapse. That is, if realistic and competitive alternatives are not developed in the meantime. For this, research efforts are being made around the world to develop novel devices for the efficient harnessing of earth's natural energy and its safe, controllable storage and transfer.

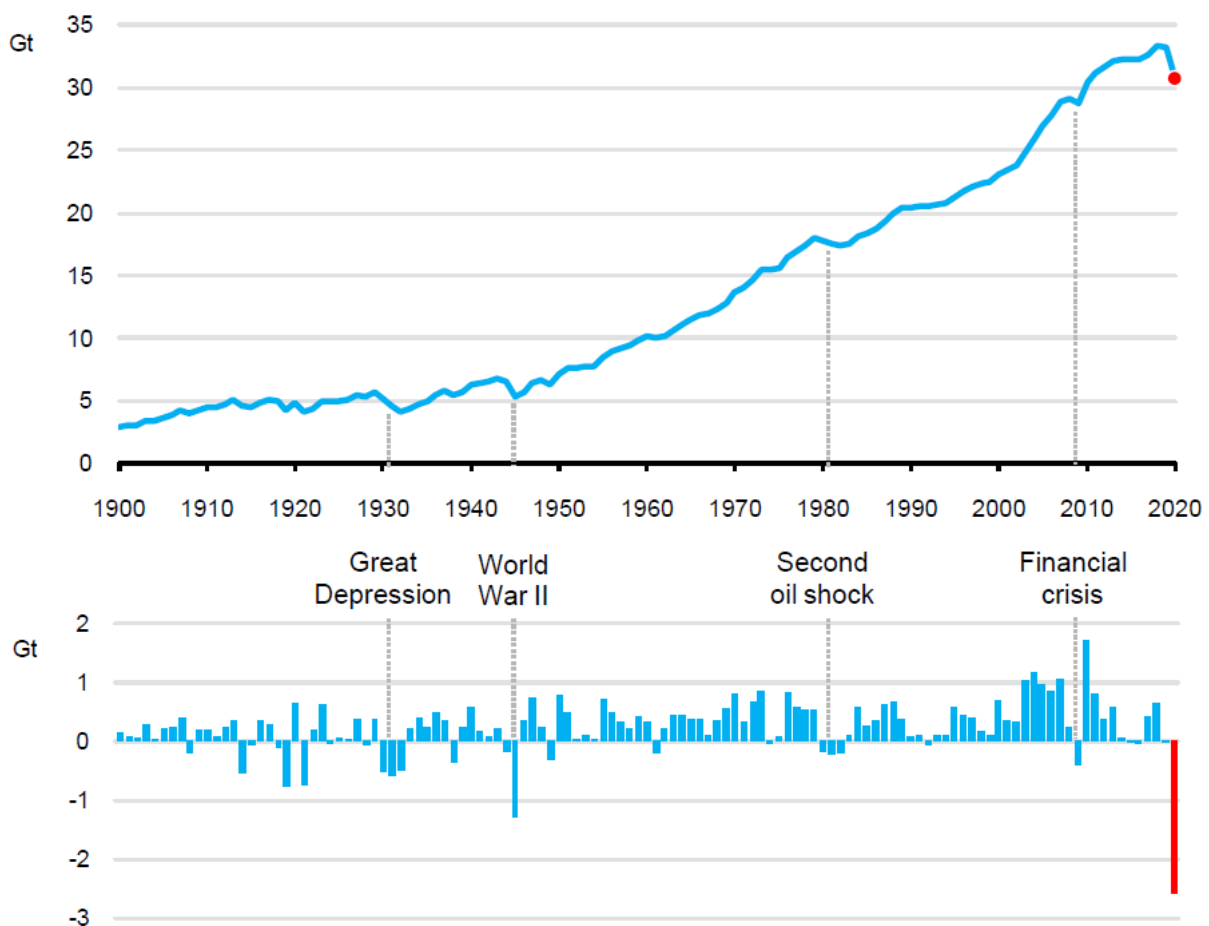


**Figure 1.0.2: Annual worldwide energy demand in gigatons since 1900, in total energy (above) and yearly fluctuation (below), per the 2020 energy report published by IEA.<sup>1</sup>**

Examples of the earth's natural energy resources include solar, wind and hydroelectric energy. The former is by far the most plentiful, providing the earth with 120,000 TW of electromagnetic power.<sup>4</sup> As of 2018, the collective efforts of alternative sources (i.e. aside from oil, coal, natural gas and nuclear) made up for just under 14% of the world's energy consumption, according to an IEA report.

## 1.1 Water Electrolysis & the Hydrogen Economy

Across the landscape of the modern-day sustainable energy field of research there exist many novel green fuels and energy storage/transfer devices. One example of a prominent fuel in research is hydrogen gas, which can be catalytically split in a device called a fuel cell in an oxidative process to produce electrical energy. The basic workings of a hydrogen fuel cell are extremely simple.  $H_2$  fuel is supplied to an anode at which it is catalytically oxidised to create protons and liberate electrons. The protons flow across an appropriate electrolyte to the cathode where they combine with  $O_2$  and an electron in another catalytically driven step to produce the  $H_2O$  by-product, all the while electrons flow in an external circuit to induce a current. The simple workings are displayed in very simplest terms in Figure 1.1.1.

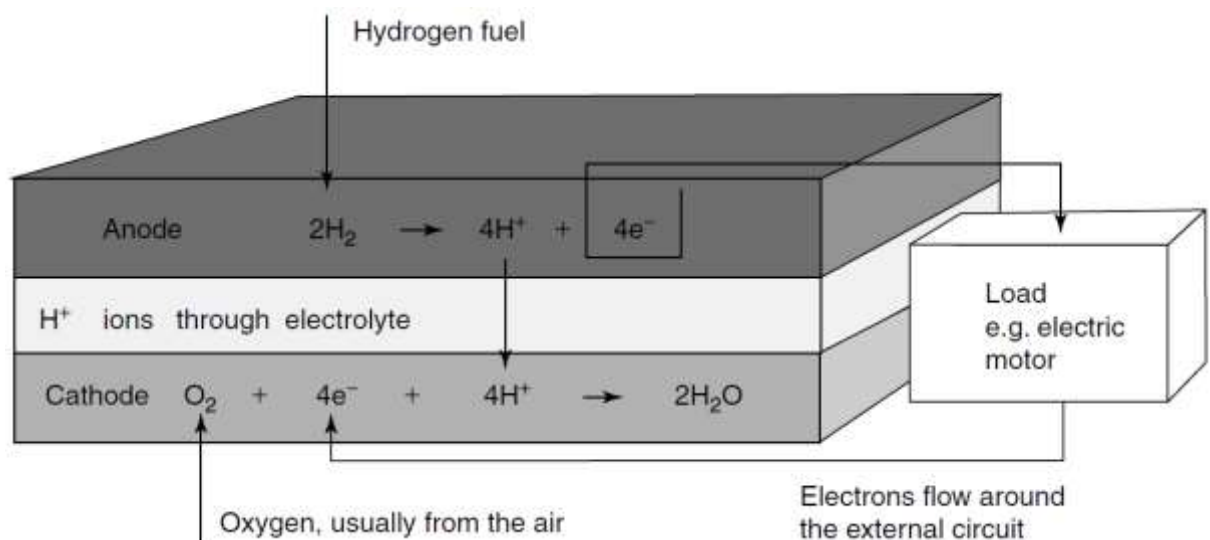


*Figure 1.1.1: Schematic illustration of the typical setup of a hydrogen fuel cell.<sup>5</sup>*

In terms of electrode components, both the anode and cathode need to be capable of oxidising hydrogen ( $\text{H}_2 \rightarrow 2\text{H}^+$ ) and reducing oxygen ( $\text{O}_2 + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$ ) respectively. To date, composites containing active platinum particles have been the highest performing catalysts on both sides of the fuel cell.<sup>6</sup> Without a doubt, the most advanced and well developed fuel cell design is that of the proton-exchange membrane (PEM) fuel cell. The cell, which is sometimes additionally referred to as a polymer electrolyte membrane fuel cell, includes an ionic conductive polymer membrane as an electrolyte, capable of shuttling protons across the cell. Advantages of using PEM cells include compact device assembly, low temperature operation and the lack of corrosive acidic or alkaline fluids.<sup>5, 7, 8</sup> All of this makes the cell design highly compatible in high interest areas of application like hydrogen powered vehicles and other portable devices.

The idea of deriving energy from a ‘green’ fuel like hydrogen is an attractive prospect and brings about the concept of the Hydrogen Economy.<sup>9</sup> It is a concept which could bring to pass a fully self-sustaining energy cycle, with water at both ends of the reaction order. Additional to this, there is the attractive energetic properties of hydrogen itself.  $\text{H}_2$  gas has potential as a clean fuel which combusts in air (Equation 1.1) and has more chemical energy than common battery materials.<sup>1</sup>



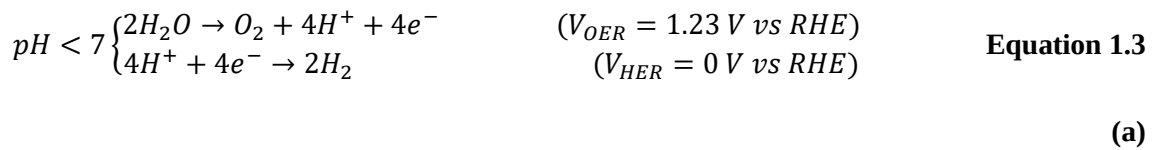
The underlying issue to this point which has caused major doubt on the scheme is that hydrogen gas is not naturally available and must be produced. Critically, this means that it cannot be considered an energy source to the extent of natural fuels but rather a secondary vehicle for energy transfer.  $\text{H}_2$  production carries with it an energy cost and this is a significant limiting factor. The vast majority of commercial  $\text{H}_2$  production today actually derives from fossil fuels. The cheapest and most popular synthetic route for industrial scale hydrogen production is steam reforming using natural gas (a mixture of primarily methane with other hydrocarbons). This involves extreme heating of the gas in the presence of water vapour and a nickel catalyst. Methane reacts with water at such temperatures to produce large quantities of hydrogen gas, with harmful CO and  $\text{CO}_2$  by-products.<sup>10</sup> If hydrogen production cannot be realized in a clean, low energy manner and without the need for a

non-renewable source then it cannot serve the desired purpose in future research. However, a cleaner method of production can be achieved via the extraction of  $H_2$  from water by electrolysis (Equation 1.2).



The reaction, in theory, has no environmentally harmful by-products and can be catalysed to lower the energy cost and hence boost the potential for commercialization. To this day however, water electrolysis accounts for just 4% of the world's hydrogen production<sup>11</sup> because the energy cost remains high, meaning more efficient catalysis is imperative.

Hydrogen evolution via water electrolysis is energetically costly mainly because of the oxygen evolution 'step' which must take place for the reaction to proceed. For this reason, catalysis of the oxygen evolution reaction (OER) more so than the hydrogen evolution reaction (HER) has been intensively studied. General, simplified versions of the formula for water splitting in acidic and basic conditions are outlined in Equation 1.3 (a) and (b) respectively, emphasizing the separate 'half-reactions' which take place for oxygen and hydrogen evolution. The most significant detail here is the potential associated with the OER step,  $E \approx 1.23 \text{ V}$  vs reversible hydrogen electrode (RHE), compared to the hydrogen evolution step which has no associated potential in theory.



As the equations show, the evolution of  $O_2$  from water requires the transfer of four electrons. The reaction proceeds by way of a multi-step process, each step involving one electron transfer.<sup>12, 13</sup> The kinetic effects associated with such a sluggish mechanism means there is always some overpotential ( $\eta$ ) associated with the reaction mechanism. The  $\eta$  value is the difference between the

measured potential vs RHE and that which is predicted by thermodynamic calculations (i.e. the energetic deviation from a ‘perfect’ reaction with no kinetic effects). Minimizing this  $\eta$  value is essential for any commercial applications of devices involving OER. Electrocatalysis will play the central role in commercialising such a process and huge efforts have been made in recent years to develop effective catalysts for OER with the aim of minimising  $\eta$ .<sup>21, 22</sup>

Once large-scale production of isolated  $H_2$  becomes possible via catalysis, it is important that the fuel is used in applications which allow for efficient and effective energy extraction. The Ragone plot in Figure 1.1.2 demonstrates the trade-off between specific energy and power capabilities of a number of modern energy storage devices. From the plot it can be seen that fuel cells possess a high energy output compared with batteries and electrochemical capacitors and comparable even to common combustion engines. Fuel cells also generally possess higher energy efficiency than combustion engines. It is clear that highly optimized fuel cells, along with the preceding electrolyser (water-splitting) cells hold great significance in our energy future.

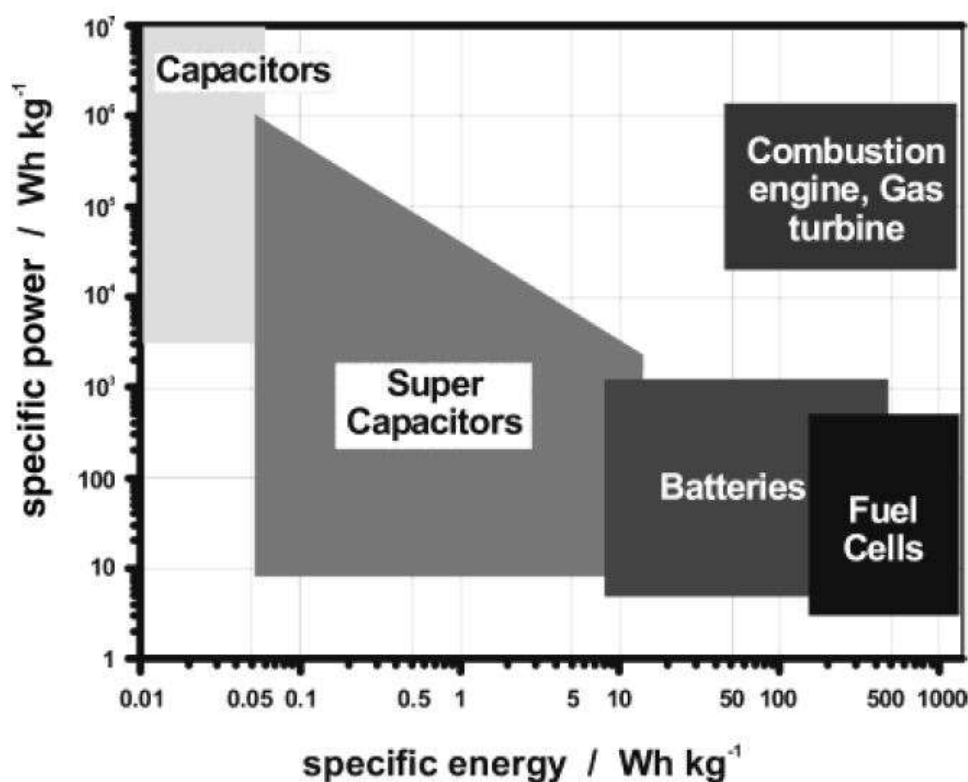


Figure 1.1.2: Ragone plot of various energy storage devices (reproduced with permission, Copyright 2004, American Chemical Society).<sup>23</sup>

Many catalysts have been considered for minimizing an overpotential, including rare earth metal oxides, various perovskites and layered materials. However, common problems often include availability, cost and stability. Layered double hydroxides (LDH, section 1.2), have exhibited exceptional OER catalysis due in part to the relatively open brucite-like structure which facilitates fast diffusion of reactants and products during catalysis as well as their large scale availability of active sites.<sup>21, 24, 25</sup> Nickel-iron (NiFe) LDH has been shown to exhibit the most promising catalysis, improving the overpotential and stability (in alkaline conditions) compared to previous competitive catalyst materials in various systems such as the rare earth catalysts RuO<sub>2</sub>, IrO<sub>2</sub> and Raney Nickel (alkaline water electrolysis).<sup>26, 27</sup> Such catalysts had other limitations in terms of commercialization due to their high cost, low earth abundance and toxicity, meaning NiFe LDH, upon discovery of its catalytic properties, has become a prime candidate for commercial hydrogen evolution catalysis. Active sites in the material are located at the edge of the platelets, meaning the average size of the LDH flakes in a given dispersion will affect the edge-site density and hence, the overall catalytic activity. Efforts are made in this study to control edge-site density of platelets after synthesis using size control techniques.

## 1.2 Layered Double Hydroxides for OER Catalysis

LDHs in general are among the materials of highest interest in research today, owing to their desirable chemical and electrochemical properties, with applications not only in the area of electrocatalysis,<sup>21</sup> but also energy storage, drug delivery, among others.<sup>28, 29</sup> LDHs belong to the layered materials family and exhibit properties of an anionic clay (i.e. swollen interlayer domains occupied by both water, and an anionic species). They consist of edge-shared octahedra (brucite-like) layers with hydroxide ions at the octahedral sites and mixed divalent and trivalent metal centres, as schematically presented in Figure 1.2.1.

Their general formula of LDHs is given in Equation 1.4, where M<sup>II</sup> and M<sup>III</sup> represent divalent and trivalent metal cations respectively, and A<sup>n-</sup> is an anionic species with valence n, which exist between layers.<sup>30</sup>

$$[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}[A_{x/n}^{n-} \cdot yH_2O]^{x-} \quad \text{Equation 1.4}$$

LDH materials with this general formula can have a range of compositions, with Mg, Fe, Ni, Cu, Zn and Co being common divalent species and Al, Fe, Cr, Mn or Ga often found as the trivalent metal.<sup>31</sup>  $Mg^{2+}$  and  $Al^{3+}$  are the metal species found in the mineral hydrotalcite, with chemical formula  $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ , which was the first realised member of the LDH family (hence, often referred to as hydrotalcite-like materials). As such, there is a condition that the divalent and trivalent metal species at octahedral centres in an LDH structure must have similar atomic radii to  $Mg^{2+}$  and  $Al^{3+}$ . There is another limitation in LDH composition, that the trivalent metal fraction  $x$  must be in the range  $0.2 \leq x \leq 0.4$  because of a limit in lattice parameters of the ‘host’  $M(OH)_2$  structure. Outside of this range, electrostatic repulsion takes over between trivalent metal centres and also between interlamellar anions which can result in the formation of some additional hydroxide species and metal salts.<sup>30, 32</sup> The necessity of the  $A_{x/n}^{n-}$  species in Equation 1.4 comes from the mixed valency of the metal centres in the brucite-like layers which causes a net positive charge within the layered framework of the material. There lies the need for counter anions between layers to balance the charge.<sup>33</sup>

Carbonates ( $CO_3^{2-}$ ) are the most stable counter anion commonly available during synthesis and therefore often exists at intercalation sites within the as-prepared material. Its stability is owed to its planar morphology as well as hydrogen bonding which exists between oxygen atoms on the carbonate and hydrogen atoms in octahedral hydroxide layers. The carbonate anion is also divalent which enhances its coulombic interaction with layers compared to monovalent species. Below is a general order of stability which is observed for some common LDH counter anions.<sup>33, 34</sup>



This trend is supported well by experimentation, with Liu *et al.*<sup>35</sup> producing data which suggests a correlation between counter anion stability and basal plane spacing. The counter anion species can be varied and facile anionic exchange at intercalation sites can give rise to some of the materials most

interesting and promising applications in the areas of energy storage and drug delivery.<sup>28, 29, 36</sup> The promise in these fields is due in part to the strong bonding between LDH layers and counter anions meaning they can swell as much as 20 Å to accommodate intercalated drugs or foreign ions without damage to the structure.<sup>28</sup> LDH materials also generally possess attributes such as low toxicity, biocompatibility and pH-dependant solubility, which favour them for *in-vivo* applications. Intercalation of some of the less stable anions from the list above can also serve the purpose of promoting exfoliation by weakening the bonds that hold layers together.

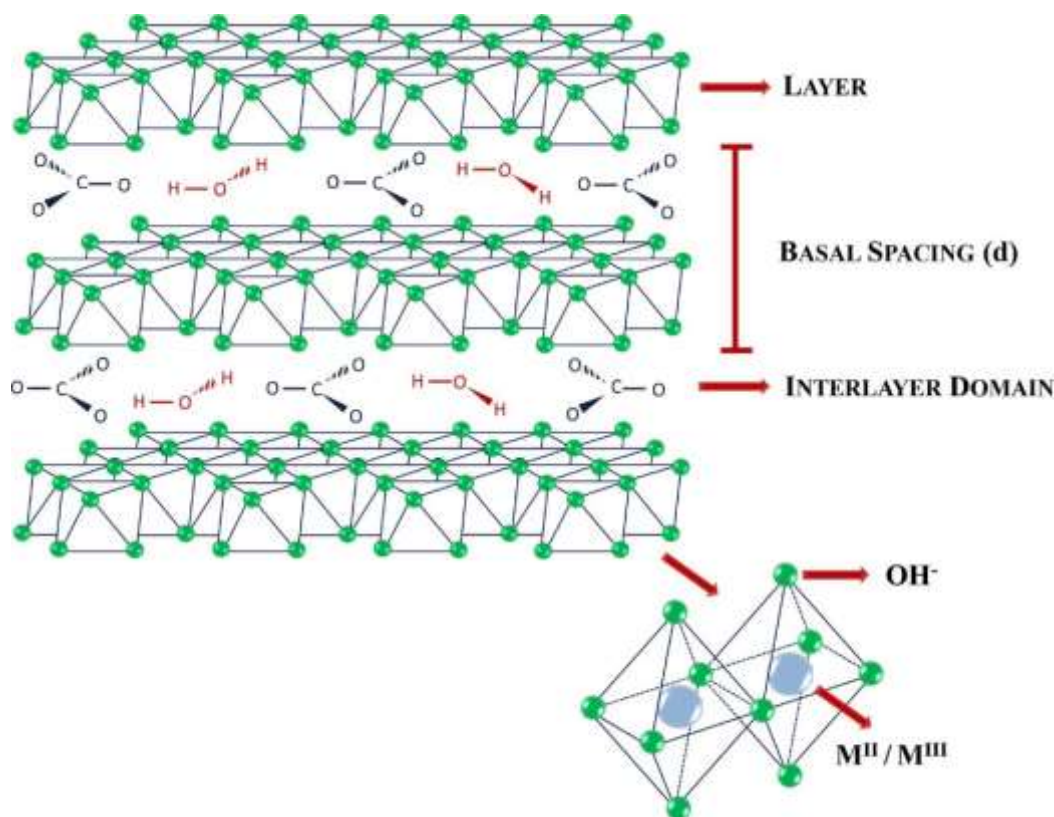


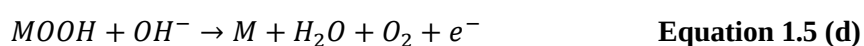
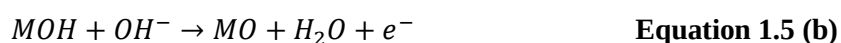
**Figure 1.2.1: Representative LDH structure, indicating edge-shared octahedron layers with interlayer water and  $\text{CO}_3^{2-}$  counter anions.<sup>37</sup>**

In the presented work, it is the catalytic abilities of LDH materials which will be exploited. NiFe LDH will be the material of focus because of the impressive catalytic properties which have been observed with this particular combination of transition metals.<sup>26, 38, 39</sup> The presence of Fe within the structure has the effect of advanced catalytic activity with respect to the parent  $\text{Ni}(\text{OH})_2$  for reasons which are not yet completely clear. A study by Trotochaud *et al.* revealed that incorporation of  $\text{Fe}^{3+}$  as alternative metal centres into the ‘host’  $\text{Ni}(\text{OH})_2$  crystal structure can result in a > 30-fold

increase in conductivity,<sup>40</sup> but this cannot alone account for the observed enhancement in activity as is seen for OER. It was also observed that an increase in crystallinity and interlayer spacing were caused by Fe<sup>3+</sup> inclusion but it did not have a direct effect on its catalytic properties. In fact, it is believed that the catalytic activity of NiFe LDH is enhanced, in comparison to the pure Ni(OH)<sub>2</sub>, because of a partial Ni-Fe charge transfer activation upon Fe<sup>3+</sup> inclusion. The enhancement is analogous to the improved activity observed when a Ni(OH)<sub>2</sub> catalyst is deposited on a more electronegative metal substrate such as Au.<sup>41</sup> The difference here is that Fe<sup>3+</sup> is incorporated within the Ni(OH)<sub>2</sub> structure rather than just the surface layers, meaning a complete electron transfer activation occurs throughout the bulk of the material.

When attempting to rationalise how the charge-transfer activation may take place between the metal centres, the intuitive conclusion is that the more electrophilic metal, Fe<sup>3+</sup> in this case, should act as a Lewis acid in the system pulling charge density from the Ni<sup>2+</sup> sites and hence creating electron deficient nickel sites. In alkaline systems this train of thought would lead to active sites at the Ni surface termination sites as the electron deficiency would promote the approach of OH<sup>-</sup> electrolyte ions. However, when one looks at the intricacies of the source of electrocatalytic activity in NiFe LDH and attempts to locate the active sites, the findings are in fact not so intuitive. For example, Friebe *et al.*<sup>42</sup> use *in-situ* x-ray absorption (XAS) and extended x-ray absorption fine structure (EXAFS) techniques to view the oxidation states and local bond lengths respectively for the metals at different points of OER activity by varying the cell potential. They observed an unexpected contraction of Fe-O bond lengths at elevated potentials when the catalyst becomes OER active. The extent of the contraction is similar to that observed for Ni-O under similar conditions, the difference being that in the case of nickel the observation is well accounted for as the pre OER oxidation of Ni<sup>2+</sup> to Ni<sup>3+</sup>, which is known to take place. In contrast, *in-situ* XAS cannot detect enough Fe<sup>2+</sup> oxidation to account for the change in Fe-O bond lengths. In the literature this has been considered the prime early indication of some activity at iron sites within a well-integrated, homogeneously packed Ni-Fe crystal.

Further mechanistic studies to understand OER activity involve density functional theory (DFT) calculations. The methods involve selecting potential candidates which may act as surface active sites and determine the free energies involved when approached by electrolyte ions,  $\text{OH}^-$  in the alkaline case. This ionic approach will kick start the four-electron transfer which is involved in simplified metal-catalysed OER reaction mechanism (Equations 1.5, represented graphically in Figure 1.2.2 for an ideal catalyst). Each electron transfer step brings about its own associated potential barrier, the greatest of which will limit the reaction rate.



It is around this model of alkaline catalysis that the DFT calculations are built. According to the Friebe paper,<sup>42</sup> such calculations suggest the lowest overpotential for catalysis taking place at  $\text{Fe}^{3+}$  sites. Most recently however, Dionigi *et al.*<sup>43</sup> have combined *in-situ* crystallographic characterization of NiFe LDH alkaline OER activity with DFT calculations to suggest that the mechanism is activated by deprotonation of a surface hydroxyl group in a Mars van Krevelan-type mechanism. The rate limiting step and the free energy cost are minimized when the hydroxyl group is bridged in a Ni-OH-Fe conformation which accounts for the superior catalysis of the mixed-metal case compared with pure Ni or Fe based catalysts. It is obvious then that there remains a certain level of uncertainty around the precise, agreed upon site of activity and surface mechanism for  $\text{OH}^-$  ion approach. One point which is not argued though is that  $\text{Fe}^{3+}$  is the component which activates the hydroxide structure to perform with such exceptional efficiency for OER catalysis, something which can be seen for its inclusion in similar hydroxide structures.

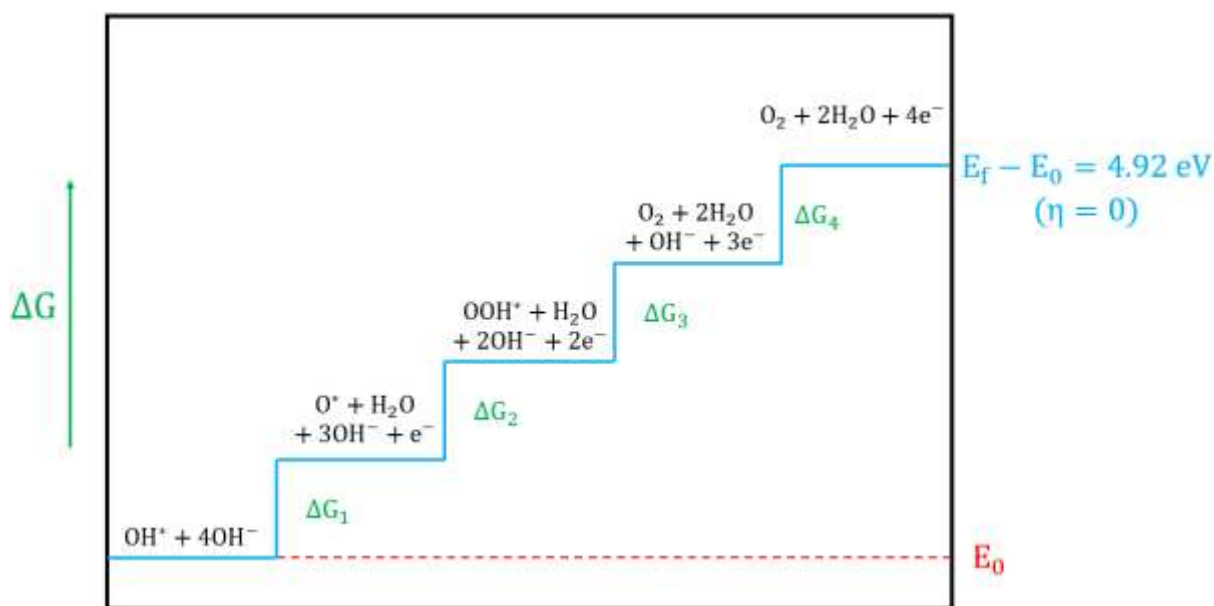


**Figure 1.2.2: Plot of Gibbs free energy of the oxygen evolution reaction in alkaline media with an ideal catalyst i.e. each step requiring 1.23 V vs RHE to overcome with no overpotential.**

NiFe LDH was synthesized here using a wet chemistry method at moderate temperatures, using a ‘capping agent’ to facilitate homogeneous decomposition and precipitation of nickel and iron metals from their intermediate states into the crystalline hydroxide product.<sup>44</sup> Full details of the synthesis are available later in section 3.1

One of the goals of this work will be to systematically study the extent to which techniques of particle size reduction and size selection can be used to enhance the catalytic abilities of NiFe LDH for oxygen evolution by alkaline water electrolysis based on active site enhancement at platelet edges. The catalytic ability will be judged based on the overpotentials which can be achieved using just the treated material deposited on a nickel foam substrate to form an electrode. Ultimately it is hoped that such a study will allow for a comprehensive understanding of the relationship between particle size and catalysis to be achieved which may help us understand the nature of electrocatalysis in layered materials in a more general sense, as well as enhancing the outlook for NiFe LDH specifically for this application.

## 1.3 Lithium Ion Batteries

A battery is an electrochemical device with the ability to store chemical energy within an enclosed system while being able to convert energy to electricity on demand. Chemical energy is stored within the bonds of reactants (cathode, anode and electrolyte) in an electrochemical cell in its charged state. Upon discharge, redox reactions take place between electrolyte ions in solution and two solid electrodes (a more positive cathode and more negative anode) in a classical battery setup (Figure 1.3.1). The redox reaction is stimulated by the application of an onset potential across the two electrodes and in doing so, electrons are liberated to flow in an external electrical circuit.

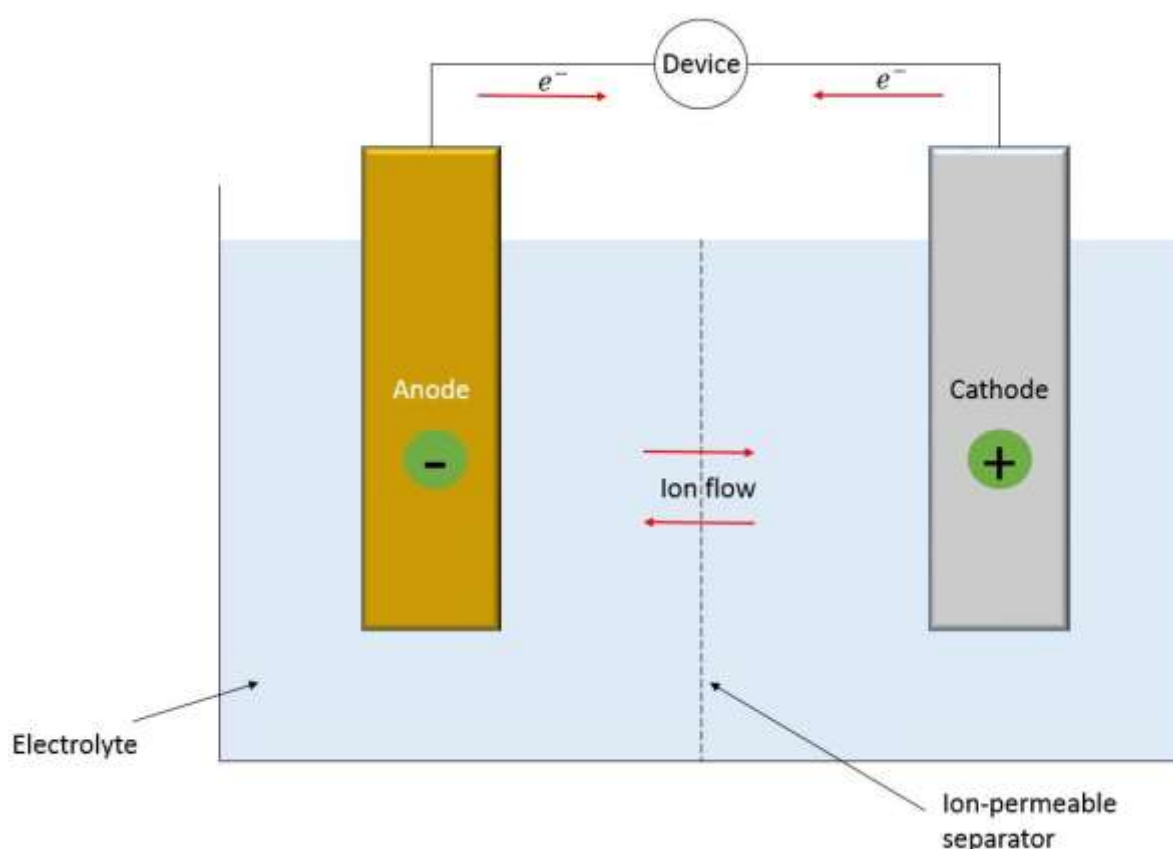


**Figure 1.3.1: Basic electrochemical battery setup.**

A battery can be classed as primary if it is non-rechargeable or secondary if rechargeable, and this depends on the nature of the materials used. A battery can be recharged if the redox reactions involved are reversible to some extent. Both primary and secondary batteries have had huge commercial success as energy sources for low-power electrical devices and efforts are still actively being made by research institutes worldwide to improve battery commercialization. To do this,

developers concentrate on four critical aspects of battery assembly, which are cost, performance, reliability and appearance.<sup>23</sup> While the factor of cost simply calls for the adoption of readily available, earth-abundant materials in battery components, factors such as performance and reliability are much more challenging and require detailed studies into advanced material processing and compatibility of battery components. Battery performance is the most pressing factor in that more progress is necessary to push batteries towards the growing demand of volumetric and gravimetric capacity into the fields of ‘alternative’ and ‘sustainable’ energy solutions, in the face of an imminent global energy crisis.

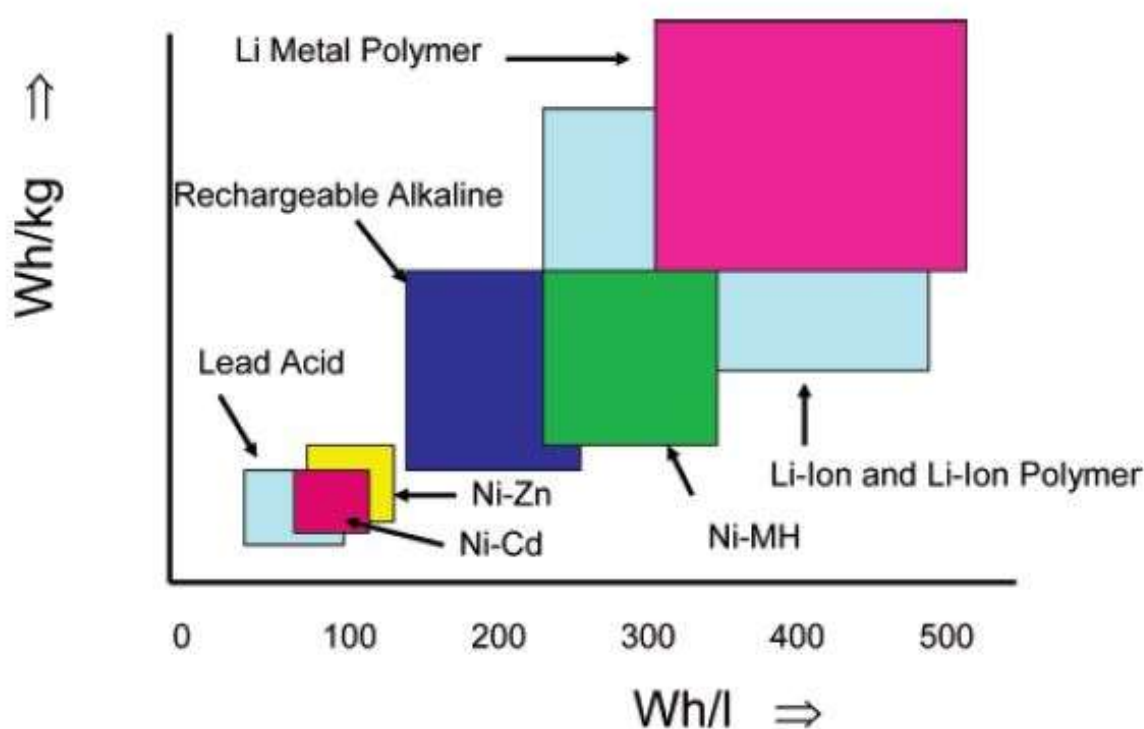
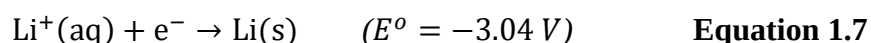


*Figure 1.3.2: Volumetric and gravimetric capacity limits for common secondary battery designs (reproduced with permission, Copyright 2004, American Chemical Society).<sup>23</sup>*

Commercially, the most successful rechargeable battery design to date has been the Lead-Acid battery.<sup>45</sup> In this design, metallic Pb at the anode is oxidised during discharge and combines with  $\text{SO}_4^{2-}$  in the electrolyte (sulphuric acid solution) to form a  $\text{PbSO}_4$  precipitate at the electrode-electrolyte interface, which dissolves again when the system is recharged leaving behind metallic Pb deposited on the surface. Despite their moderate energy density (Figure 1.3.2) and cycle life (50 –

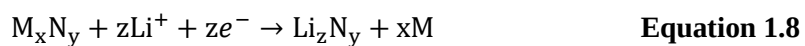
500 cycles), commercial success for these batteries was realised due to their affordability of production, high rate capability, durability in challenging conditions and a well-established recycling system of the active materials.<sup>23</sup> However, in order to push battery design for higher energy applications, as is the apparent global requirement, an alternative approach to battery assembly is necessary. Looking at Figure 1.3.2 the most promising designs are those based on lithium ion systems.<sup>46, 47</sup> Lithium Ion Batteries (LIBs) are designed such that upon charging, lithium atoms located in the cathode are oxidized and  $\text{Li}^+$  ions dissolve into the electrolyte solution. These ions shuttle between electrodes during charge-discharge cycles. There are a number of key factors which allow lithium-based systems to exhibit impressive capacity. Firstly,  $\text{Li}^+$  has a standard reduction potential of -3.04 V, the lowest of any element which allows the overall cell potential to be maximised to this extent.



Secondly, lithium is the third lightest element. This favours the storage mechanism when  $\text{Li}^+$  ions are taken up by the foreign anode material in the charged state. Another factor is the monovalent state of lithium in its ionised form. This monovalency improves ionic diffusion within solid electrodes, which is generally a limiting factor in electrochemical energy storage systems.

The extent to which a LIB can perform depends heavily on the choice of anode, cathode and electrolyte components and their compatibility. When choosing an appropriate electrolyte, one must consider how it can facilitate cell reactions and shuttle ions from anode to cathode, as well as its stability at working cell potentials. Aqueous electrolytes often consist of salts of strong acids or bases ( $\text{H}_2\text{SO}_4$  in common lead acid batteries), can demonstrate good ionic conductivity compared to non-aqueous ones but are limited in stability because of the relatively low potential at which water hydrolyses occurs ( $\approx 2 \text{ V}$ , including kinetic effects). Non-aqueous electrolytes use organic solvents which decompose at higher potentials, allowing for a higher energy electrochemical cell. Organic solvents with high ionic conductivity are generally more viscous which can have effects on the cells power, so combinations are often used to maximise the performance.<sup>48</sup>

In contrast to the relatively well-established nature of electrolytes, electrode materials have been the matter of much research, due to the huge potential for improvement on conventional battery design in aspects like specific capacity and cycle life using new technologies based around nanocomposites as well as the implementation of more novel nanomaterials.<sup>47, 49</sup> In research, anodes and cathodes are generally studied separately and optimized against some counter electrode. Examples of good counter electrodes in LIBs are graphite (anode) and pure lithium metal (cathode). Upon discharge, the anode is said to be the  $\text{Li}^+$  source while the cathode is the  $\text{Li}^+$  sink. The electrode materials in lithium batteries are required to be redox active, reversibly reactive with lithium, conductive and also affordable. High-performance materials have additional requirements of having high capacity to store lithium (i.e. good lithium-host atom ratio), rapid lithium insertion-removal capability (for high power applications) and high (low) operating voltage for the cathode (anode). Electrode materials can be classified in terms of how they store foreign atoms. They are generally classed as intercalation, alloying and conversion materials.<sup>50</sup> Intercalation-type materials have layered structures with interlayer spacing capable of storing foreign atoms or molecules. In doing so, the host material is not chemically modified but may ‘swell’ or ‘contract’ in the direction perpendicular to the basal planes in response to intercalation. Conversion materials and alloying materials are similar in that they store energy by forming intermediate intermetallic compounds. Conversion materials consist mostly of transition metal oxides, phosphides, sulphides, and nitrides with a charging mechanism outlined in Equation 1.8 below, where M is a transition metal and N is O, S, P or N.



The pure metal product from the equation then acts as an alloying material with similar qualities to elemental alloying materials like Si, Ge, etc. Conversion materials suffer from volume expansion and irreversible capacity loss.

Considering first cathode options, transition metal oxides account for the most promising candidates. Commercially, the most significant material to date has been  $\text{LiCoO}_2$  (and others like it),

with a reasonable theoretical capacity of  $274 \text{ mAhg}^{-1}$  and high operating voltage ( $\approx 3.8 \text{ V}$ ) compared to other layered materials, and also good stability (low self-discharge) and cycle life, making it an attractive option for commercial applications, despite the ability of other alloying/conversion type materials such as transition metal chalcogenides/halides to store much more energy. Such conversion type materials often suffer from poor conductivity and irreversible capacity loss due to extreme swelling in response to lithium insertion.

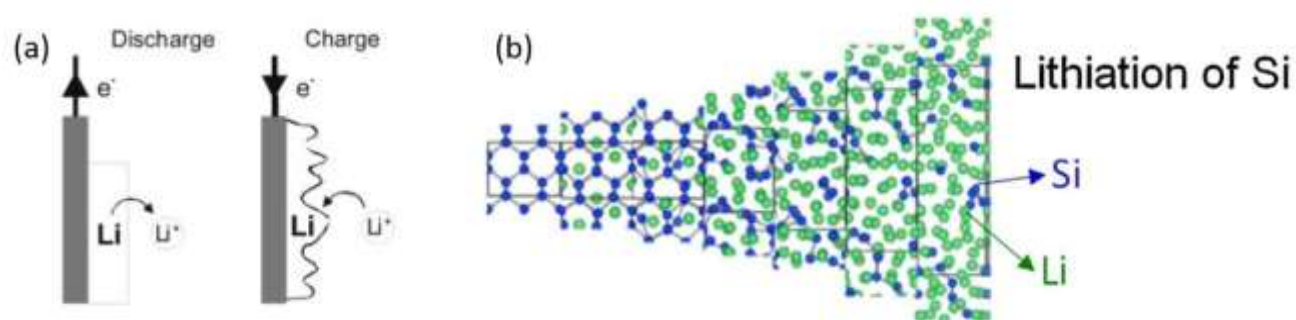
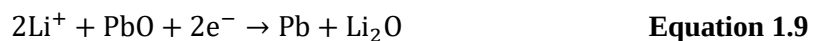


**Figure 1.3.3:** (a) Charge-discharge mechanism of a pure lithium anode LIB (reprinted with permission from Winter et al.<sup>23</sup>. Copyright 2004 American Chemical Society) and (b) first cycle lithiation of pure silicon anode, and subsequent crystal-swelling and fracture (reprinted with permission from Chan et al.<sup>51</sup>. Copyright 2012 American Chemical Society).

Choosing an appropriate anode material for next generation battery capabilities poses many of the same problems as in cathode studies, with promising conversion materials being hindered by issues like capacity loss and poor cycle life. Although pure lithium may seem the most sensible anode material for a high capacity LIB, there is one key feature of such a design which prevents it from having any commercial potential. That is, the growth of dendrites when the battery is repeatedly recharged (and discharged). Figure 1.3.3 shows graphically how  $\text{Li}^+$  ions fall into solution after being oxidised when the cell is discharged and how the ions re-deposit on the surface as dendrites (branch-like crystal growth) when it is re-charged. Lithium dendrites are extremely dangerous in electrochemical cells because they can pierce the separator and cause the cell to become shorted. This in turn can lead to a dangerously high current passing across the cell. So, alternative anode materials are required. Graphite is a prime example of a layered anode material with promising  $\text{Li}^+$  ion storage properties, which include low working potential (lithiation at 0.07, 0.10 and 0.19 V) and a good cycle life, owing to the robust host structure which resists fracture upon cycling of  $\text{Li}^+$  ion in

and out of interlayer spaces.<sup>52</sup> However, graphite can only host one Li<sup>+</sup> ion per six host carbon atoms, resulting in a low theoretical capacity of 372 mAhg<sup>-1</sup> (compared to that of pure lithium, 3860 mAhg<sup>-1</sup>). Li<sup>+</sup> ions also suffer from slow diffusion in graphite which impedes its power capabilities. Alloying materials such as silicon and germanium can demonstrate exceptional capacities (4200 mAhg<sup>-1</sup> and 1623 mAhg<sup>-1</sup> respectively) compared to graphite but suffer from poor cycle life. Alloying materials store charge by forming intermetallic compounds with lithium metal with the capacity being governed by the lithium to host atom ratio (Li<sub>22</sub>Si<sub>5</sub> and Li<sub>22</sub>Ge<sub>5</sub> are the limits for silicon and germanium). Most alloying material swell on first charge-discharge cycle to the point of fracture (Figure 1.3.3 b) and in doing so suffer huge initial capacity loss and subsequent capacity fade with cycling. Lead (II) oxide (PbO) is a layered polymorph and a good example of a high capacity conversion type anode material. PbO can be synthesized as the orthorhombic mineral ‘massicot’ or the tetragonal ‘litharge’ form. As a conversion type material, PbO undergoes reduction from Pb(II) to Pb(0), as shown in Equation 1.9, upon reaching its activation potential with Li<sup>+</sup>. From there, Pb forms various alloys with lithium, and in doing so stores energy electrochemically.



Improved mechanical stability for materials like PbO can be achieved in theory using simple processing techniques such as dimension reduction and composite formation, among others. Dimension reduction refers to the method of downsizing particles to the nanoscale where they are more promising for high energy and high-power applications, owed to physical properties such as high surface area, low diffusion paths into the nanoparticles and high intrinsic conductivities. Also, nanoparticles can show improved mechanical stability compared to their bulk counterparts because they experience less stress when swollen. Composite formation refers to the introduction of some other material within the electrode with desirable properties which can improve the electrodes overall performance. Carbon allotropes such as graphene and carbon nanotubes (CNTs) are frequently used as composite materials as they can provide mechanical support and high conductivity and connectivity within an anode or cathode matrix. If nanotechnology can be used to rectify the issue of poor cycle life in conversion type electrode materials it may be possible to fully utilize their

exceptional capacity capabilities in practical rechargeable systems. Chapter 5 will build on such principles applied to the highly promising PbO anode materials.

At present, the future of LIBs as potential next generation batteries relies heavily on the ability of research to come up with new materials and technologies which can push the energy and power densities to the degree of ‘next generation’ energy storage (i.e. to compete with combustion engines and other novel systems such as fuel cells).<sup>5, 53</sup> The majority of LIB technologies currently being studied are sensitive systems which are affected by things like over charging/discharging and over cycling and cannot be utilized for large-scale commercialization for those reasons.

## **1.4 Aims and Objectives**

Broadly speaking, the goals for this work are tailored towards the development and implementation of novel approaches to material processing, specifically concerning layered nanomaterials with applications in energy systems, such that the intrinsic capabilities can be improved upon and the specific performance considered ‘optimized’. With that, the most heavily weighted consideration in this work are sustainability, reproducibility, and industrial compatibility.

The world of electrochemical applications is broad and diverse. LIBs and alkaline water electrolyzers represent two distinct examples, sharing only fundamental similarities. It is for this reason that layered nanomaterials (namely, NiFe LDH and PbO) are considered for their energy transfer and energy storage properties, respectively. With that, the work in this thesis can highlight the broad applicability of the simple processing techniques which are proposed here for optimizing cell performance. For this research, the specific objectives involve post-synthesis particle size treatment as well as composite system integration, in an attempt to realize improved performance with minimal additional input in terms of cost or time concerns.

In order to address industrial compatibility, prepared devices will be tested in a practical, relatively long-term capacity. With that, the stability of the device components in the active environment are questioned. Particularly in the case of NiFe LDH OER catalysts in alkaline media,

the degradation mechanism of the active component will be attempted to be elucidated with the goal of potentially rectifying and improving the chances of fully realizing the material's performance. In essence, I believe the materials in question are examples of important oxide and hydroxide families, in terms of potential for sustainable energy solutions, and the low-cost improvement of their electrochemical performance after synthesis must be an invaluable consideration.

## 2 Experimental Techniques

Characterization techniques were chosen for this project such that relevant and conclusive information could be drawn in relation to the as-synthesized NiFe LDH and PbO materials as well as the processed material after post-synthesis treatment, and their composites. The synthesized materials were characterized for properties which are important for applications in electrochemistry. Namely, crystallinity, morphology and chemical composition. From an electrochemistry standpoint, the materials were tested for their electrochemical properties using techniques such as voltammetry, chronopotentiometry and charge-discharge characterization. These methods, plus a host spectroscopic, compositional and morphological characterization technique will be introduced in this section.

### 2.1 Electron Microscopy

Microscopy operates on the basis of an incident beam of light interacting with a sample, and measurement of the resulting signal. Conventional optical microscopy uses an electromagnetic wave beam and is limited in that there is an inverse proportionality between the resolution and wavelength ( $\lambda$ ) of the incident light. This derives from the Rayleigh criterion (for optical microscopes) which describes the minimum resolvable detail ( $\delta$ , inversely proportional to resolution) in terms of  $\lambda$ , as in Equation 2.1, where NA is the numerical aperture of the lens and describes the range of angles over which the system can accept scattered light.<sup>54, 55</sup>

$$\delta = \frac{0.61\lambda}{NA} \quad \text{Equation 2.1}$$

Considering visible light is limited to a fixed wavelength window (390 – 700 nm), there is an associated limit to the achievable resolution. This value lies between 200 and 400 nm. Beyond visible light, shorter wavelength electromagnetic radiation does not work as a microscope source because light at such wavelengths does not reflect or refract easily. Herein lies the necessity to

implement an alternative beam source for imaging on the nanometre scale. According to the de Broglie relation, an electron's (de Broglie) wavelength relates to energy E, as in Equation 2.2.<sup>56</sup>

$$\lambda = \frac{1.22}{\sqrt{E}} \quad \text{Equation 2.2}$$

In this criterion, an electron of energy 100 keV, for example, will have a wavelength of 4 pm, and in theory could image with resolution on a similar scale. However, in reality factors such as lens aberrations limit the resolution substantially.<sup>57</sup> Despite this, high energy electrons still represent a far superior resolution capability compared to light.

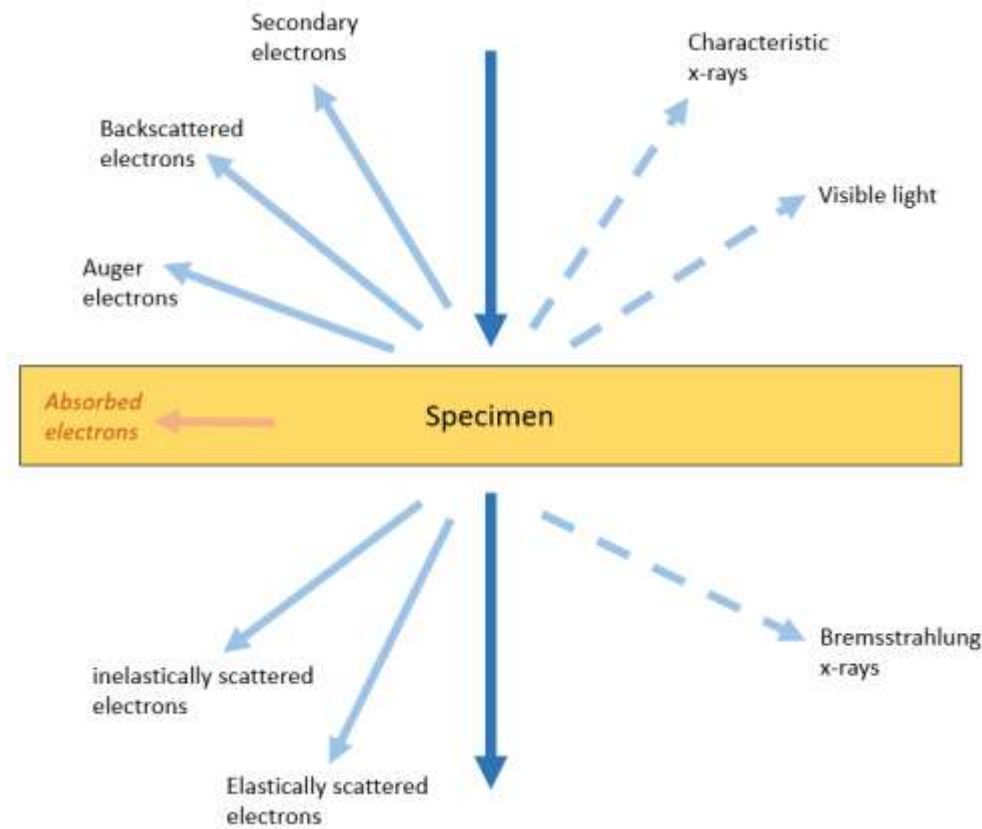


**Figure 2.1: Different signals from interaction of an electron beam with sample specimen.**

The range of signals in Figure 2.1 are indicative of the dynamic nature of electron microscopy. Depending on which electron-specimen interaction is probed, different information regarding the sample's morphological and compositional nature can be measured. Energy-dispersive x-ray spectroscopy (EDX) and selected area electron diffraction (SAED) are examples of analytical electron microscopy (AEM) techniques which can extract compositional and/or crystallographic

information, using inelasticity scattered electrons and x-rays, respectively. In terms of direct imaging (i.e. morphological information), electron microscopy can be divided into two primary techniques. Transmission electron microscopy (TEM), which probes elastically scattered ‘transmitted’ electrons, and scanning electron microscopy (SEM) which is concerned with the reflected signals (either elastically scattered or inelastically scattered secondary electrons) with respect to the specimen (Figure 2.1). Not only do the two techniques differ in what signals they measure, but also in how the electron probe is introduced to the sample surface. A static, parallel beam is used as a probe for conventional TEM (cTEM) while a convergent incident beam is rastered across the surface in SEM (Figure 2.2).

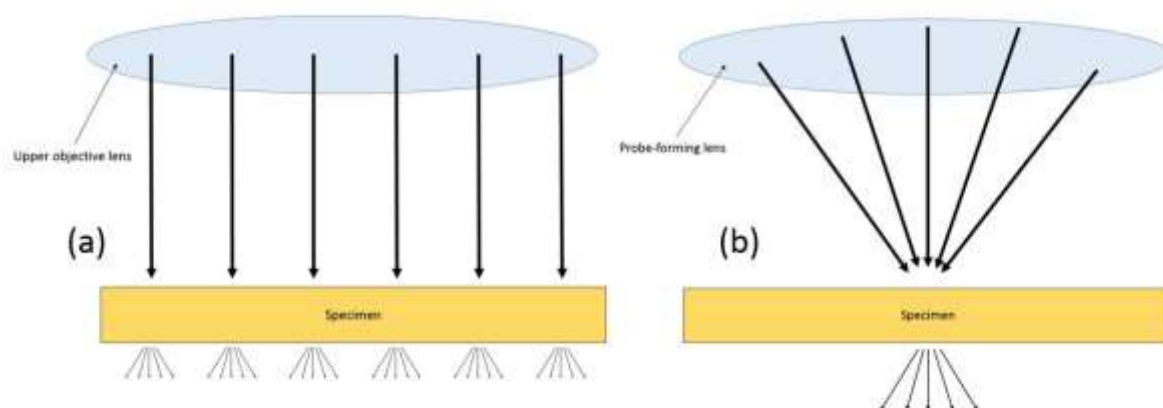


**Figure 2.2: (a) Parallel incident beam, typical of cTEM and (b) convergent incident beam for SEM/STEM.**

TEM can be an extremely dynamic analytical technique with a wide range of *in-situ* capabilities depending on the specific microscope in question. Some common ‘modes’ of image acquisition include high-resolution TEM (HRTEM), scanning TEM (STEM) and high-angle annular dark field (HAADF) STEM with various capabilities and advantages in each case. The mode of choice very much depends on the nature of sample in question and what information is desired. For example, if one wanted to acquire spatially resolved crystallographic data via SAED acquisition, STEM imaging is the appropriate mode. One may consider STEM to be the mode which marries the functions of conventional TEM and SEM imaging as it can allow for high resolution to the extent of atomic scale imaging in some cases while the beam can also be rastered across the sample surface,

choosing particular sites of interest where further analytical measurements can be applied. The ability to move across the surface is possible because of the beam configuration. Instead of a parallel beam source as in the conventional case, with STEM an objective lens situated before the sample produces a convergent beam whose spot, or ‘probe’, focuses on a point on the surface and whose position can be rastered and controlled (Figure 2.2). Rastering allows for spatially resolved imaging while precise position control allows for a high spatial selectivity for carrying out further analysis.<sup>58</sup>

Additionally, dark-field imaging can be considered as a method of achieving z-contrast in low z (thin) samples as well as phase clarity for crystalline specimens. Dark-field imaging is a diffraction-specific mode of imaging which utilizes those scattered electrons diffracted into annular positions around the non-scattered ‘bright-field’ electrons (Figure 2.3). In order to avoid inelastically scattered electron contributions in the dark-field signal, the dark-field signal is normalized with (divided by) the inelastic signal acquired via electron energy loss spectroscopy (EELS). The problem here is that there is a fundamental limitation of EELS with low angle signals which can cause unclear results. For that reason, only high-angle scattered electrons are considered, hence the HAADF mode of STEM follows.<sup>59</sup>

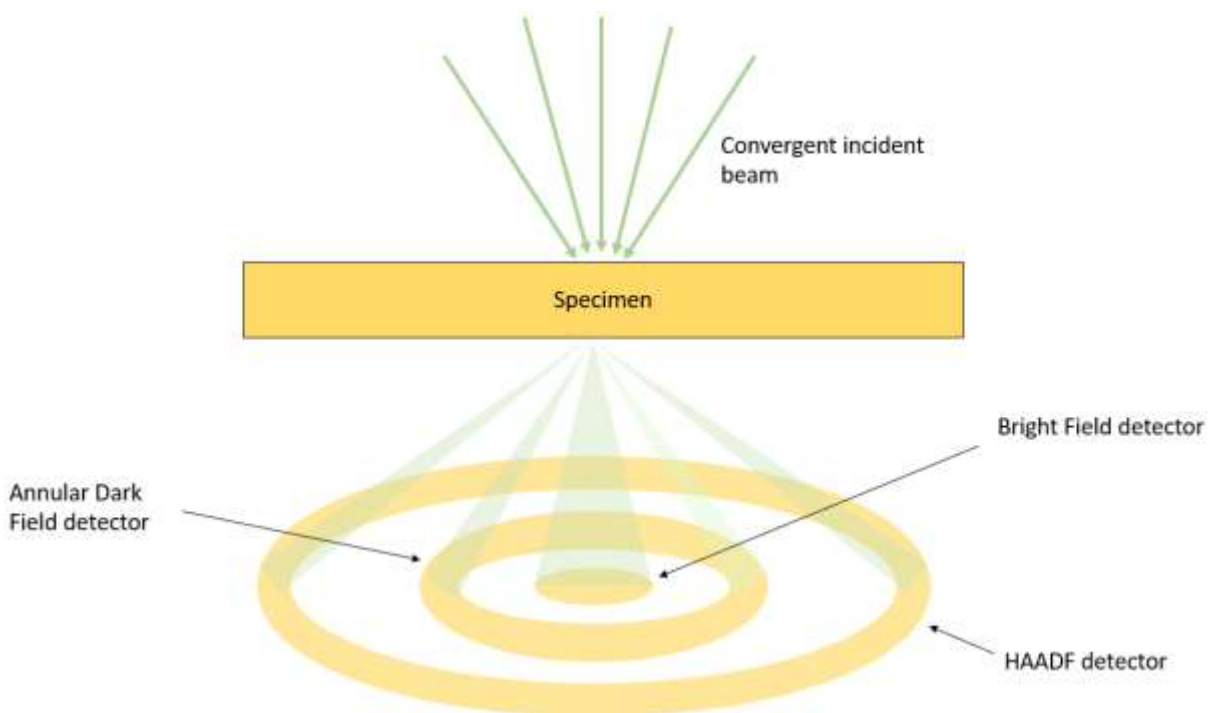


**Figure 2.3: Schematic representation of high and low angle signals in a STEM HAADF setup.**

In this work, SEM was carried out using Zeiss Ultra Plus field-emission microscope with a Gemini column and a secondary-electron detector, operating in accelerating voltage range 2–5 keV and TEM images were taken using an FEI Titan 80 – 300 kV FEG S/TEM microscope (operating at 300 kV accelerating voltage) and a JEOL 2100 LaB TEM (operating at 200 kV). Samples were prepared by drop casting onto a lacey carbon 200 mesh copper grid with approx. 97  $\mu\text{m}$  hole size (Ted Pella) unless otherwise specified.

## 2.2 Spectroscopy

Spectroscopy accounts for a wide variety of characterization techniques whereby some form of electromagnetic radiation is passed through a sample and the transmitted fraction of radiation (T) is measured for analysis. T depends on the extent to which the sample can absorb the incident light which itself depends on the energies involved. Depending on the wavelength of the incident light, spectroscopy can withhold information regarding a samples rotational, vibrational, electronic and first-ionization energies. Some of the most common spectroscopic techniques (and those utilized in the presented work) are infrared (IR), Raman, ultraviolet-visible (UV-Vis), energy dispersive x-ray (EDX) and x-ray photoelectron spectroscopy (XPS).

### Infrared Spectroscopy

Infrared (IR) light exists at a longer wavelength than both visible and ultraviolet light and as a result it has less associated energy ( $E=hc/\lambda$ ). The IR spectrum stretches from 780 nm for near-IR, up to 300  $\mu\text{m}$  in the far-IR region. The relatively low-energy radiation is not enough to stimulate an electronic transition within an atom or molecule but is enough to cause transitions in a molecules rotational or vibrational state. The vibrational frequency ( $\nu$ ) of a particular bond within a molecule can be determined by drawing comparison to a spring with spring constant  $k$  and using Hooke's law as in Equation 2.3, where  $\mu$  is the reduced mass of the two atoms in question.<sup>60</sup>

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

**Equation 2.3**

Any given molecule can have a number of vibrational modes, each of which describes unique movement of atoms relative to one another, either along or perpendicular to the bond direction. Nonlinear molecules with  $n$  atoms have  $3n-6$  vibrational modes while linear molecules will have  $3n-5$ . Vibrational energies at the molecular level are quantized, meaning they are limited to discrete energy levels. Only when the incident infrared light matches the transition energy between vibrational states (i.e.  $\Delta E = h\nu$ ) can the light be absorbed and produce a spectroscopic 'peak'. However, not all vibrational modes are IR 'active'. There is a requirement that there must be a change in dipole moment between two atoms when vibrating. This essentially means that symmetrical, nonpolar molecules are inactive in IR and most polar molecules are active.

Fourier Transform IR (FT-IR) differs from classical dispersive IR spectroscopy by how the beam wavelength is scanned. Instead of monochromatic light, here the beam contains an IR *spectrum* that's passed through a Michelson interferometer to produce an interferogram which is used to probe the sample. By mathematically performing a Fourier transform on the output interferogram, one can instantaneously produce an absorption spectrum for the material. FT-IR allows for rapid data acquisition of broad spectral frequencies with high sensitivity.<sup>61</sup> In this work, a Perkin Elmer Spectrum 100 FT-IR spectrometer was used to obtain FT-IR spectra in the range  $4000 - 550 \text{ cm}^{-1}$ .

## **Raman Spectroscopy**

While polar functional groups give rise to strong bands in IR spectroscopy, non-polar bands can still be characterized using an infrared source through Raman spectroscopy. Sir Chandrashekhara Venkata Raman won the Nobel Prize for Physics in 1930 for his discovery of the effect by which light incident on a sample can be scattered inelastically, without being absorbed. The inelastically scattered light accounts for a small fraction of the scattered photons and will have a frequency ( $\nu$ ) slightly above or below that of the incident beam. The 'shift' in energy of a given photon as a result is called as Stokes' shift if the photon has lost energy and Anti-Stokes' shift if the photon has gained energy.

$$\nu = \nu_{\text{incident}} - \nu_{\text{vibrational}}$$

**Equation 2.4**

As is the case with IR spectroscopy, the phenomenon here comes about as a result of light interacting with vibrational and rotational energy levels within the sample. This interaction is known today as the Raman Effect.

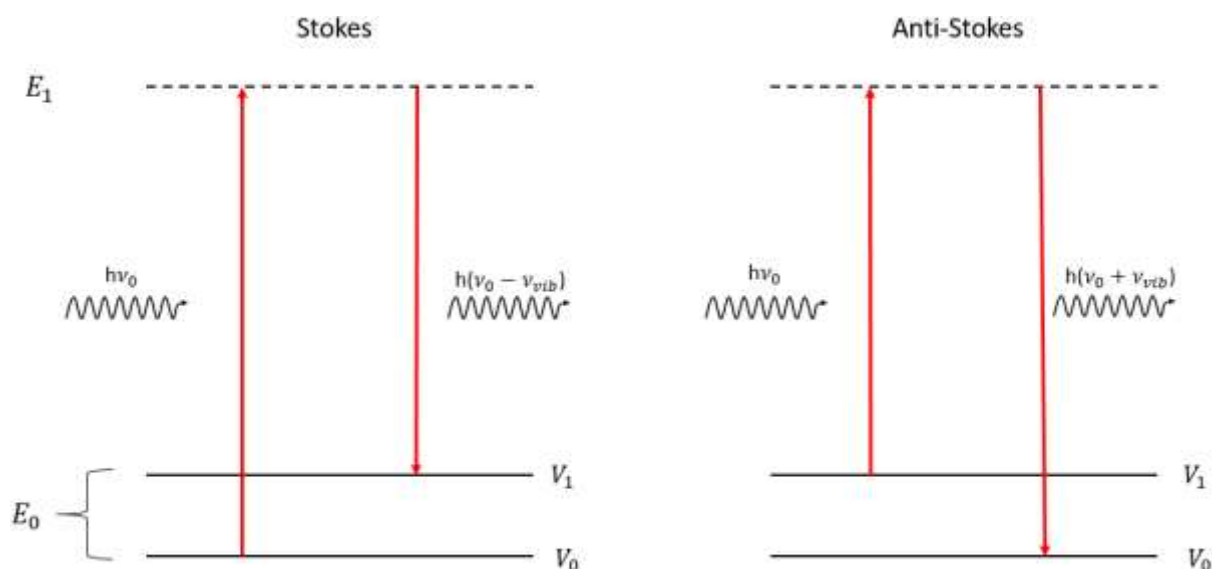


**Figure 2.4:** Schematic demonstration of the Stokes' and anti-Stokes' shift, stimulated by an incident IR photon with frequency  $\nu_0$ .

The one defining designation which separates Raman spectroscopy from classical IR spectroscopy is that there must be a change in the electric polarizability of the analyte molecule if it is to be Raman 'active'. The polarizability of a molecule ( $\alpha$ ) is the proportionality constant between its dipole moment ( $\mathbf{P}$ ) which is induced by some external electrical field ( $\mathbf{E}$ ), as in Equation 2.5. When the electric field is changed, the molecule will respond by changing its dipole moment (IR active) or polarizability (Raman active) and this is the key IR-Raman distinguishing factor. There is a rule of thumb that symmetric molecules are generally Raman active while asymmetric molecules are generally IR active.

$$\mathbf{P} = \alpha \mathbf{E}$$

**Equation 2.5**

The most important feature of Raman spectroscopy is its ability to compliment IR spectroscopy by characterizing non-polar molecules but additionally it exhibits a high degree of

specificity (making it an ideal tool for fingerprinting), compatibility with aqueous systems and also produces spectra with a generally high signal-to-noise ratio. In addition to conventional Raman techniques, more advanced methods of data acquisition have been developed. Resonant Raman Spectroscopy (RRS) operates by matching the wavelength of the incident laser with the electronic absorption of the molecule to achieve higher intensities of the Raman-active vibrations by as much as a factor of  $10^4$ . Surface Enhanced Raman Scattering (SERS) occurs when some adsorbate is added to a conventionally ‘rough’ surface and has the effect of enhancing Raman scattering by achieving surface plasmon resonance (and hence, exceptionally large electromagnetic field experienced by the surface molecules) and a charge transfer complex between surface molecule and adsorbate.<sup>62</sup> Raman spectra for this work were acquired using a WITec Alpha 300R with a 532 nm excitation source.

### Ultraviolet-Visible Spectroscopy

UV-Vis spectroscopy operates in the wavelength range 160 – 780 nm. In this range, photon energy is such that electronic transitions can occur upon photon absorption. The most probable transition within a molecule's electronic structure is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Figure 2.5 indicates what transitions are possible. Here  $\sigma$  and  $\pi$  are bonding molecular orbitals (MOs),  $n$  is a non-bonding MO and  $\sigma^*$  and  $\pi^*$  are anti-bonding orbitals (Figure 2.5).

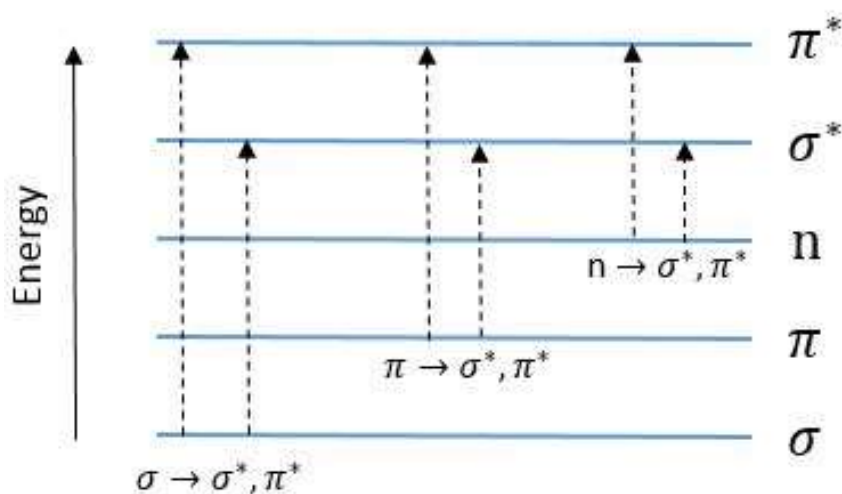


Figure 2.5: Energy-level diagram indicating the possible electronic transitions upon photon absorption.

The Beer-Lambert equation (Equation 2.6) is very important for quantitative analysis using UV-Vis spectroscopy.<sup>63</sup> It relates the samples ‘absorbance’  $A$ , to its concentration  $c$  (and path length  $l$ ) with a proportionality constant  $\epsilon$ , known as the extinction coefficient.  $\epsilon$  is a value specific to a given compound and describes how strongly light is absorbed at a given wavelength.

$$A = \epsilon lc \quad \text{Equation 2.6}$$

In this work, UV-Vis measurements were carried out using a Biochrom Libra S22 UV/Vis spectrophotometer at 200 – 900 nm.

### Energy Dispersive X-Ray Spectroscopy

EDX operates by observing the outcome of an inelastic interaction between electron and sample.<sup>64</sup> Looking at Figure 2.6 (b), more than one signal can be detected from such an interaction. Firstly, there is the inelastically scattered incident electron (red), whose detection is the basis of EELS measurements. Secondly, there is a secondary electron signal (blue) resulting from an electron being omitted from a core shell due to energy exchange from the inelastic interaction. Secondary electrons can be used in SEM imaging. In response to electron ejection from the core shell, an electron from a higher energy level can fill its place and in doing so, undergo an energetically unique transition accompanied by the release of a characteristic x-ray. This electromagnetic signal is used in EDX and indirectly in Auger electron spectroscopy (the x-ray energy being transferred in this instance to more loosely bound ‘Auger’ electrons, causing them to be emitted). Both EELS and EDX can be used to

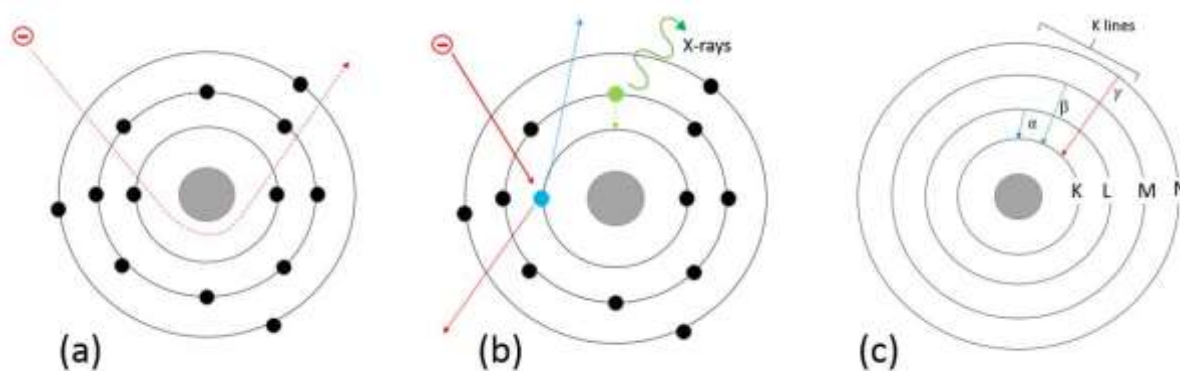


**Figure 2.6:** (a) Elastically and (b) inelastically scattered electrons, with release of characteristic x-rays (and secondary electrons). (c) K line transitions typical of characteristic x-ray emission.

extract similar information but complement each other well. Both can help obtain atomic composition but EELS works best for low atomic number atoms and EDX is more sensitive at higher atomic numbers. The way in which atoms can be characterized based on x-ray emission is described by Moseley's equation (Equation 2.7), which relates the x-rays energy (E) to the host atoms atomic number (Z) with some constants ( $c_1$ ,  $c_2$ ) which are specific to the emission lines of the transition (Figure 2.6 c).<sup>65</sup>

$$E = c_1(Z - c_2)^2 \quad \text{Equation 2.7}$$

'Characteristic' x-rays, used for EDX, differ from Bremsstrahlung x-rays in that they come from electron transitions to the K shell, making up the K lines (Figure 2.5 c). Bremsstrahlung x-rays are associated with transitions whose final energy level is above K (i.e L, M, N etc.). EDX is an incredibly useful way to gain compositional information using the same (convergent) electron beam that's used for imaging in SEM or STEM systems. Additionally, it is possible to prepare spatially resolved EDX maps over a defined area by rastering the convergent beam in SEM or STEM. In this work, EDX was carried out using the Zeiss Ultra Plus field-emission SEM at 15 keV and an FEI Titan 80 – 300 kV FEG S/TEM instrument. EDX data was analysed using Bruker-ESPRIT 2.0 software.

### **X-Ray Photoelectron Spectroscopy**

Targeting core-level electrons, once considered inaccessible, is the basis of XPS analysis, where an x-ray probe is used to induce the emission of photoelectrons from within the core shells (i.e. K shell, Figure 2.6 c) of a coordinated atom. Given the limited mean free path of electrons in solid state environments, this is primarily employed as a surface technique, giving compositional information in terms of elements present as well as their chemical state. Photoelectrons may be emitted from a sample after radiation exhibiting a range of kinetic energies (KE) which can be used to directly measure binding energies (BE) from surface species (< 10  $\mu\text{m}$  depth) according to Equation 2.8, in which  $h\nu$  represent the incident x-rays photon energy and  $\phi_s$  is the spectrometer work function.<sup>66</sup>

$$KE = h\nu - BE - \phi_s \quad \text{Equation 2.8}$$

X-rays are generally sourced for XPS analysis from Mg or Al K $\alpha$  lines via electron bombardment of the metals as in Figure 2.6 (b). Once the incident monochromatic x-ray collides inelastically with core levels, the resulting photoelectrons travel to a detector where the KEs (and hence BEs) are measured. The energy readings can provide a host of information regarding the atoms of origin, including their oxidation state and chemical environment.<sup>67</sup> For this work an Omnicron XPS model was used with a monochromatic Al K $\alpha$  source.

## 2.3 Crystallographic Characterization

In 1913, W. L. Bragg discovered that a unique interaction occurs when an x-ray is incident on the surface of a crystalline solid. He noticed that at certain angles and wavelengths, there are sharp peaks in the scattered signal.<sup>68, 69</sup> This phenomenon was concluded to be a result of x-rays ‘reflecting’ from various lattice planes of the crystal structure. Within a crystal there exist a number of so-called high symmetry directions, each perpendicular to a set of parallel lattice planes. Each plane consists of regularly ordered ions and are separated by a distance  $d$ . X-rays are unique in this circumstance as they have wavelengths comparable to the general inter planar distance of crystal structures (Cu K $\alpha$ : 1.54 Å, Mo K $\alpha$ : 0.71 Å) and so are capable of probing these features by diffraction. Two important conditions must be upheld in order to observe diffraction peaks. Firstly, the x-rays should reflect off the crystal plane specularly so that the incident and diffracted beam have the same angle ( $\theta$ ) with respect to the crystal plane. Secondly, the reflected beams from successive planes must interfere constructively (Figure 2.7). The Bragg equation (Equation 2.9) describes the angle ( $\theta$ ) and wavelength ( $\lambda$ ) which are necessary to diffract from a group of planes with separation  $d$  with constructive interference.

$$n\lambda = 2d \sin \theta \quad \text{Equation 2.9}$$

In the equation,  $n$  refers to the diffraction ‘order’. This can be understood by looking at Figure 2.6 which shows two parallel x-ray beams diffracting off parallel lattice planes. The difference

in path length of the two diffracted beams must be some integer (n) multiple of the wavelength in order for complete constructive interference of scattered beams to be observed.

There are two principle methods of experimentally taking XRD patterns from a sample crystal. Namely, single-crystalline and powder XRD. As the name suggests, the single-crystal method uses one bulk crystal which is rotated through various angles about some fixed axis with respect to a monochromatic x-ray source, using an instrument called a goniometer.<sup>70</sup> The scattered signal is the averaged over all crystal orientations and in this way, any diffraction planes will be revealed by the presence of some peaks in the diffractogram. Alternatively, the powder method utilizes the random orientation of crystal grains within a powder to average over all crystallographic directions without the necessity of sample rotation. Powder XRD was carried out in the presented work using a Bruker Advance Powder X-ray diffractometer with a molybdenum K $\alpha$  and copper K $\alpha$  emission sources in the Bragg-Brentano configuration.

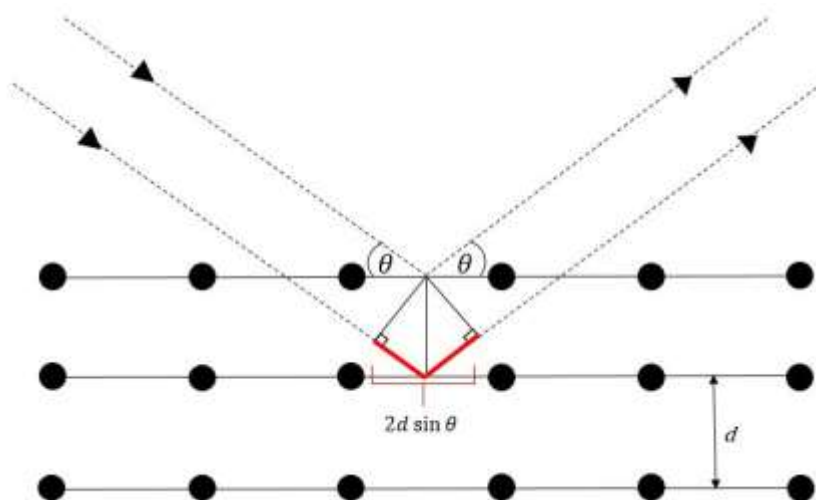


**Figure 2.7: Schematic representation of the Bragg condition.**

Selected area electron diffraction (SAED) is another technique based on diffraction for crystallographic characterization. This takes diffracted electron signals from a local area of the sample and uses a simplified version of Bragg's equation ( $n\lambda = 2d\theta$ , for smaller electron wavelengths) to produce crystallographic information. In this case electrons are used as a source and can be operated within a TEM setup.<sup>57</sup> An FEI Titan microscope was used in the case of this work.

## 2.4 Compositional Characterization

Thermogravimetric analysis (TGA) is a technique which measures the mass of a sample as a function of temperature. The sample is heated, and the temperature is ramped up at a constant rate while mass is simultaneously monitored. Information gathered with this technique includes thermal stability of the components within the sample as well as weight percentage of volatiles. This is important for determining precise chemical quantitative formulae.<sup>71</sup> For this project, TGA measurements were carried out using Perkin Elmer Pyris. Approximately 10 mg of powder was heated at a rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  and purged in air at  $20\text{ ml}\cdot\text{min}^{-1}$ .

Atomic absorption spectroscopy (AAS) gives both qualitative and quantitative information regarding the composition of a sample. Each element absorbs a specific wavelength of light, which gives qualitative information about the sample composition. At the same time, the amount of the light absorbed correspond to this element's concentration in a sample.<sup>72</sup> The metals content was measured with a Varian 55 Atomic Absorption spectrometer. The exact Ni and Fe concentration were determined by comparison with reference standards.

Inductively coupled plasma mass spectrometry (ICP-MS) is another technique capable of elemental labelling with a higher degree of sensitivity than AAS. It uses a plasma (ionized gas) which is formed by inductive heating of some starting component, argon in this case, to ionize the sample in question through high energy collisions.<sup>73</sup> The ions are subsequently captured by a carrier gas, separated from the plasma and the resulting ionized sample is then analysed on the basis of mass-spectrometry in this case, but is often alternatively examined through optical emission spectrometry (ICP-OES). Analyses were performed using a Thermo Scientific iCAP-Qc ICP-MS and Elemental Scientific (ESI) SC-2 DX autosampler equipped with a microFAST injection system. Samples were mixed with a multielement internal standard ( $^6\text{Li}$ , Rh, Re, Bi,  $^{235}\text{U}$ ) to monitor internal drift to a nominal gravimetric dilution factor of 2, 10 or 100. Calibration and external drift corrections were performed using a 0 – 500 ppb dilution series of an AcuStandard multielement solution containing Si, Al, Ti, Mg, Mn, Fe, Ca, Na, K and P. The experimental set-up and measurement followed that of

Eggins et al.<sup>74</sup> ICP-MS measurements were carried out by Cora McKenna in the Trinity Technology and Enterprise Centre (TTEC) in TCD.

## 2.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) measures the interaction between an extremely sharp tip (probe) and a sample surface to obtain an atomically precise height profile.<sup>75</sup> The oldest method of AFM is contact mode, where the tip (usually silicon or silicon nitride) is ‘dragged’ across a surface in a rastering motion. The atoms in the tip and sample interact electrostatically forcing the tip to fluctuate perpendicular to the surface in response to the sample’s height profile. The tip is attached to a sensitive piezoelectric cantilever (with low spring constant,  $k$ ) such that the tip’s movement is accurately monitored. The movement is measured by a laser beam which is being reflected from the surface of the cantilever (Figure 2.8). The subtle bending of the cantilever is interpreted by an equivalent change in the reflected laser signal.

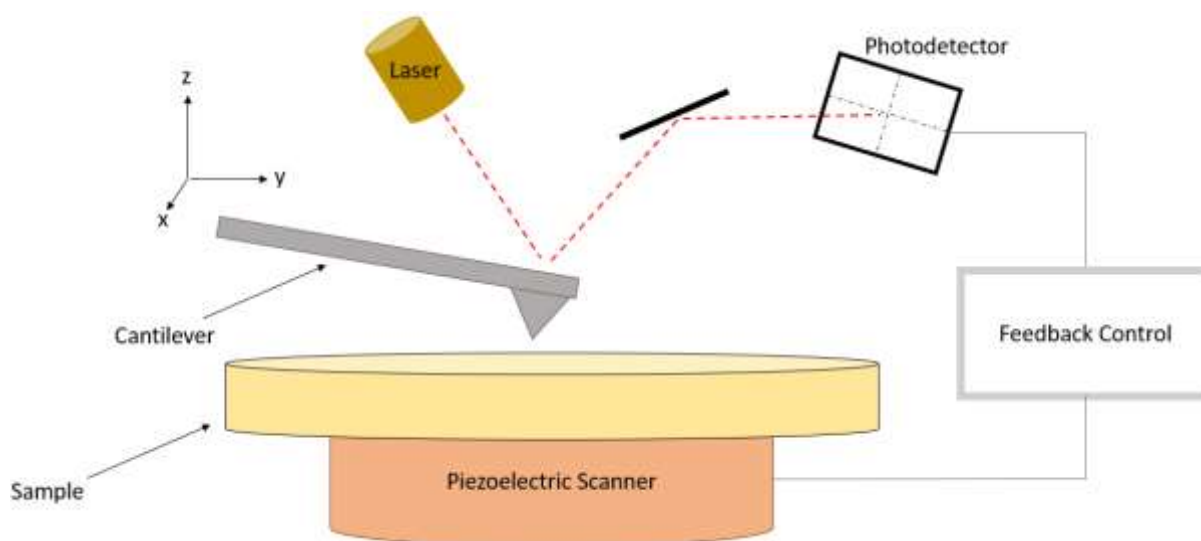


**Figure 2.8: Schematic representation of AFM operation.**

A significant problem with contact mode AFM is the damage caused to both tip and sample during measurements. To avoid this, an alternative non-contact mode exists. In this setup, the tip oscillates at its resonant frequency at some distance from the sample surface. Without contact, long range electrostatic interactions (e.g. van der Waals) can still be felt from the sample surface, enough

to damp the tip frequency. An external piezoelectric force-transducer then alters the tip-sample distance in response, so that the resonant frequency of the tip remains unchanged. The Z-contrast of the cantilever is monitored using the same laser system as for contact mode (Figure 2.8). One drawback here compared to contact mode AFM is the high sensitivity to liquid molecules which may adsorb to the sample surface in ambient conditions. Unlike with contact mode where the tip can penetrate such molecules, non-contact mode will be forced to image the liquid layer instead of the sample, meaning ambient conditions will not suffice. For this work, intermittent contact (or tapping) mode is used. This technique is essentially a hybrid, where the applied tip oscillation has a large enough amplitude to pass through the surface's attractive proximity to the region of repulsion. A force-transducer is also used in tapping mode to maintain a constant resonance frequency and hence, produce a height profile with sub-nanometre resolution. Tapping mode is generally considered the most useful AFM technique for measurements in ambient conditions where there is a significant probability of liquid molecules depositing on the sample surface. In this case, tapping mode can 'penetrate' a liquid layer on the surface to achieve short-range interactions with the sample surface while not having to worry about the tip sticking to the surface, as may be the case with contact mode.

For this project, imaging was carried out using an Asylum Research MFP 3D microscope operating in tapping mode. Silicon tips were used with aluminium reflex coating, from supplier Budget Sensors. They have a resonant frequency of 300 kHz and a spring constant ( $k$ ) of  $40 \text{ N}\cdot\text{m}^{-1}$ . All measurements were taken in ambient conditions at scan rates between 1-2 Hz. Gwyddion software was used to process AFM data. All samples were prepared by drop casting on pristine silicon wafers and drying with argon.

## 2.6 Electrochemistry

An electrochemical process occurs when a redox reaction takes place and liberates electrons which can be 'collected' and supplied to an external circuit. Hence, there is a conversion here between chemical and electrical energy. In an electrochemical cell (e.g. battery, supercapacitor, electrolyser cell etc.) this redox reaction occurs at the interface between electrode and electrolyte

material (usually solid and liquid phase, respectively). In a basic electrochemical cell setup ions flow between anode and cathode via an ion-permeable separator while electrons flow in a circuit as a current source for some external device during cell discharge. When a material is being tested electrochemically, it is generally good practice to prepare a half-cell. That is, a cell where one active material (anode or cathode) is tested against a material with a well-known, intermediate potential so that the active materials performance can be accurately quantified. For example, when testing LIBs, it is useful to test half cells using pure lithium foil as a counter electrode. The electrode containing active material is generally referred to as the ‘working’ electrode.

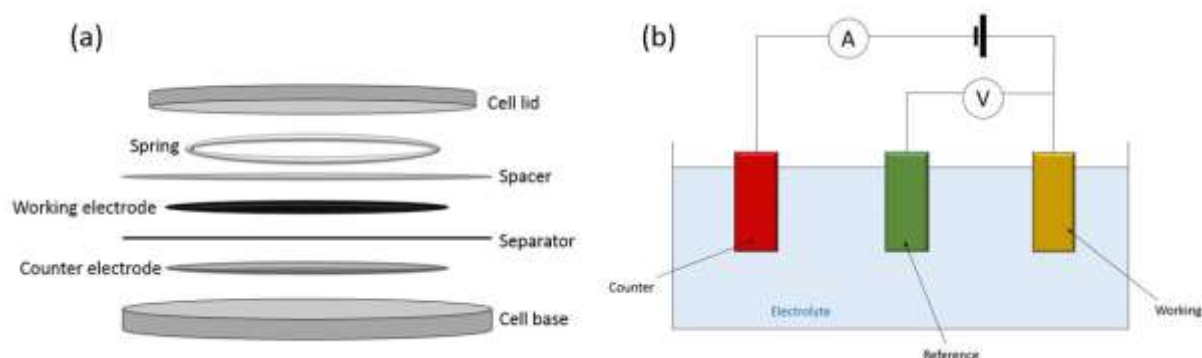


**Figure 2.9: (a) Coin cell components and (b) three-electrode electrochemical setup.**

Voltammetry is an electrochemical analysis technique in which the potential difference between working and counter electrode is varied while measuring the current which flows in response, due to redox reactions at electrode-electrolyte interface. There are two principle setups that are considered in this work when preparing electrochemical half-cells for this kind of testing. Firstly, there is a simple coin cell consisting of two electrodes (working and counter) separated by some electron-insulating separator (Figure 2.9 a). One important shortcoming of this setup is the difficulty in maintaining a constant potential at the counter electrode as it exchanges substantial amounts of current in response to redox reactions at the working electrode during voltammetry sweeps. The uncertain potential of the counter electrode makes it difficult to accurately know the cell voltage during sweeps and this is the reason for introducing an alternative setup, the three-electrode system. A three-electrode system contains an additional ‘reference’ electrode (Figure 2.9 b). A reference electrode has a well-defined reduction potential and has the sole purpose of acting as a reference with

which the potential of the working electrode can be accurately known. No current passes to or from the reference electrode. Within the three-electrode setup, a potential difference is applied between working and reference electrodes, while the resulting current is measured across the working and counter electrodes.

Voltammetry can be carried out in a number of ways depending on how the voltage is swept. The most common methods are linear sweep voltammetry (LV, sometimes LSV) and cyclic voltammetry (CV) while others include staircase and square wave voltammetry, all of which depend on the 'shape' of the voltage signal applied to the cell.<sup>76</sup> Data is presented by plotting applied voltage (x-axis) against cell current (y-axis). Such a graph is called a voltammogram. Voltammetry is generally used to characterize electrochemically active materials by observing characteristic oxidation or reduction peaks in the voltammogram. Additionally, by studying hysteresis effects in CVs it is possible to deduce information regarding the kinetics and hence operating limits of the cell in question. Galvanostatic Cycling with Potential Limits (GCPL) is an alternative method to voltammetry in battery testing whereby a constant current is applied across the sample cell and allowed to fully charge (and discharge) between defined potential limits. This is useful method to compliment CV or LV data as it is a more direct way to measure cell capacity using a simple conversion of Amperes to Amp-hours per gram ( $\text{Ah}\cdot\text{g}^{-1}$ , usually  $\text{mAh}\cdot\text{g}^{-1}$ ).

Additionally, there are a number of electrochemical techniques one would consider when testing devices beyond the scope of batteries and supercapacitors. In the field of OER electrocatalysis it is useful to examine the extended catalyst lifetime of active catalyst materials in a working cell using chronopotentiometry (CP) and chronoamperometry (CA). These methods essentially hold the cell at a defined cell current (potential) and measure their respective potential (current) in response, over some fixed time scale. All voltammograms were acquired out using a BioLogic VMP 300 while GCPL experiments were performed with a LANDt battery testing system CT2001 model. A Sentek Ag/AgCl single junction reference electrode was used for all three-electrode cells with a Pt rod counter in 1 M KOH solution.

### 3 NiFe LDH Platelet Size Control for Improved OER Electrocatalysis

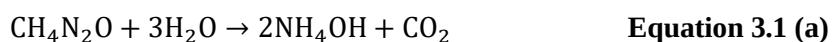
NiFe LDH is a layered, hydrotalcite-like bimetallic compound which exhibits impressive OER electrocatalytic properties compared to other similar multi metal compounds, owing largely to its high density of active sites and some intrinsic properties relating to the subtle electronic behaviour between nickel and iron in the octahedral coordinated crystals, as discussed briefly in section 1.2. Similar to the majority of materials in applied electrochemistry, the most impressive performance of NiFe LDH in literature is noted in composite systems. Composite materials made of NiFe LDH and various carbons, such as carbon nanotubes, graphene and graphene oxide, have been shown to reach overpotentials as low as 230 mV with impressive Tafel slopes as well as high, sustainable anode currents at low overpotentials.<sup>39, 77</sup> An understanding of the intrinsic catalytic properties within the raw NiFe LDH material is imperative in the scope of this study where the goal is to maximise the water-splitting performance.

From previous literature studies, it has been recognized that all or most of the catalytically active sites in LDHs and other platelet-like catalysts are located at the platelet edges rather than along basal planes. One such study carried out by Song *et al.*<sup>38</sup> explored the effect of exfoliation of NiFe LDH into single nanosheets on the OER catalysis. Exfoliation was achieved by swapping anionic intercalation species between LDH layers with less stable anions by etching, followed by sonication. The LDHs with less stable interlayer anions should exfoliate at relatively low sonic power. It was intuitively thought that increasing the electrochemical surface area (ECSA) of the material by exfoliation would enhance the electrochemical reaction kinetics and hence, the catalytic activity. While improvements in electrochemical performance are observed after exfoliation of NiFe LDH, it cannot be attributed to the increased ECSA as only a small change in ECSA was observed and could not account for the considerable changes in catalytic capabilities. Instead, the higher activity was deemed to be due to a higher density of edge sites exposed as the particles undergo downsizing simultaneously with exfoliation.

This suggests that particle size control (i.e. mean lateral platelet length,  $\langle L \rangle$ ) should allow for some control of the catalytic properties of the material by way of increased/decreased active site density within an electrode of given mass of material. This work will attempt to exploit this effect as acutely as possible. In addition, it is hoped that some understanding of the relationship between overpotential and particle size can be elucidated. In doing this, I attempt to move the research in this area a step closer to clarifying the nature of LDH activity in electrocatalysis in general and also present a facile, transferable processing route for platelet-like catalysts to fully optimize the potential they have as high-performance components in catalyst systems.

### 3.1 Synthesis of NiFe LDH Platelets

NiFe LDH was synthesized here using a wet chemistry method with the aid of a ‘capping agent’,<sup>78</sup> to produce hexagonal platelets with high crystallinity and purity as well as a regular morphology throughout.<sup>44</sup> There are a number of methods of LDH wet synthesis, one of the most common being homogeneous precipitation, where a precipitating agent ( $\text{OH}^-$ ) is produced *in-situ* during thermal decomposition of amides<sup>79</sup> such as urea (Equation 3.1 a) or amines such as hexamethyltetramine.<sup>80</sup>



This causes a slow pH increase upon dissolution of the resulting ammonium hydroxide (Equation 3.1 b) and, in the presence of divalent ( $\text{M}^{2+}$ ) and trivalent ( $\text{M}^{3+}$ ) metal ions,  $\text{M}(\text{OH})_3$  starts precipitating until the  $\text{M}^{3+}$  species is completely consumed, at which point  $\text{M}^{2+}$  is incorporated in the structure via a dissolution/precipitation mechanism, resulting in the formation of stable  $\text{M}^{2+}\text{-M}^{3+}$  LDH. However, the dissolution/precipitation process takes place only for an amphoteric  $\text{M}^{3+}$  species (like  $\text{Al}^{3+}$ ) because the changing  $\text{OH}^-$  concentration within the reaction solution will be the stimulus for dissolving the reaction intermediates which is the first chemical step of the coprecipitation reaction mechanism. For a species like  $\text{Fe}^{3+}$ , this is an issue. The issue arises because of the  $\text{Fe}(\text{OH})_3$

intermediate which is non-amphoteric at any appreciable concentration, meaning this synthesis route is essentially blocked and can result in inhomogeneous precipitation, poor crystallinity of the product and its contamination with  $M^{3+}(\text{OH})_3$ .<sup>80</sup> The nature of a material like NiFe LDH in electrochemical applications though, means it may rely on properties like good crystallinity to enhance its performance in terms of facilitating electronic and ionic transport during activity. So, synthesis of highly crystalline NiFe LDH was achieved using a triethanolamine (TEA) capping agent to accompany the homogeneous precipitation reaction to ensure both metal ions are incorporated uniformly in the final product.

TEA in this reaction has a dual purpose. Firstly, it causes a change in the pH of the starting solution from about 2 to 6.6. At this pH,  $\text{Fe}^{3+}$  ions precipitate as thermodynamically metastable iron oxyhydroxide, which is less stable than the  $\text{Fe}(\text{OH})_3$ . Secondly, TEA molecules coordinate  $\text{Ni}^{2+}$  forming an octahedral Ni-TEA complex. When the entire reaction mixture (iron oxyhydroxide, Ni-TEA and urea) is then heated to 100 °C to stimulate pH increase, both  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  are gradually released from their respective intermediates and they recombine with the  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  from urea hydrolysis forming crystalline NiFe LDH platelets.<sup>81</sup> Additionally, facile exchange of the  $\text{CO}_3^{2-}$  counter ion to some other anion can be performed by acid and salt treatment. Experimental details for all of the above are provided in section 3.6.

## 3.2 Material Characterisation

The NiFe LDH homogeneous co-precipitation synthetic route described above has been shown to yield pure, highly crystalline NiFe LDH hexagonal platelets with planar morphology.<sup>44</sup> A study by Jaskaniec *et al.*<sup>44</sup> confirmed that a relatively low reaction temperature (100 °C) and an initial TEA: $\text{Fe}^{3+}$  ratio of 4:1 maximise the products crystallinity and morphological regularity for this synthetic route. The as produced NiFe LDH was characterized based on morphology, crystallinity and chemical composition.

The planar, hexagonal platelet morphology of NiFe LDH synthesized by the coprecipitation method was confirmed by SEM (Figure 3.2.1 a). By studying high and low magnification SEM images over an extended sample area, it is clear that well defined platelets have been formed throughout with a high degree of regularity in terms of platelet morphology and size. A particle size study was carried out by measuring individual particle lateral dimensions (L, measured between adjacent corners, inset Figure 3.2.1 b) across a broad area of the sample. This study revealed that the as produced hexagons had an average lateral length of  $0.78 \pm 0.02 \mu\text{m}$  (with standard deviation  $\sigma = 0.19 \mu\text{m}$ ), the majority of which exist in the relatively narrow size range  $0.4 - 1 \mu\text{m}$ . This is consistent with the sub-micron NiFe LDH lateral dimensions reported in literature (smaller than most LDH species) which is known to be one of the materials significant built-in features in terms of electrochemical activity.<sup>38</sup>

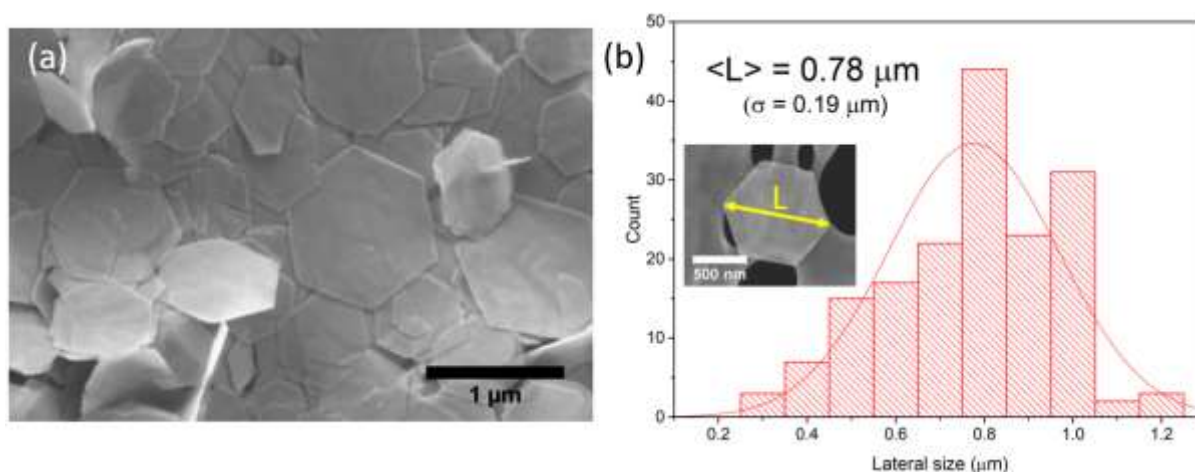


**Figure 3.2.1:** (a) SEM micrograph of as-prepared NiFe LDH platelets and (b) histogram representing the size distribution in the synthesized dispersion.

The height profiles of individual platelets were observed using tapping mode AFM. Figure 3.2.2 shows two individual representative platelets with similar height. A thickness of  $12 \pm 2 \text{ nm}$  was observed using AFM, which corresponds to about 10 layers.<sup>28, 38, 78</sup> Previously published reports of AFM imaging for NiFe LDH materials suggest thicknesses in the range of tens of nanometers.<sup>77, 81</sup> The AFM height profiles also indicate sharp edge features for the hexagonal platelets. It is believed that the observed ‘roughness’ across the surface is due to some impurities gathered there before the microscopy was carried out, perhaps residual TEA from synthesis, and the material is otherwise believed to possess a smooth surface profile based on SEM and TEM imaging.

Similarly to AFM, TEM imaging (Figure 3.2.3 a) demonstrates the sharp edges and relatively homogeneous surface of the as-synthesized hexagonal platelet, with some patches indicating the presence of potential impurities (again, possibly residual TEA on the surface which have accumulated during preparation). This is similar to what can be seen across the AFM surface profile (Figure 3.2.2). Beam damage could also be a contributor to the apparent roughness across the surface. The sharp hexagonal features and regular planar morphology have significance because they are qualities which have been shown to improve catalytic activity for the OER relative to other morphologies which may result from different synthetic routes.<sup>81</sup> The material's SAED pattern (Figure 3.2.3 d) was acquired using the electron source from the FEI Titan TEM. The bright spots in the SAED pattern are indicative of the high crystallinity of the synthesized material. The hexagonal orientation of the diffraction pattern is characteristic of the symmetry<sup>38, 79</sup> within an LDH crystal structure. This is complemented by the highly ordered atomic resolution observed via HAADF-STEM in Figure 3.2.3 (c).

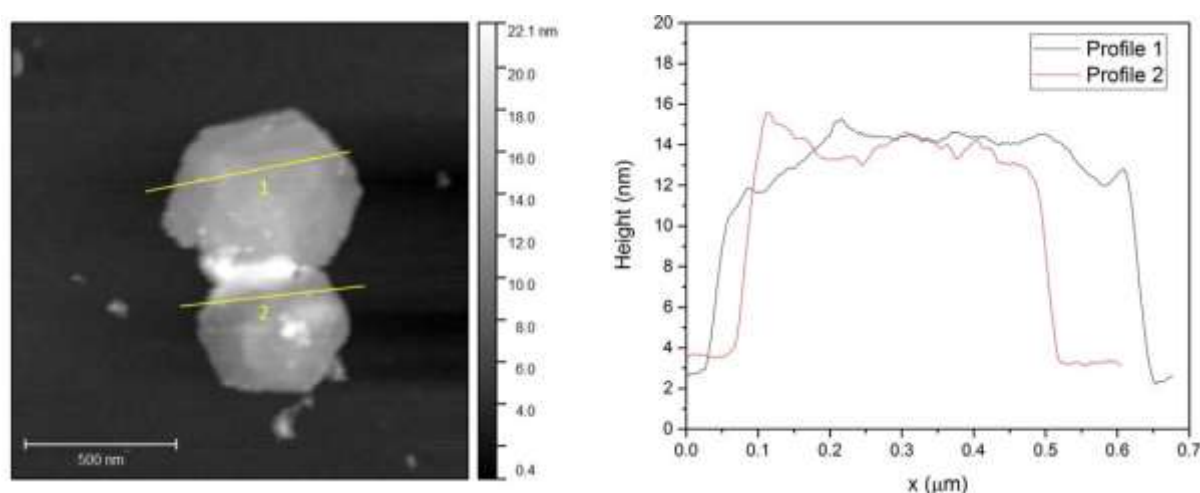


**Figure 3.2.2:** AFM image of NiFe LDH platelets, with height profiles (over distances marked by yellow lines 1 & 2) of individual platelets.

The XRD pattern (Figure 3.2.3 b) was indexed as hexagonal symmetry with lattice parameters  $a = 3.08 \text{ \AA}$ ,  $b = 23.55$ .<sup>78</sup> The high intensity peaks in the diffractogram such as (003) and (006) represent high-symmetry directions within the crystal and suggest a highly crystalline nature of the sample.<sup>26, 38, 39</sup> The accurate peak matching also shows that the sample is mostly pure. Two unmatched peaks (labelled \* in Figure 3.2.3 c) indicate the presence of some minor secondary phase

contamination. This is proposed to result from areas where residual TEA has intercalated the material resulting in a minor phase which is swollen relative to the major  $\text{CO}_3^{2-}$  intercalated phase (TEA is a larger intercalant), hence the shifted d-spacing relative to the high intensity (003) and (006) peaks. Using the indexed lattice parameters from XRD peak matching, the first two families of bright spots in the SAED pattern can be indexed as (012) and (110) directions.

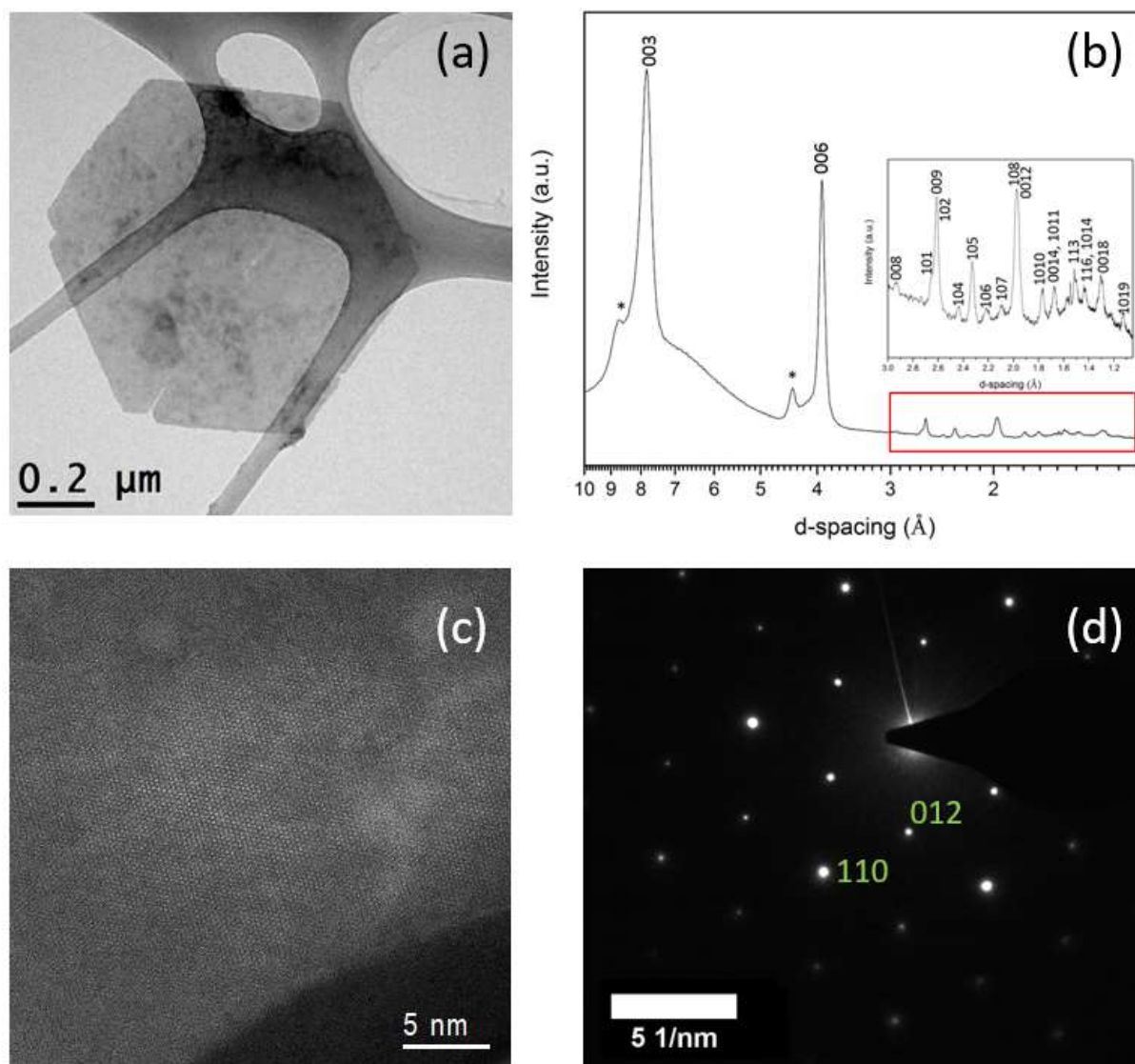


**Figure 3.2.3:** (a) TEM micrograph, (b) XRD diffraction pattern (inset, zoomed signals for the 1.3 – 3 Å d-spacing region), (c) atomic resolution HAADF-STEM and (d) SAED pattern for as-synthesized NiFe LDH.

To ensure that complete homogeneous precipitation of  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  at octahedral centres has been achieved, EDX mapping was performed on individual hexagons. This technique was carried out using an SEM probe which was scanned across the sample in a rastering motion to produce an elemental map to view the distribution of constituent species within the materials extended crystal

structure. Figure 3.2.4 shows maps for Ni, Fe and O across an imaged platelet. The data confirms that the divalent and trivalent metal centres are homogenously distributed, as well as O atoms which are found throughout the structure in hydroxides (in-layer) as well as carbonate and water molecules (inter-layer). The most important result is the confirmation that  $\text{Fe}^{3+}$  ions have been uniformly integrated into the brucite-like host structure, because it is this feature which stimulates charge-transfer activation within the material and enhances its catalytic ability.<sup>40</sup>

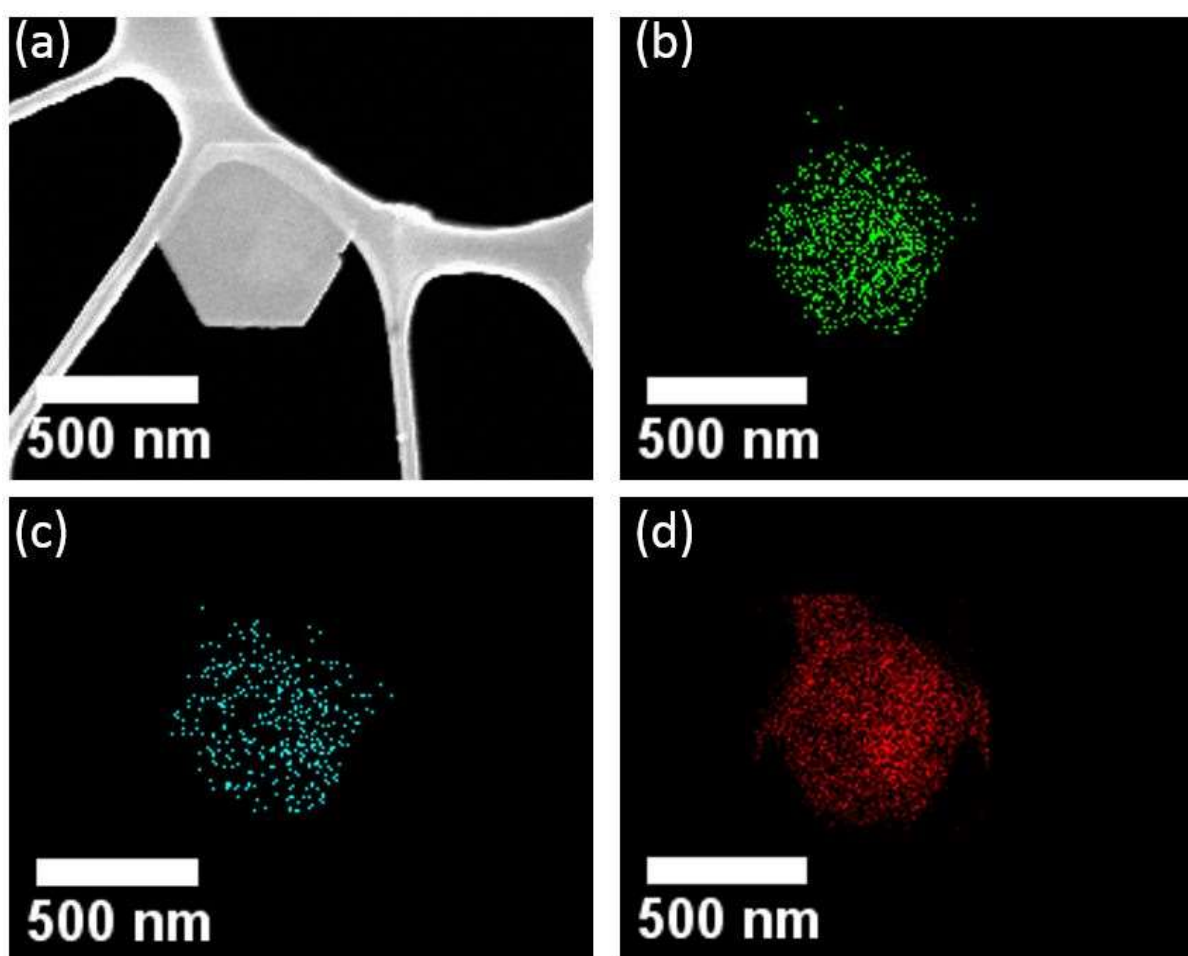


**Figure 3.2.4:** (a) SEM micrograph and EDX mapping of (b) Ni K $\alpha$ 1 (c) Fe K $\alpha$ 1 and (d) O K $\alpha$ 1 signals within a NiFe LDH platelet.

While the initial Ni:Fe ratio can be precisely controlled in the reaction solution, it is impossible to ensure their complete uptake into the final LDH structure. AAS was performed on the synthesized material to accurately determine the  $\text{Ni}^{2+}$  to  $\text{Fe}^{3+}$  ratio. This revealed that the value after coprecipitation was not exactly 3:1 but rather 3.54:1, suggesting that the  $\text{Fe}^{3+}$  uptake was sluggish compared to  $\text{Ni}^{2+}$ . This ratio was then used to produce a value for x in Equation 1.4, which describes

the fraction of  $\text{Fe}^{3+}$  relative to  $\text{Ni}^{2+}$  within the LDH layers. Complimentary to this, TGA analysis was carried out (Figure 3.2.5) and revealed a total 34% mass loss upon heating in the range 100 – 800 °C. After reaching the first plateau in the TGA curve, it can be observed that 9% mass has been lost in the temperature range 30 – 200 °C. This loss is attributed to the presence of water.<sup>82</sup> The sharp plateaus in this region suggest that only water, and no other impurities are contributing to the 9 % mass loss. However, infrared spectroscopy assisted TGA may be a useful method of confirming this in future work. The weight percentage of water within the material could be used from here to calculate the molar ratio of  $\text{H}_2\text{O}$  to the other components in the compound ( $y$  in Equation 1.4) using a stoichiometric calculation. The further 25 % mass loss in the 200 – 800 °C range is due to decomposition of the intercalated counter anions and dehydroxylation at octahedral sites within the layers.<sup>33</sup> With the quantitative information from AAS and TGA measurements, the molecular formula can be estimated accordingly as  $\text{Ni}_{0.78}\text{Fe}_{0.22}(\text{OH})_2(\text{CO}_3)_{0.11} \cdot 0.5\text{H}_2\text{O}$ .

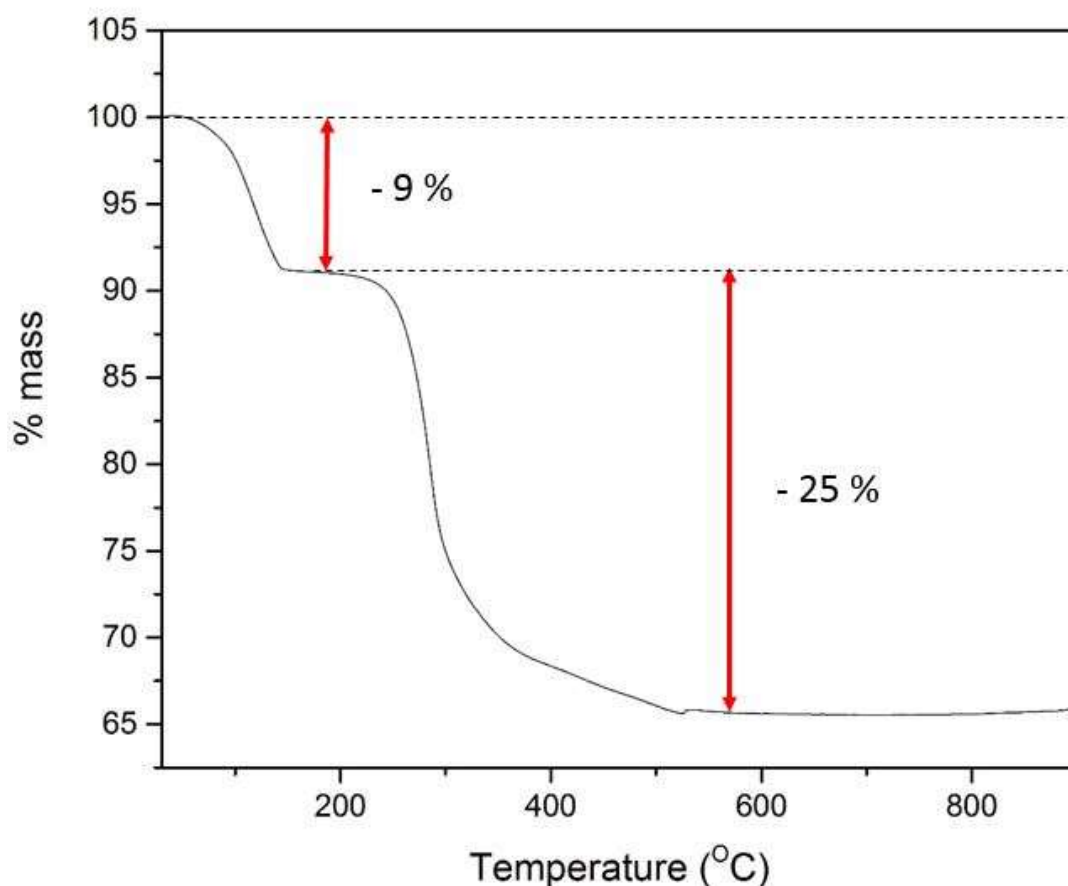


**Figure 3.2.5: TGA analysis of NiFe LDH.**

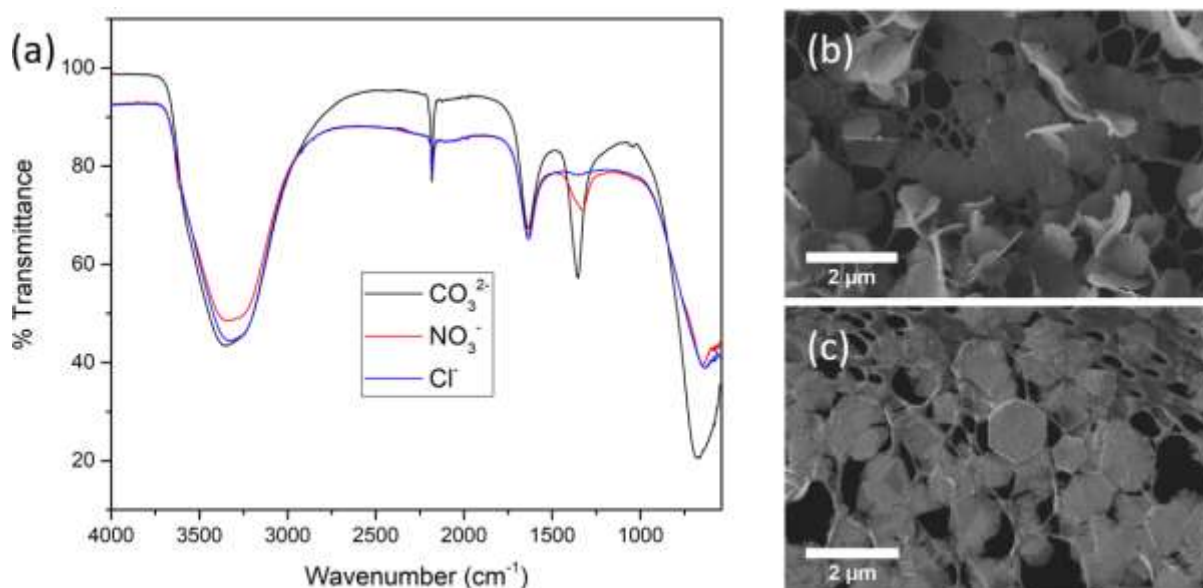


**Figure 3.2.6** (a) FT-IR spectra of NiFe LDH with  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  interlamellar counter anions. (b) and (c) SEM micrographs of  $\text{NO}_3^-$  and  $\text{Cl}^-$  intercalated platelets, respectively.

Careful characterisation of the material thus far has demonstrated the two-dimensional (2D), layered nature of NiFe LDH. One of the most important features of layered materials is the extent to which they can become exfoliated to produce its fully/partially delaminated equivalent. Delaminated 2D materials have unique, and often superior, physical and electronic properties compared to their ‘bulk’ counterparts.<sup>83</sup> Intercalated species can often play an important role in exfoliation. The as produced NiFe LDH possesses  $\text{CO}_3^{2-}$  at intercalation sites. These counter anions act to strengthen the inter layer bonding due to coulombic interactions with the positively charged layers and also hydrogen bonding between the oxygen atoms in the anion and hydrogen atoms within the layers. As a result, layers require a relatively high energy input to become exfoliated. The difficulty then lies in the intricacy required to apply just enough shear stress to the structure to separate layers without destroying the material. So here it is useful to perform an anion exchange reaction to replace strongly binding  $\text{CO}_3^{2-}$  with some weaker bonded counter anions. LDH materials have good intercalation exchangeability properties meaning that anion exchange can easily be achieved. In doing so the interlayer forces may be weakened if a less stable counter anion is chosen, which can promote exfoliation when a shear stress is applied in the appropriate solvent. Anion exchanges were carried out in this study using  $\text{Cl}^-$  and  $\text{NO}_3^-$  as alternative counter anions (method in section 3.6) so as to

observe the ease of exchangeability of these anions, an important LDH property and one which will be utilized later in this work.

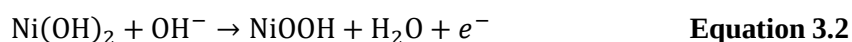
FT-IR spectroscopy was used to characterize the NiFe LDH material before and after anion exchange. Figure 3.2.6 (a) shows the FT-IR spectra for  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  intercalated material. The peaks at  $3350\text{ cm}^{-1}$  are attributed to the  $\nu_{\text{O-H}}$  vibrational mode (symmetric and asymmetric O-H stretching) in octahedral hydroxide groups as well in  $\text{H}_2\text{O}$  (additional peak at  $1645\text{ cm}^{-1}$  from O-H bending completes the  $\text{H}_2\text{O}$  signal). Common peaks for all three samples at around  $700\text{ cm}^{-1}$  are typical of collective LDH lattice vibrations, namely M-O, M-O-M, O-M-O vibrations (M = Ni, Fe).<sup>33,</sup>

84, 85

Of most interest are the three peaks of various intensity in the narrow region of  $1350 - 1400\text{ cm}^{-1}$ . Here we see the characteristic stretching modes  $\nu_{\text{NO}_3^-}$  ( $1384\text{ cm}^{-1}$ ) and  $\nu_{\text{CO}_3^{2-}}$  ( $1354\text{ cm}^{-1}$ ).<sup>79</sup>  $\text{Cl}^-$  will have no active IR modes because it is monatomic. The weak peak in the  $\text{Cl}^-$  spectrum in this region is likely residual  $\text{CO}_3^{2-}$  intercalated material within the sample. Nevertheless, this FT-IR data provides evidence that the anion exchange reaction was successful for NiFe LDH. This is hugely significant as it suggests near complete anion exchange using a simple acid-salt treatment, which essentially alters the chemical and structural properties of the layered material. In fact, it has been shown that appropriate LDH intercalation can facilitate exfoliation in formamide dispersions without the necessity of ultrasonic treatment.<sup>38</sup> An additional novel application for complete anion exchange in the material will be introduced later in the thesis. The accompanying SEM micrographs in Figure 3.2.6 (b) and (c) demonstrate the consistent hexagonal morphology even after complete anion exchange.

NiFe electrodes were prepared for electrochemical testing by spraying liquid suspensions of active material onto Ni foam using an ultrasonic assisted spray tool (USI Prism Ultracoat 300). An accurate mass loading was achieved by performing low-volume spray patterns repetitively and observing mass changes with a microbalance. Good quality NiFe LDH material can improve the OER overpotential value  $\eta$  (potential energy in excess of the thermodynamic minimum) for water

splitting when compared with the working electrode support (Ni foam) alone (Figure 3.2.7 d). The figure indicates relative overpotentials for Ni foam and NiFe LDH electrodes of 387 mV and 361 mV, which is comparable to that reported by Lu *et al.*<sup>39</sup> for NiFe LDH grown on Ni foam. The CV curve for pure NiFe LDH on Ni foam (Figure 3.2.7 c) shows well defined redox peaks at 1.32 V (cathodic) and 1.41 V (anodic) vs RHE, giving a redox couple at around 1.36 V, before onset of the OER current (beyond 1.55 V). This couple is the signal of the Ni foam substrate material oxidizing from hydroxide to its oxyhydroxide form, as in Equation 3.2 below. This Ni(OH)<sub>2</sub> redox couple is observable repeatedly in the literature, as well as for pure nickel control experiments for this work (Figure A1 a in Appendix A).<sup>39, 86</sup>



In the initial anodic sweep of Figure 3.2.7 (c), there are no observable oxidation peaks from the NiFe LDH active material.<sup>87</sup> It is thought that the oxidation occurs with a subtle current output and at potentials beyond the onset of OER activity and is therefore not visible. Lu *et al.*<sup>39</sup> reported that the apparent ‘delay’ in onset potential for the Ni<sup>2+</sup>/Ni<sup>3+</sup> redox couple within a NiFe LDH crystal compared to pure nickel is because of highly charged Fe<sup>3+</sup> and interlayer counter anions in the surrounding sites which inhibit nickel oxidation and push the reaction to a higher potential. There is, however, a cathodic signal at 1.37 V which accounts for nickel reduction from oxyhydroxide to hydroxide (i.e. the opposite of Equation 3.2) for nickel within the NiFe mixed metal LDH environment. This is in good agreement with the expected reduction potential for the catalyst.<sup>39</sup> Subsequent cycling (Figure A1 b in Appendix A) sees an increasingly visible oxidation peak for nickel within the LDH, setting up a redox couple at 1.41 V. The cathodic jump for this redox couple between cycles one and two is not entirely clear but thought to be a response to some significant structural changes in the crystal in response to the initial voltage sweep. There will be more detail on this point later in the thesis. For now, the peaks of the respective redox couples can be definitively assigned to the Ni<sup>2+</sup> ↔ Ni<sup>3+</sup> conversion.<sup>26, 39</sup> This assignment is based on the knowledge that, although LDH materials have been known to occupy a significant proportion of Ni<sup>4+</sup> sites, it is also known that redox peaks of this kind will appear beyond the onset potential of the OER catalysis and

will not be visible in this case.<sup>88-90</sup> High oxidation state iron may also exist within this LDH oxidation scheme, believed to be made possible by the deprotonation of interlamellar  $\text{H}_2\text{O}$  and  $\text{OH}^-$  ligands.<sup>91</sup> However, studies by Beverskog and Puigdomenech<sup>92</sup> confirm that at pH 14 (1 M KOH solution), the oxidation of  $\text{Fe}^{3+}$  to  $\text{Fe}^{5+}$  in the form of oxo-species, occurs at identical potentials as the hydroxide-oxyhydroxide couple. So, what is likely seen in the 1.41 V redox couple (Figure 3.2.7 c & Figure A1 b) is primarily  $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$  with some minor potential contributions from more highly oxidised iron species.

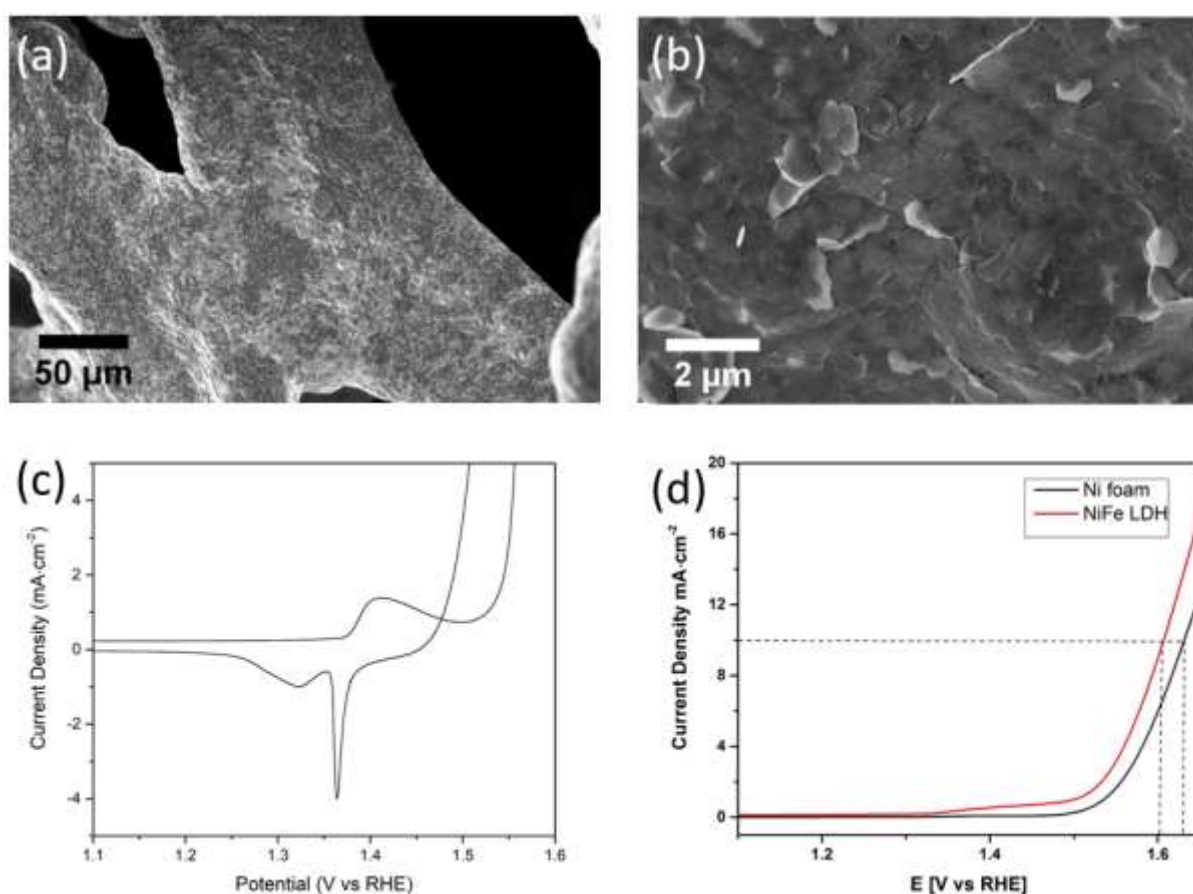


**Figure 3.2.7: (a) & (b) SEM micrographs showing the homogeneous deposition of NiFe LDH onto Ni foam. (c) First cycle CV curve for NiFe LDH electrode. (d) Polarization curves for pure Ni foam and NiFe LDH (on Ni foam) at  $5 \text{ mV} \cdot \text{s}^{-1}$  in 1 M KOH. The overpotentials are quoted at  $j = 10 \text{ mA} \cdot \text{cm}^{-2}$ .**

Based on the characterization of the wet-chemistry-synthesized  $\text{Ni}_{0.78}\text{Fe}_{0.22}(\text{OH})_2(\text{CO}_3)_{0.11} \cdot 0.5\text{H}_2\text{O}$ , the material has been demonstrated to be highly crystalline and regular in its hexagonal morphology with mean platelet lateral dimensions of  $0.78 \pm 0.02 \mu\text{m}$  and ten layers thick on average. Additionally the crystals show facile anion exchange ability as well

as an activity for OER catalysis in alkaline conditions. These features provide a base on which to build this study which will involve, for the most part, post synthetic processing techniques performed on the as produced material. Additionally, this material will provide a standard against which subsequent ‘modified’ NiFe samples can be evaluated in terms of OER catalytic performance.

### 3.3 Platelet Size Reduction & Selectivity

Adachi-Pagano *et al.*<sup>79</sup> reported that, for MgAl LDH synthesis using a classic coprecipitation method, by precise control of the reaction conditions it was possible to control the size of as produced hexagons for that particular combination of metals. By changing the pH evolution rate (i.e. initial urea concentration), reaction temperature and reaction time, the particle size and the Mg:Al ratio were controlled. However, in the case of NiFe LDH such modification could not be achieved, most probably due to the non-amphoteric nature of the  $M^{3+}$  species, as well as the necessity of a capping agent. As a result, size control based on post-synthetic treatment will be implemented in this work in an attempt to optimize the electrocatalytic behaviour and understand its relationship with particle size.

A systematic study will be carried out involving high-power ultrasonication and centrifugation techniques to control LDH platelet sizes within pure liquid dispersions to find out the extent to which the techniques can be used to build upon the intrinsic catalytic capabilities of NiFe LDH for oxygen evolution by alkaline water electrolysis. The catalytic ability will be judged based on the overpotentials which can be achieved using the treated material deposited on a nickel foam substrate to form an electrode. LV, CV and CP data will be studied to observe how performance of the electrode changes during the course of its active lifetime. Ultimately, such a study should allow for a better understanding of the relationship between particle size and their catalytic activity, which may help us understand the nature of electrocatalysis in layered materials in a more general sense, as well as enhancing the outlook for NiFe LDH specifically for this application.

Particle size selection for colloidal dispersions can be achieved using centrifugation. Khan *et al.*<sup>93</sup> demonstrate for exfoliated graphene dispersions, controlled centrifugation could achieve a range of dispersions whose mean flake length ( $\langle L \rangle$ ) varied from 1  $\mu\text{m}$  to 3.5  $\mu\text{m}$ . The process involves carefully choosing centrifugation conditions i.e. time and rate in rotations per minute (rpm). The specific conditions need to apply enough centrifugal force to the colloids to cause sedimentation of some, but not all of the dispersion. After a successful centrifugation step, the material is separated into the ‘supernatant’ (smaller  $\langle L \rangle$ ) and sediments (larger  $\langle L \rangle$ ). Size selection using this method is approached in steps, starting (for this research) from a low centrifugation rate and increasing stepwise, gradually removing the sediments after each run for size study with SEM, and then centrifuging the supernatant at a higher rpm (Figure 3.3.1). Alternatively, removing some supernatant after each cycle will also results in particle size separation being observed from high to low rpm.

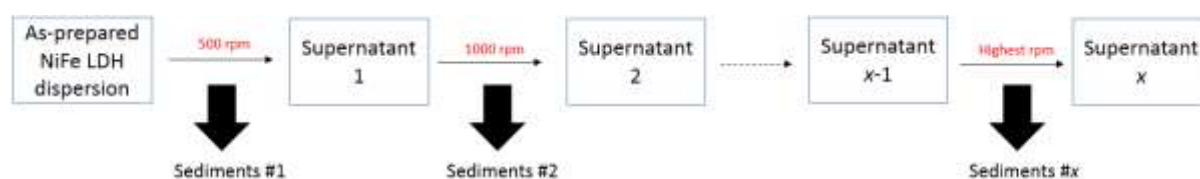


**Figure 3.3.1: General scheme for centrifugation-driven size selection.**

After homogeneous precipitation, the material’s relatively narrow size distribution posed certain problems compared to size selection of graphene flakes,<sup>93</sup> for example, because centrifugation is not a particularly sensitive technique for narrow size distributions. Regardless, the method was carried out using the scheme in Figure 3.3.1 whereby the starting material was centrifuged at 500 rpm intervals from 500 rpm to 3000 rpm in order to see the extent to which particles could be separated in this range.

Aggregation effects can be detrimental to this process because if a dispersion is highly aggregated, the material will be separated based on the sizes of aggregated clusters rather than the individual particles, and  $\langle L \rangle$  of successive dispersions will essentially become more randomized. Aggregation is especially prominent in smaller NiFe LDH platelets so it is an important consideration in situations like this one where the goal will ultimately be to isolate particles with small  $\langle L \rangle$ . Dispersions were sonicated using a Fisherbrand 11207 (330 W maximum power) operating at 37

kHz and 60 % power before each run to prevent aggregation. It can be seen from Figure 3.3.2 (a) – (f) that in the range 500 – 3000 rpm, centrifugation can in fact cause reasonable selection from successive supernatants with  $\langle L \rangle$  from  $0.85 \pm 0.03 \mu\text{m}$  ( $\sigma = 0.18$ ) down to as small as  $0.47 \pm 0.01 \mu\text{m}$  ( $\sigma = 0.14$ ). The accuracy with which size selection can be performed is proportional to centrifugation time which is why the standard deviation decreases steadily for samples further along in the centrifugation scheme. This is an indication that, should we want to minimize or abolish overlap of particle sizes between successive samples this could be done by increasing treatment times and/or repeating the steps in figure 3.3.1, with some probable loss of concentration in the resulting dispersions.

One issue with attempting to perform size-selection this way on as produced platelets with high selectivity is that it becomes wasteful. One must disregard the majority of the platelets in order to isolate the desired size range. In the scope of this work where smaller particle sizes are expected to be more electrocatalytically active, it is the larger particles which are wasted. A far more economical method would be to perform some mechanical fracture and breaking of the particles to drive down the mean particle size within a given dispersion to begin with, resulting in a smaller basis with which to begin centrifugal size selection. This mechanical ‘fragmentation’ method uses all of the as-synthesized platelets meaning a much larger portion of the material can be used in the final dispersions. Tip-sonication will be used as the primary method of downsizing in this way.

Tip sonication is a technique similar to bath sonication in that it uses high power ultrasound to apply energy to a sample in a liquid medium. The application of an ultrasonic signal within a liquid suspension creates small bubbles in a process called cavitation. The bubbles will expand rapidly before ‘imploding’ in a violent manner creating a high energy ‘hot spot’ which sends shock waves out into the extended volume of liquid.<sup>94</sup> Sonication of liquid dispersions is a technique used frequently in materials science for exfoliating material to produce 2D nanosheets. Tip-sonication uses an ultrasonic probe which operates directly in the sample dispersion and exhibits superior homogeneity and up to 1000 times the power capability of bath sonication. It is for this reason that the method was employed to achieve NiFe LDH platelet breaking. When such high power is applied,

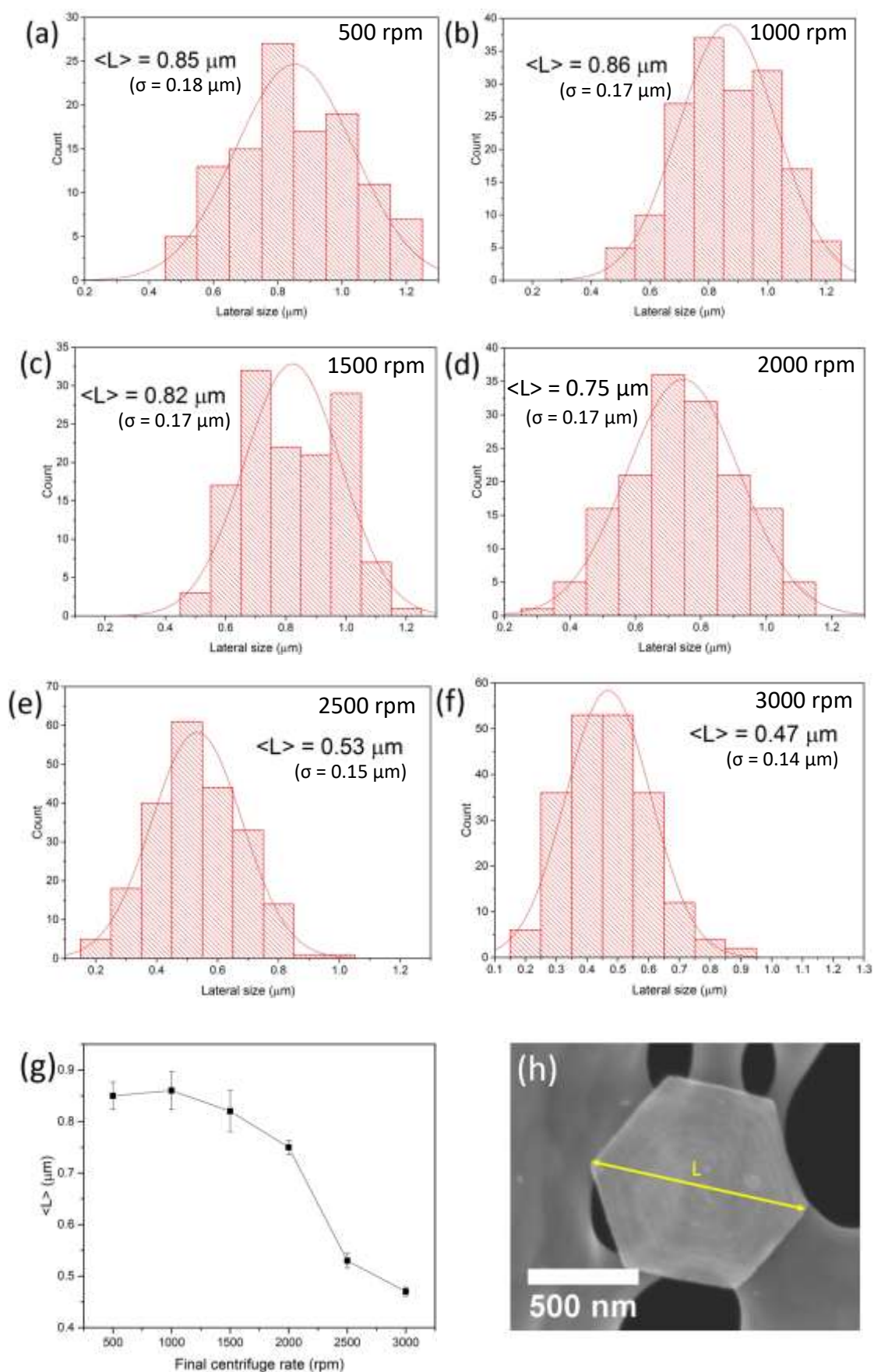


**Figure 3.3.2:** (a) – (f) Size-distribution histograms after size-selection by centrifugation in the range 500 – 3000 rpm (standard deviations quoted), (g) Graph of mean particle size vs final centrifugation rate and (h) representative SEM micrograph indicating the method of lateral particle size measurement.

the shear stress required for exfoliation is surpassed and out-of-plane particle breaking dominates. Figure 3.3.3 indicates the effect on the particle lateral size distribution by tip-sonicating dilute dispersions of NiFe LDH using a Fischer Scientific Sonic Dismembrator Ultrasonic Processor at 40% power for 1 hour (with Fisher Scientific Isotemp refrigerated bath circulator cooling system held at 5 °C). One can notice not only the drastic decrease in  $\langle L \rangle$  value but also the narrowing of the size distribution, something which goes hand-in-hand with fragmentation and continues to decrease with sonication time (Figure A2 in Appendix A).

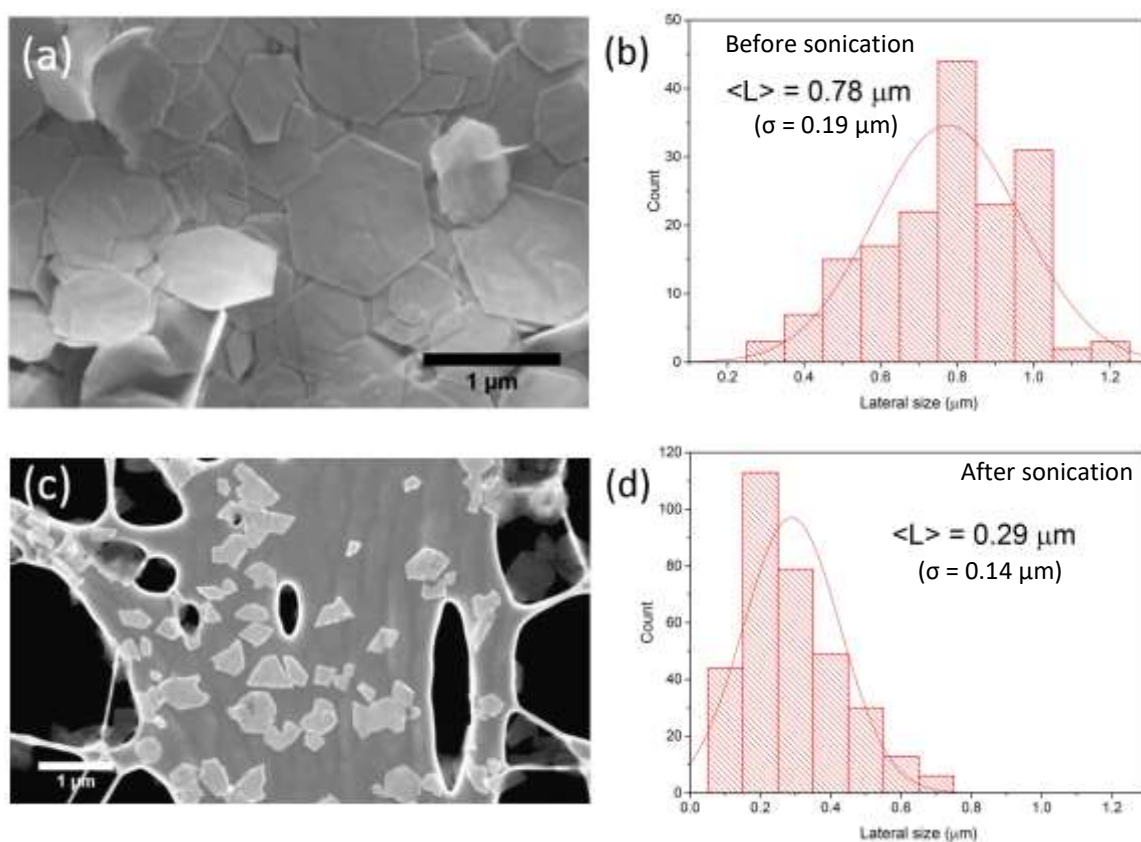


**Figure 3.3.3: (a) & (c) SEM micrographs of as produced and fragmented NiFe LDH platelets respectively and (b) & (d) associated platelet size distributions indicating mean platelet size.**

As outlined previously, this work is based on the principle that fractured platelets can have, in theory, more exposed active edge sites than their larger, as produced hexagonal precursors. However, it is difficult to quantify by how much the density of active sites will improve. In terms of electrochemistry, the active site density will vary across the surface area of a platelet (i.e. relatively high at edges and low along planar surface). Taking this into consideration, it becomes difficult to quantify with conventional surface area characterization techniques, even approximately how much

the active site density has improved within a given suspension after size reduction. It is believed that the best insight to this end is through electrochemistry which will be covered later in this chapter. Short of that, size distributions are a useful insight into how electrochemically active a material like this could be.

However, the aim remains to have the ability to not only downsize but also to selectively tailor the platelet dimensions and ultimately isolate the smallest size distribution within a useable dispersion i.e. high enough concentration for practical use with little to no impurities, as they can drastically affect the mass loading process during electrode preparation. Impurities can most notably be introduced during tip-sonication steps (this will be analysed in subsequent sections). Additionally, controlling platelet size within a given range may help to elucidate some observable relationship between the abundance of exposed edges and the electrocatalytic activity and potentially give insight into how edge sites exposed by fragmentation compare to those intrinsic sites formed during synthesis.

The results for centrifugal size-selection of the size reduced platelets (sr-NiFe LDH) with final rates in the range 500 – 5000 rpm are shown in Figure 3.3.4 (a) – (f), where it is indicated (Figure 3.3.4 h) that measurements are taken along the long edge of each particle when they appear to be lying flat on the substrate. In this rpm range, a steady drop in mean lateral size of particles in the respective dispersions can be observed, again with a narrowing distribution further down the sequence (Figure 3.3.4 g). This means that despite the shift down in platelet size upon sonication, centrifugation remains an adequately sensitive tool for further tailoring of platelet dimensions. The method allowed for the isolation of dispersions with  $\langle L \rangle = 0.17 \pm 0.02 \text{ } \mu\text{m}$  with satisfactory concentration and sample purity. With a highly selective and facile method established for LDH platelet size control, the next task is to determine what effect will be had on the electrocatalytic performance and in doing so approach an optimized platelet dimensionality that will further build upon the materials intrinsic OER catalytic properties.

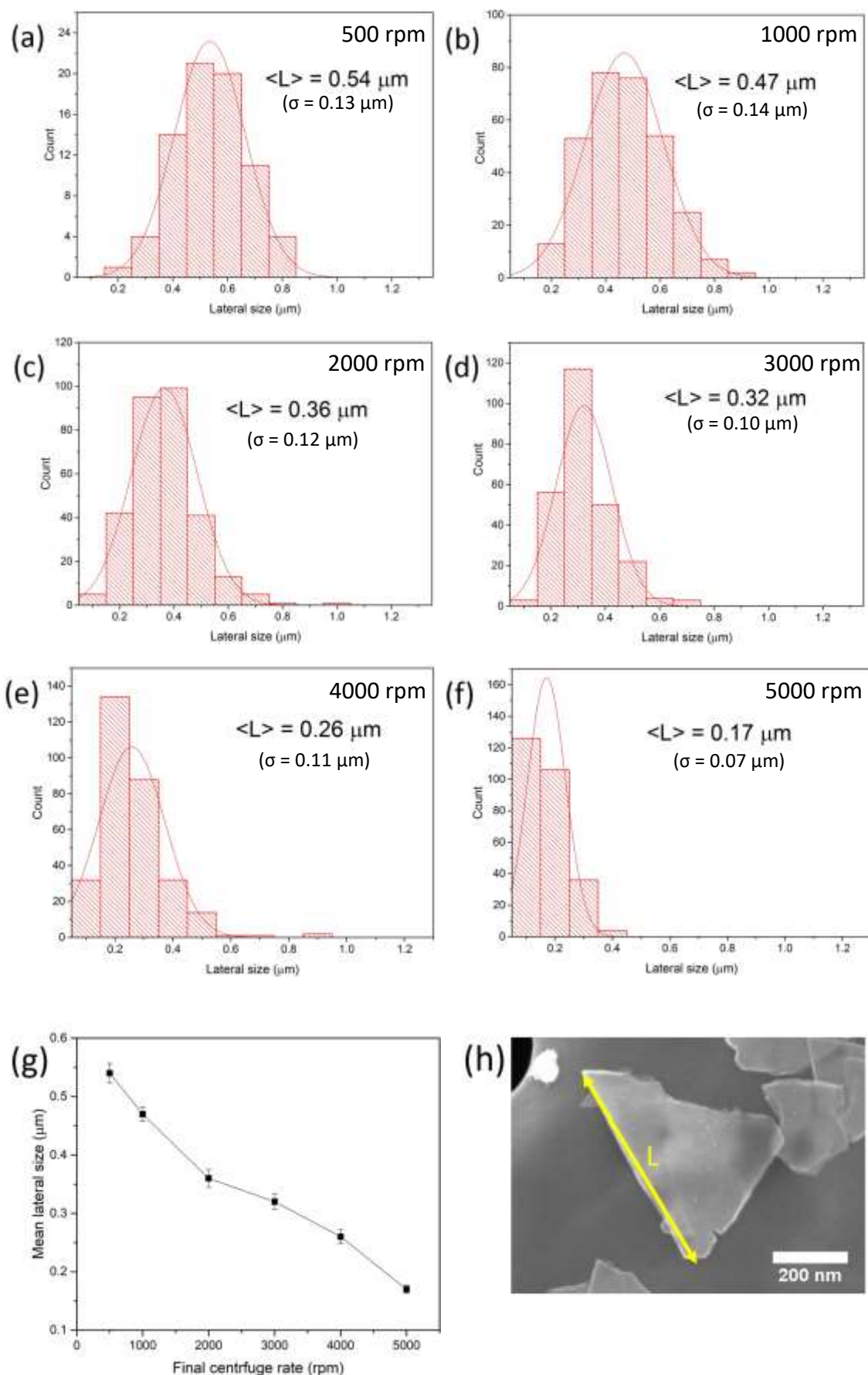


**Figure 3.3.4:** (a) – (f) Size-distribution histograms of sr-NiFe LDH after size-selection by centrifugation in the range 500 – 5000 rpm (standard deviation  $\approx 0.2 \mu\text{m}$ ), (g) Graph of mean particle size vs final centrifugation rate and (h) representative SEM micrograph indicating the method of lateral particle size measurement.

### 3.4 Electrocatalytic Evaluation of Platelet Size Control

As was suggested in the previous section, perhaps the most insightful method of elucidating the relative density of active sites for NiFe LDH dispersions of different mean lateral size is via electrochemical testing. In this section, linear and cyclic voltammetry, chronopotentiometry (CP) and Tafel slope (denoted 'b') determination will be used as tools for characterizing the material of varying sizes in terms of preliminary performance (i.e. overpotential) as well as more practical considerations (i.e. cycling and ageing electrodes in working conditions). CP, the only technique not introduced thus far, is another simple mode of electrochemistry which compliments CV cycling data nicely. It works by applying a constant current density (say,  $10 \text{ mA} \cdot \text{cm}^{-2}$  for convention) and how the potential in the cell responds over time to the constant current. CP is a very relevant, practical characterization tool for electrolyser cell components (OER, HER catalysts) and will be used here in conjunction with other methods to clarify the active life of sr-NiFe LDH in alkaline OER catalysis.

#### 3.4.1 sr-NiFe LDH Processed in Organic Solvents

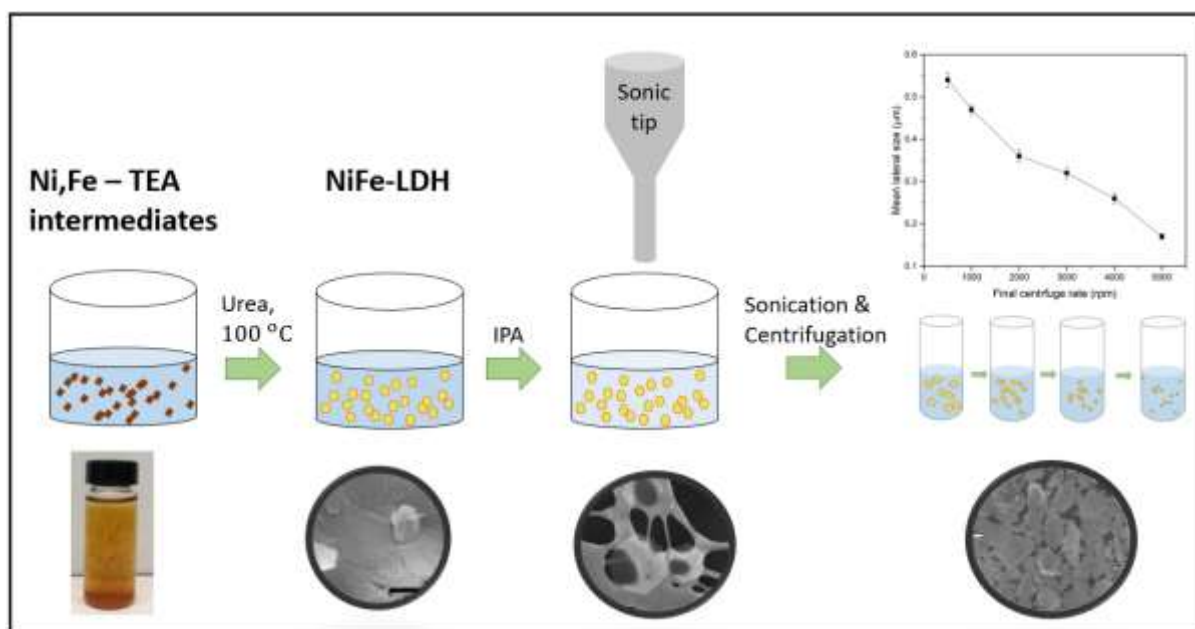


Figure 3.4.1: Schematic showing the NiFe LDH size-selection steps involved from wet synthesis to centrifugation.

Firstly, we consider the material which was processed as above (sonication & centrifugation steps) in organic solvent dispersions (namely IPA), with aqueous processing being alternatively

considered in section 3.4.2. As depicted in the process scheme on Figure 3.4.1, the as-synthesized material is transferred to and washed in IPA by centrifugation after synthesizing in aqueous conditions. This was done to reduce stress on the sonic tip. Deionized (DI) water has a greater affinity for ions as well as a greater surface tension when compared to organic solvents like IPA meaning it will cause more rapid degradation of the titanium head of the sonic dismembrator and cause contamination of the NiFe dispersion with metal ions and clusters stripped from the tip (demonstration in the following section). While not necessarily the most damaging additive to contaminate the material in terms of conductivity, titanium is a bad OER catalyst. Any significant amount of such material will affect the gravimetric performance as well as the ability to accurately mass load the active material onto a substrate. So, for that reason it is crucial that contamination is minimized and therefore basing the active dispersions in IPA is one useful precautionary step. IPA was chosen because it can create adequately stable suspensions of both sr-NiFe LDH and carbon nanotube additives which will be used in this research, without the necessity of stabilizing components (surfactants etc.).

In electrocatalysis, the Tafel slope for a given catalyst can give an indication of the rate capability as well as the sensitivity of the rate to a change in potential. It's an interesting parameter to start with because it can give some insight into a materials' intrinsic electrochemical properties. The Tafel equation (Equation 3.3) relates the overpotential  $\eta$  to the current density  $j$  (and exchange current density  $j_0$ ) so that the proportionality constant  $b$  (Tafel slope) will give information regarding the sensitivity of the reaction rate to a change in potential across the cell.

$$\eta = b \times \log_{10} \left( \frac{j}{j_0} \right) \quad \text{Equation 3.3}$$

The inverse proportionality between  $b$  and  $j$  mean that a low  $b$  value is desirable as it implies good rate capability within a given cell. Figure 3.4.2 indicates low values for NiFe and sr-NiFe LDH compared with pure nickel foam. Upon fragmentation, no great change is observed. In fact, the Tafel slope increases slightly. This is perhaps a consequence of some impurities being introduced during the sonication procedure. What the Tafel slopes seem to suggest is that although fragmentation may

increase active site density with an effect on OER overpotential values (Figure 3.4.2), the intrinsic rate capabilities are not enhanced. This effectively points to the lack of any change in the catalyst's compositional makeup here. There should be no expectation of any great shift in the intrinsic rate capabilities but rather an increase in the number of catalytic events happening per LDH platelet.

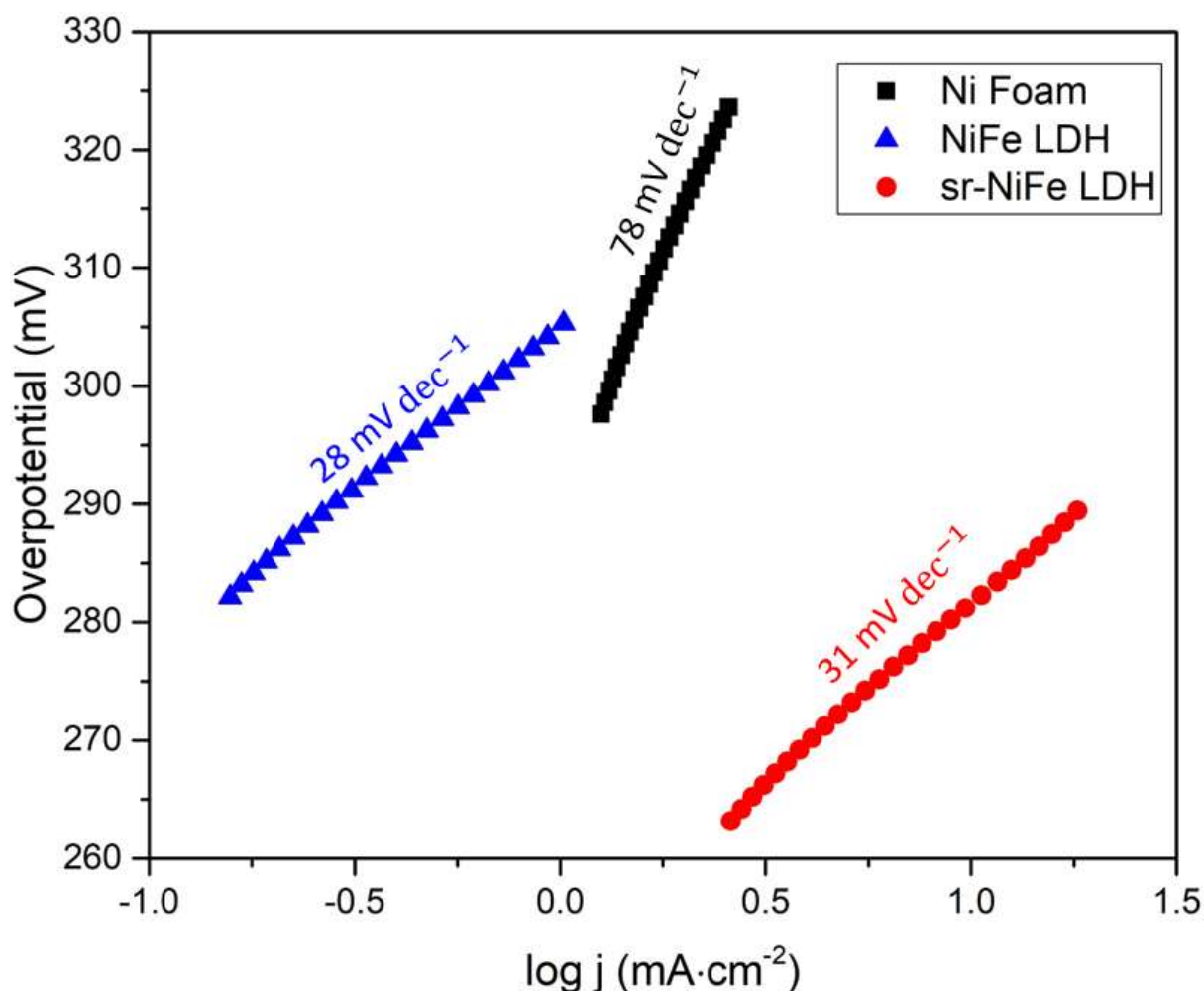


**Figure 3.4.2: Representative Tafel plots and quoted slopes,  $b$ , for pure nickel foam, as-synthesized NiFe LDH and the size-reduced material.**

In order for the catalytic improvements to be allocated to an increase in edge site density specifically, it is an important step at this point to attempt to dispel any possible alternative effects. There are a number of studies which deem exfoliation to be a significant source of OER performance enhancement for NiFe and other LDHs.<sup>103, 104</sup> This necessitates that the planar surfaces of the platelets contain a significant density of active sites. This, in turn, depends on the grade of the material. Large numbers of defects and vacancies across such surfaces may result in more activity and can be engineered to improve surface catalysis.<sup>105</sup> The material reported in this work is synthesized such

that it displays a high degree of crystallinity, regularity and compositional purity and hence, any observable increase in active site density upon exfoliation should be minimal compared to that of the highly active edge sites. One method of approach in examining this point is to observe by AFM the average platelet thickness in the samples before and after sonication to try and detect whether or not there actually is any exfoliation (Figure 3.4.3). The observable height profiles of the respective cases, sampled over similar number of particles, demonstrate no clear sign of exfoliation. In fact, the sonicated material produces a larger mean thickness value overall with an unsurprisingly broader distribution of values and reduced correlation between lateral platelet dimensions and thickness (Figure A3 in Appendix A).

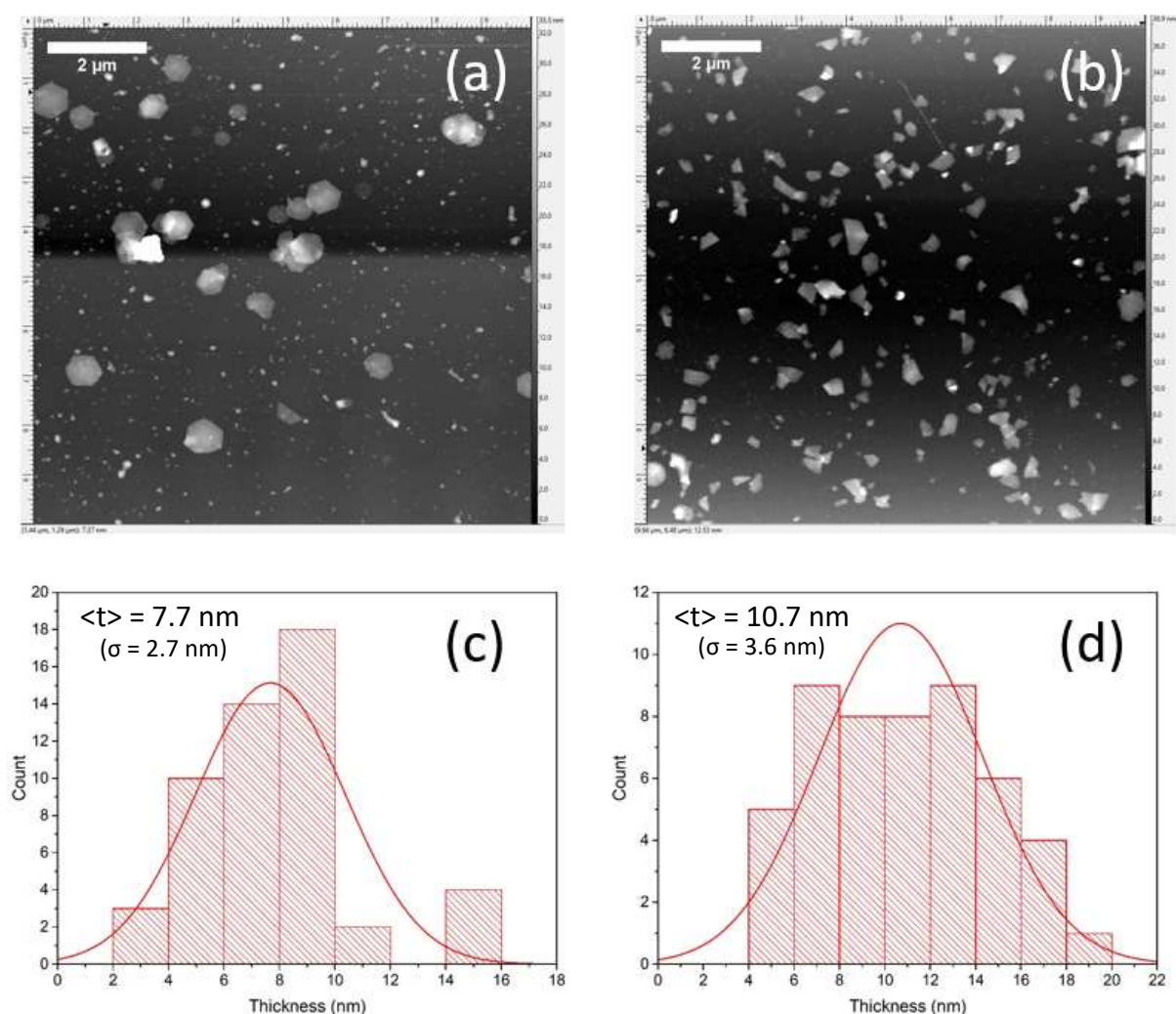


**Figure 3.4.3: Typical height profile areas and associated platelet thickness distributions for the as-synthesized (a, c) and post-sonication (b, d) NiFe LDH.**

It is understood that re-stacking may play its part in the AFM result as the sample is allowed to dry, but even so exfoliation would be detected. An additional electrochemical approach can be applied here called electrochemical surface area (ECSA) analysis. This method allows one to estimate that area across the sample surface which is electrochemically active by utilizing its relationship with the double layer capacitance ( $C_{DL}$ ) via strategic CV analysis (details in Appendix C). The results for both the as synthesized and sonicated platelets are presented in Figure 3.4.4. The ECSA values are estimated based on the anodic and cathodic  $C_{DL}$  to be 28.73 and 26.48  $\text{cm}^2$  respectively. Again, this is perhaps a non-intuitive result but one which can strongly suggest against the likelihood that active planar surfaces are exposed upon tip-sonication. With that, the demonstrated potential drop upon size-reduction (Figure 3.4.5) is encouraging but can be optimized further in terms of edge-site density with centrifugal size selection of the fragmented platelets because there remains a relatively wide size distribution after treatment (Figure 3.3.3 d). Herein lies one of the principle objectives of this work; to use size selection of sr-NiFe LDH platelets to demonstrate some degree of positive correlation between  $\langle L \rangle$  and OER catalysis ( $\propto 1/\eta$ ).

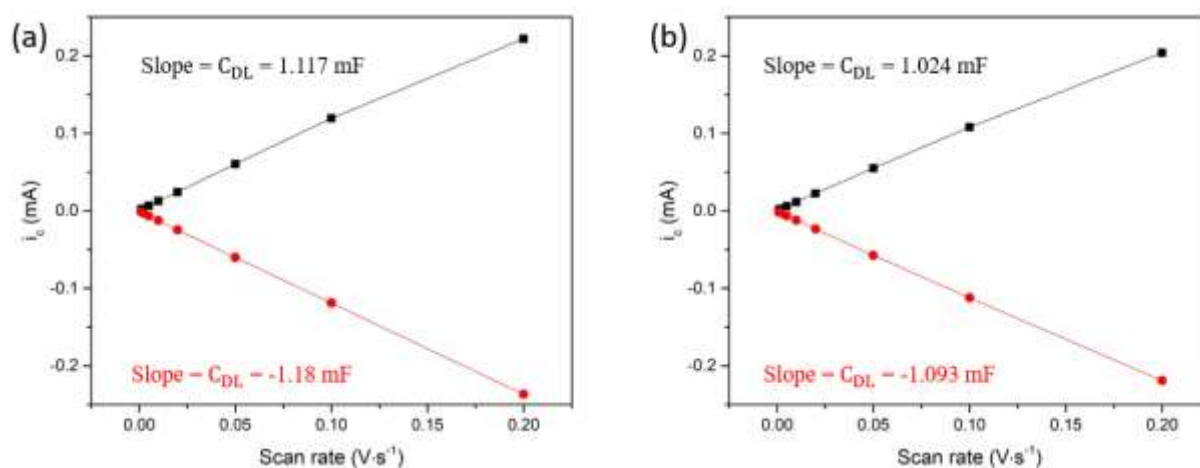


**Figure 3.4.4:** Cathodic (red circle) and anodic (black square) charging currents measured at 0.1 V vs Ag/AgCl reference at scan rates 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1 and 0.2  $\text{V}\cdot\text{s}^{-1}$  for (a) as-produced and (b) sr-NiFe LDH.

In order to demonstrate this relationship, three separate sr-NiFe LDH dispersions with unique size distributions were prepared (Figure 3.4.6) from the same batch of synthesized platelets using similar parameters as those presented in section 3.3. In an ideal situation, dispersions would be used whose standard deviations do not overlap with one another at all. Although the average particle sizes

are unique within the estimated uncertainty values, the particles are not unique when one considers the  $\sigma$  values. In fact, there is considerable overlap, as demonstrated in Figure 3.4.6 (g). The difficulty with preparing completely unique dispersions in this sense for the given NiFe LDH material is that the overall size distribution of the useable sr-NiFe LDH particles is relatively narrow to begin with. Further narrowing of the size-selected sr-NiFe platelets would require repeated centrifugation steps and longer centrifugation time which would drastically decrease the final concentrations. While very much possible this is unnecessary in the given circumstances. Particle size distributions with some slight overlap should be enough to demonstrate unique electrocatalytic behaviour in OER.

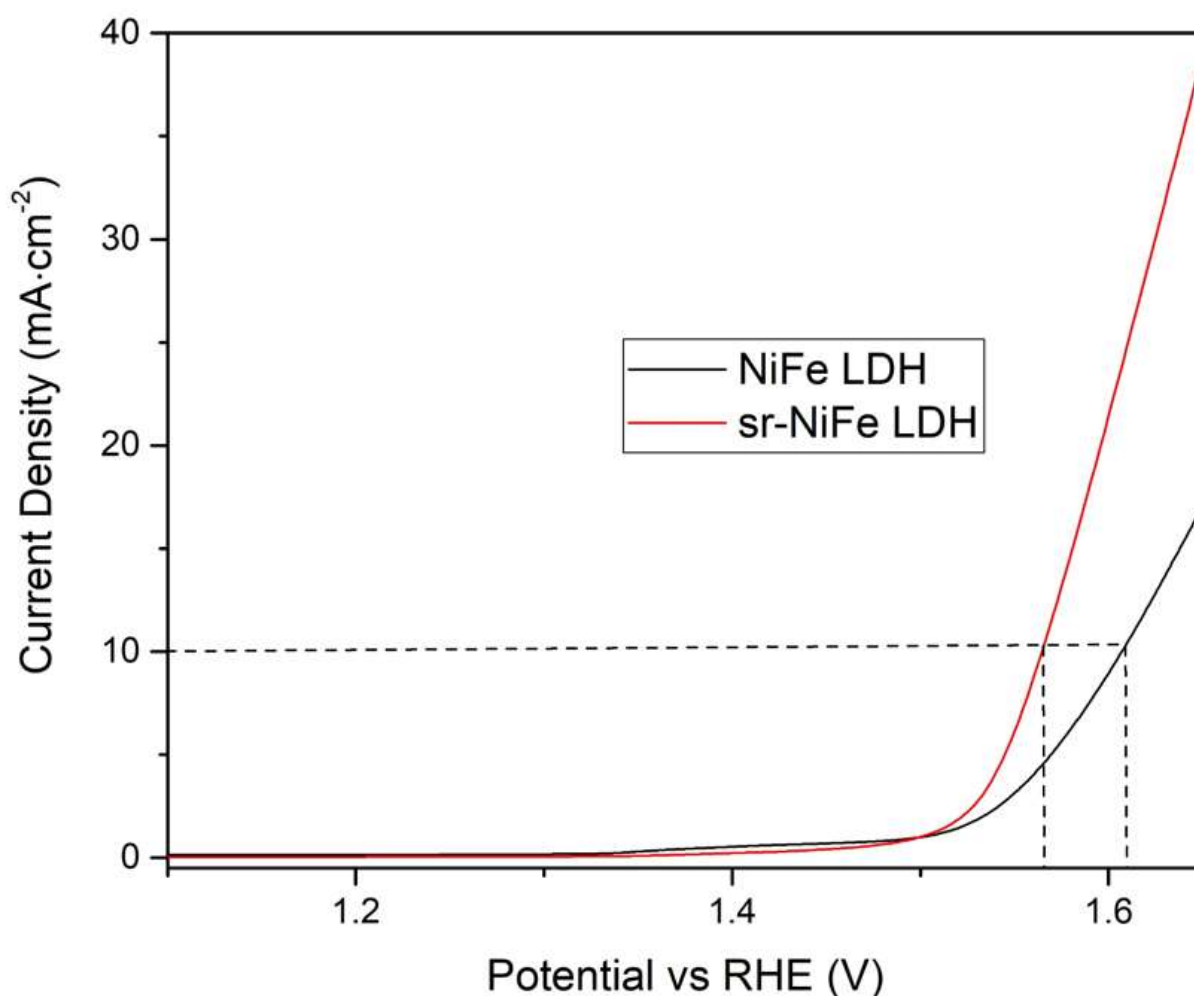


**Figure 3.4.5:** Polarization curves for electrodes prepared with as produced NiFe LDH and size reduced NiFe LDH.

Electrodes were prepared using the three respective particle dispersions by homogeneously depositing them across the surface of a 1 cm<sup>2</sup> nickel foam substrate, heated to 100 °C. Homogeneous deposition was achieved using a sonication-assisted spray tool (USI Prism Ultracoat 300) where

particles are subjected to sonic energy via a sonic tip in an *in-situ* manner as they are sprayed onto the surface. This improves not only homogeneity but also reduces clustering effects which can be prominent in smaller particle dispersion with a potentially drastic effect on the performance. It is possible to gain some insight into the homogeneity of the coverage via SEM imaging over large sample areas (Figure 3.4.7). With this, one can clearly see that complete and uniform coverage can be achieved which is expected to be reflected in the electrocatalytic performance.

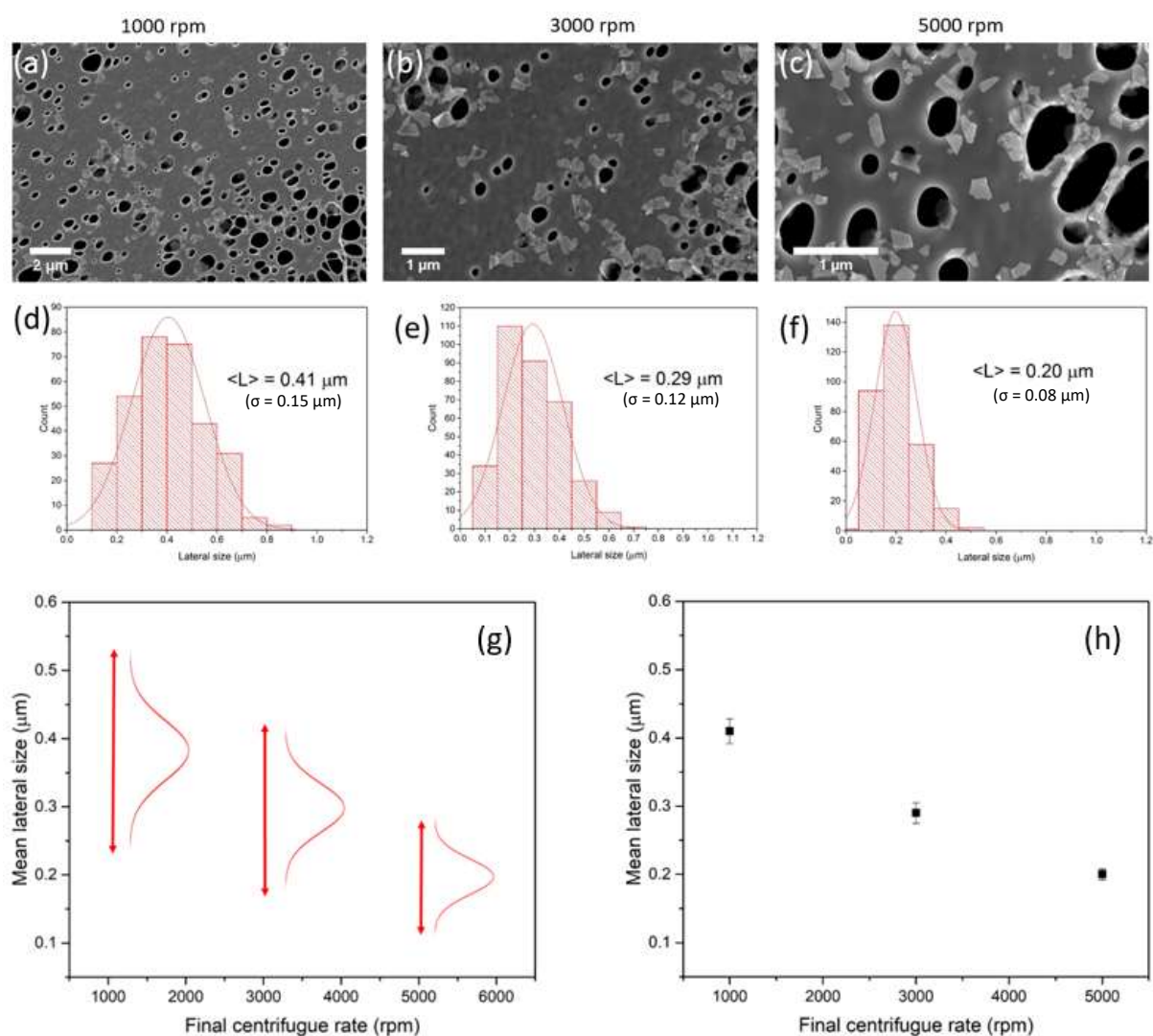


**Figure 3.4.6:** (a) – (c) SEM micrographs and (d) – (f) accompanying size-distribution histograms for sr-NiFe LDH with final centrifugation rate 1000, 3000 and 5000 rpm respectively. Also, graphs of mean particle size vs final centrifugation rate with (g) standard deviations and (h) estimated uncertainty intervals indicated.

By observation of initial polarization curves for the three samples, such as those seen in Figure 3.4.8 (a), it is not possible to see an obvious trend in the quoted onset potentials (@ 10 mA.cm<sup>-2</sup>). Instead of studying immediate linear voltammograms it is more useful to cycle the sr-NiFe LDH

electrodes using CV sweeps within a fixed potential range which should allow the materials to stabilize to some extent.<sup>40, 106</sup> This should provide a more realistic set of overpotential values for comparing electrode performances (Figure 3.4.8 b). During early cycling one can see the overpotential fluctuating quite rapidly in the range 240 - 290 mV. During this time, it is thought that a combination of subtle crystallographic phase changes and active-site degradation produce the graphs shape. Phase changes have been observed for various hydroxides based OER catalysts in alkaline media.<sup>107</sup> The transition involves an initial  $\alpha$ -hydroxide and final  $\gamma$ -oxyhydroxide phase, the latter being a more highly ordered and densely packed crystal.<sup>91, 108, 109</sup> Some hydroxides like  $\text{Ni}(\text{OH})_2$  demonstrate additional  $\beta$ -hydroxide/oxyhydroxide phases with even higher packing densities. The transitions generally take place during early cycling and allows for some improvement in electrochemical performance (i.e. lower overpotentials). This phenomenon is well established for monometallic cases like  $\text{Ni}(\text{OH})_2$  but not as much for a mixed-metal hydroxide like NiFe LDH. It is likely that the observed overpotential fluctuation is attributed, in part, to some  $\text{Ni}(\text{OH})_2$  impurities in the active material, or perhaps more likely, some exposed nickel substrate. However, the effect appears too strong to derive from minor nickel contributions alone and it seems that some phase transitions are taking place for the NiFe hydroxide/oxyhydroxide system too.

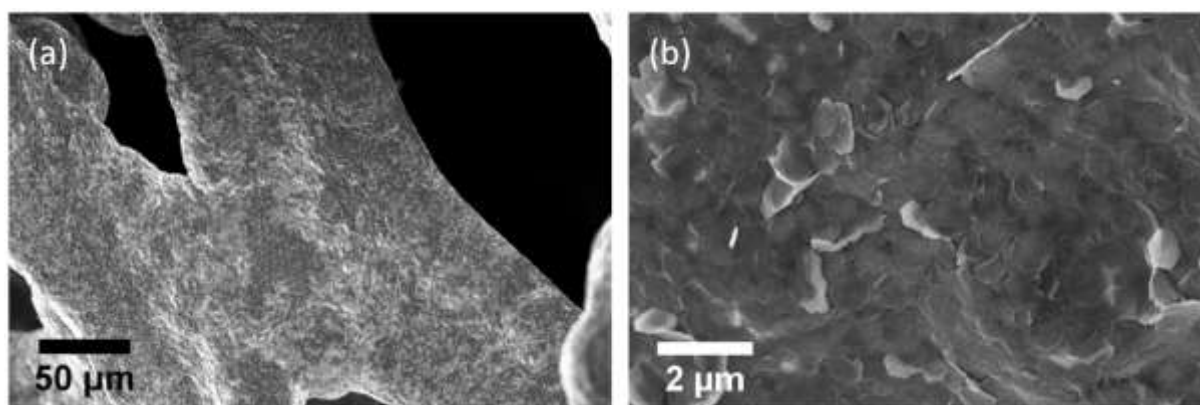


**Figure 3.4.7: Digital micrographs from SEM of NiFe LDH hexagonal platelets deposited on Ni foam substrate, at low and slightly higher magnification.**

Following this, the subsequent sharp rise in  $\eta$  in Figure 3.4.8 (b) from cycle number four onward is yet to be rationalised. In this time, it is thought that the active material undergoes considerable degradation in response the physical catalytic processes taking place at platelet edge

sites as well as the resulting electron and ion diffusion within the host structure. The precise nature of this degradation as well as the preceding apparent phase behaviour will be the focus of Chapter 4. Beyond this the  $\eta$  values approach equilibrium for the three samples and one can start to see an apparent correlation between the overpotentials and the final centrifugation rate (and hence  $\langle L \rangle$ ). This is a subtle difference between samples in this case but provides a proof-of-concept representation of the proposed theory which links platelets dimensions to catalytic performance. The entire process can be repeated with similar results. Figure A4 in Appendix A is an example of a repeated data set over a slightly narrower initial sr-NiFe LDH size distribution. In that case, there was somewhat less of an overlap between the centrifugation steps of 500, 4000 and 7000 rpm which resulted in a clearer separation of equilibrium  $\eta$  values for the cycled catalysts.

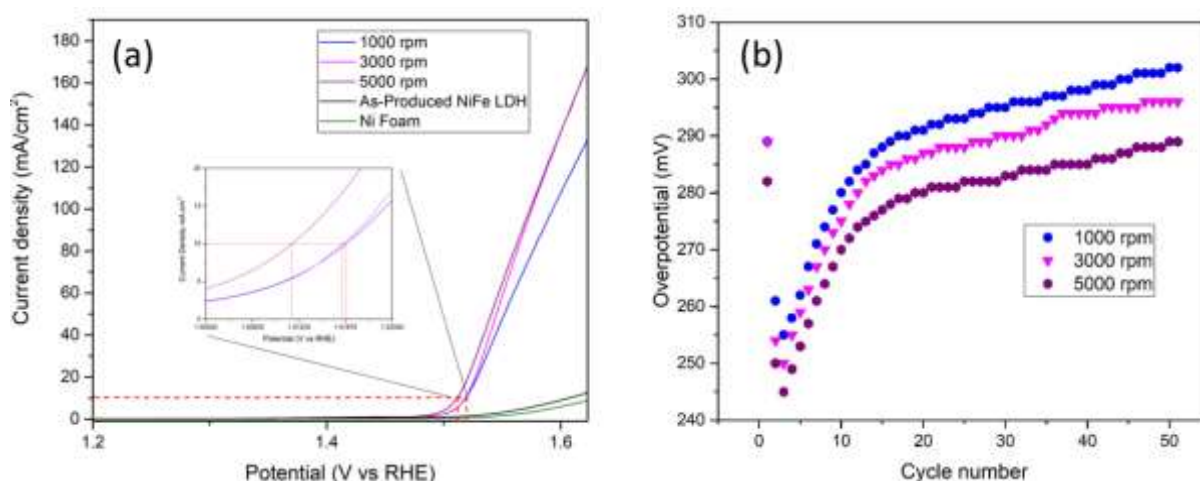


**Figure 3.4.8: (a) Initial polarization curves and (b) overpotential (@  $10 \text{ mA} \cdot \text{cm}^{-2}$ ) values as a function of cycle number for catalysts prepared using size selected sr-NiFe LDH of final centrifugation rate 1000, 3000 and 5000 rpm, cycled fifty times in the potential window 0 – 0.6 V vs Ag/AgCl.**

This simple and practical method of OER activity enhancement should extend to many of the other electrocatalytically active layered and/or planar materials under review in this field, with similar results. Families of materials with which this may be relevant include transition-metal dichalcogenides<sup>110, 111</sup> (TMDs), MXenes<sup>112</sup> (transition metal carbide/nitrides), transition-metal oxides<sup>113, 114</sup> and hydroxides,<sup>21, 115</sup> within which lies the LDH family, as well as non-metal 2D materials, most of which are considered as composite additives in this field, such as black phosphorous<sup>116, 117</sup> (BP) and graphene.<sup>77, 118, 119</sup> Along with lateral platelet size engineering, other methods of electrocatalytic improvement are regularly considered for these materials and include

defect engineering<sup>105, 120, 121</sup> and nanostructuring.<sup>20, 39, 122</sup> The goal is to take practical, affordable 2D catalysts and to optimize their performance using such treatment methods so as to enhance the electrocatalytic abilities to competitive levels within the field of alkaline water electrolysis.<sup>114, 123, 124</sup> Common metrics used in this work to evaluate the performance include the electrocatalytic overpotential, Tafel slopes, current stability and cycling capability. While the data thus far suggests successful size engineering for pure sr-NiFe LDH down to  $\eta = 245 \pm 7$  mV and Tafel slope of 31 mV dec<sup>-1</sup> (for  $\langle L \rangle = 0.2$   $\mu$ m, Figure 3.4.2), further processing is introduced to reduce the effects of cycling in alkaline conditions, which has been seen to dramatically affect the overpotential (Figure 3.4.8 b). This must be addressed should the sr-NiFe LDH material be considered as a realistic high-performance OER catalyst.

In the interest of improving cyclability and combating the  $\eta$  losses, composite studies are carried out in addition to size treatment, the aim being to minimize overlap of adjacent NiFe LDH platelets and instead providing an integrated conductive matrix which can facilitate the rapid electrochemical mechanism. A number of interesting composite materials have been suggested and researched for LDH-based OER catalysis in recent times including various carbon allotropes,<sup>125, 126</sup> metal-organic frameworks<sup>127, 128</sup> (MOFs) and more novel materials, often presenting nanowire morphologies.<sup>129, 130</sup> Carbon nanotubes (CNTs) have most notably been demonstrated as useful additives to this end, yielding improved overpotential, Tafel slope, conductivity and stability when coupled with NiFe LDH in alkaline electrolyser systems.<sup>122</sup> CNTs represent a well-established option as a conductive additive in electrochemistry while also being readily available and for these reasons will be studied here to determine their compatibility with size-controlled sr-NiFe LDH. The aim is simply to observe the extent to which the long-term performance of the catalyst can be improved in this way.

Composites of the sr-NiFe LDH and single-wall CNTs (SWCNT, utilized for their superior electrical properties compared to multi-wall nanotubes)<sup>131</sup> were made by mixing IPA dispersions of each together. With both concentrations known, the specific weight ratios of the two components were controlled. In order to achieve a well-integrated composite system, good connectivity needed

to be achieved. Simply mixing the components did not suffice. The affinity between LDHs and CNTs is weak and in addition to some aggregation effects in both starting components, it is unsurprising that the electrochemical performance is not only unimproved but in fact hindered if tested directly after mixing. Some relatively low-power tip-sonication after mixing (Fischer Scientific Sonic Dismembrator Ultrasonic Processor at 40% power for 10 min) can help achieve higher connectivity within the LDH-CNT matrix which is reflected electrochemically. Figure 3.4.9 demonstrates the effect a well-integrated CNT nanocomposite can have on the overpotentials during early cycles as well as highlighting why it is necessary to supply mild sonication after mixing the components. Using this preparation method, composites of different CNT weight percentages were prepared and compared by cycling 50 times under OER conditions.

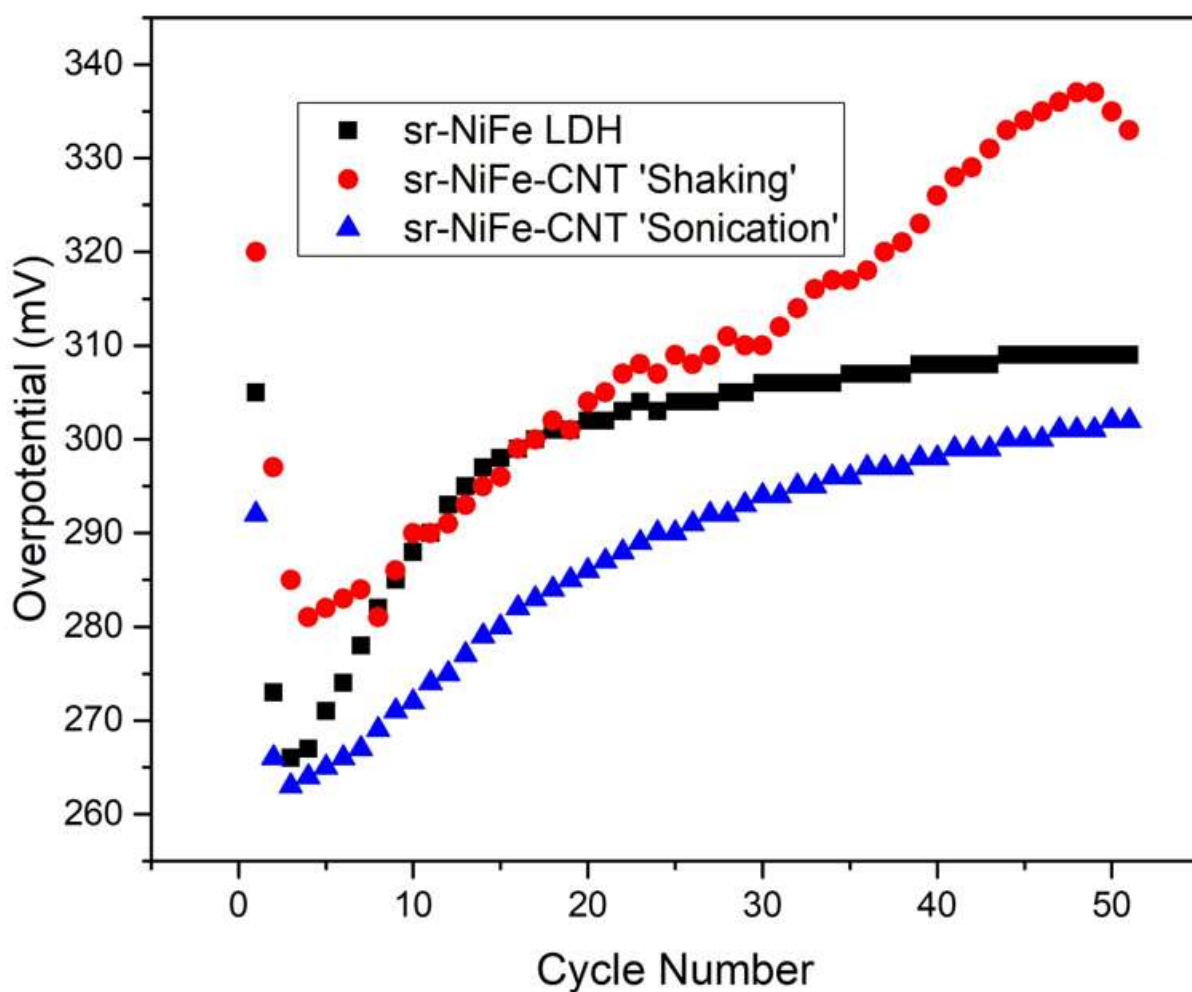


**Figure 3.4.9:** Overpotential values as a function of cycle number for catalysts of sr-NiFe LDH in composite with SWCNTs assisted by shaking or ultrasonication. Pure sr-NiFe catalyst for reference.

What is immediately obvious from the OER cycles with SWCNT additives (Figure 3.4.9 & 3.4.10) is the improved retention of the overpotential values beyond 4 – 5 cycles. This suggests perhaps a relaxation of the degradation effects observed in the pure material, which was judged to drastically hinder  $\eta$  values, or perhaps simply improved kinetics offsetting such effects in early cycle life. The next task is to optimize this effect to achieve the lowest possible stable  $\eta$  value. Although mass loading was previously optimized as  $0.12 \text{ mg} \cdot \text{cm}^{-2}$  for pure NiFe LDH electrodes, replacing some percentage of the mass with a foreign species will likely affect this. Mass loading in the range  $0.12 - 0.18 \text{ mg} \cdot \text{cm}^{-2}$  was tested for samples containing 10, 15 and 20 weight % of SWCNT with NiFe LDH. If the mass loading is kept consistent across samples of various SWCNT wt% an inverse relationship is observed with the electrocatalytic output decreasing (higher  $\eta$  values) with more SWCNT. This is expected as there would be less and less active component in each case. One can compensate for this by increasing the mass loading to a particular value for each composite. The ideal loading in each case (Figure 3.4.10 c) demonstrated similar electrocatalytic behaviour.

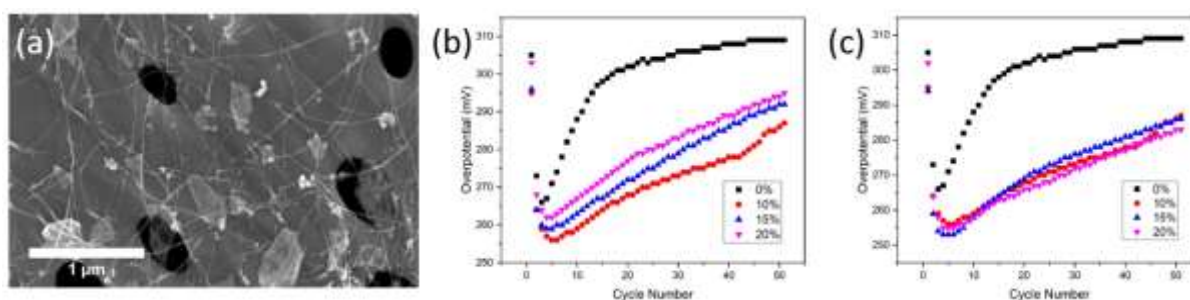


**Figure 3.4.10: (a) SEM micrograph showing the connective matrix of SWCNTs between adjacent LDH particles. Also, Overpotential values as a function of cycle number for sr-NiFe LDH composites 0, 10, 15 and 20 weight % SWCNTs, both (b) without and (c) with mass loading optimization.**

Combining fragmentation and centrifugation techniques allows for an optimized electrode performance (Figure 3.4.11). The optimized electrode was prepared by taking the fragmented material, applying centrifugal size selection and selecting the material with a final rate was 5000 rpm and finally preparing a composite with 20 wt% SWCNT in IPA before spraying on nickel foam to  $0.17 \text{ mg} \cdot \text{cm}^{-2}$  mass loading. The final product produced an impressive electrocatalytic output with the lowest overpotential observed in this work ( $237 \pm 7 \text{ mV}$  vs RHE) and more importantly, the best retention through 50 cycles with just 7% increase. Upon further cycling, a stable value is reached at

around 275 mV after 200 cycles (full cycling data in Figure A5, Appendix A). As suggested by the comparative data in Table 1 for various state-of-the-art NiFe LDH composites in the OER field today, the fully optimized catalyst in this work realizes a highly competitive performance and activity for water electrolysis, considering the facile, inexpensive nature of the processing steps.

By studying Tafel slopes (Figure 3.4.11 b) one can gain some insight into the improved electrocatalysis of the optimized electrode. The increase in  $b$  upon initial introduction of carbon additives suggests the sensitivity is inhibited but once particle size-reduction is applied, the value returns almost to that of the pure sr-NiFe. With considerable particle size reduction within a given electrode, an increase in contact area between the active material and conductive SWCNT matrix is achieved which is likely allowing for this positive affect on the Tafel slope. This in turn suggests improved kinetics within the optimized electrode which will have a positive effect in the electrochemistry.

**Table 1: Comparative OER activities for various competitive NiFe LDH catalyst systems.**

| Catalyst                        | $\eta$ @ 10 mA · cm <sup>-2</sup> (mV vs RHE) | Current density (mA · cm <sup>-2</sup> ) | Tafel slope (mV · dec <sup>-1</sup> ) | Mass loading (mg · cm <sup>-2</sup> ) | Substrate |
|---------------------------------|-----------------------------------------------|------------------------------------------|---------------------------------------|---------------------------------------|-----------|
| IrO <sub>2</sub> <sup>38</sup>  | 338                                           | 10                                       | 47                                    | 0.21                                  | GC        |
| NiFe LDH <sup>44</sup>          | 360                                           | 5                                        | -                                     | 0.12                                  | NF        |
| NiFe 'nanosheets' <sup>38</sup> | 302                                           | 9.351                                    | 40                                    | 0.07                                  | GC        |
| NiFe-CNT <sup>122</sup>         | 220                                           | 10                                       | 31                                    | 0.25                                  | GC        |
| NiFe-rGO <sup>77</sup>          | 230                                           | 10                                       | 42                                    | 0.25                                  | GC        |
| NiFe@NiCoP <sup>132</sup>       | 220                                           | 10                                       | 49                                    | 2                                     | NF        |
| <b>sr-NiFe</b>                  | <b>245</b>                                    | <b>10</b>                                | <b>31</b>                             | <b>0.13</b>                           | <b>NF</b> |
| <b>sr-NiFe-CNT (this work)</b>  | <b>237</b>                                    | <b>10</b>                                | <b>32</b>                             | <b>0.16</b>                           | <b>NF</b> |

Chronopotentiometry (Figure 3.4.11 c) represents a more practical test of performance for an electrolyser cell with no cycling but rather an overpotential gradient when subjected to constant current density. After 1 hour the overpotential value of the fully optimized catalyst (blue curve) remains around 270 mV with a relatively shallow slope (Figure A6 in Appendix A) and rises to 295 mV after 12h. This performance represents improvement over similar NiFe LDH-carbon-based composite materials in the field of OER catalysis<sup>77, 122, 133</sup>. It suggests a fully optimized NiFe LDH

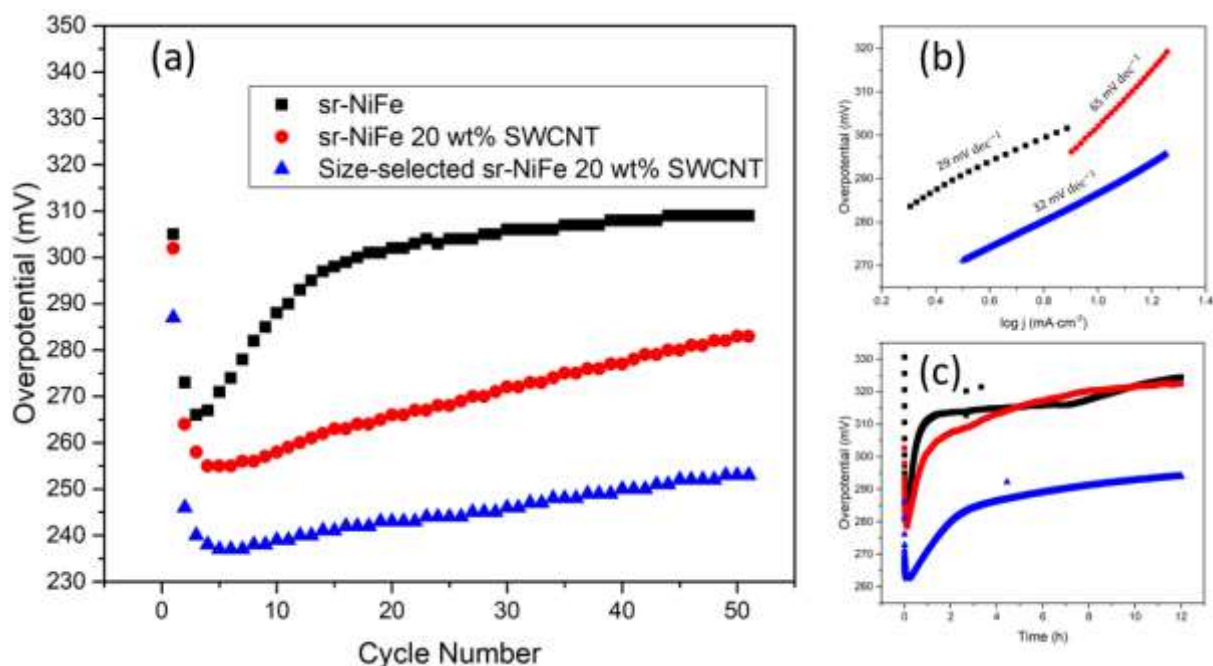


**Figure 3.4.11:** Comparison of (a) overpotentials through 50 cycles, (b) Tafel slopes and (c) chronopotentiometry curves through 12 hours at  $10 \text{ mA} \cdot \text{cm}^{-2}$  for OER electrodes prepared using size-selected sr-NiFe LDH with 20 wt% SWCNT, a non-size-selected composite and pure sr-NiFe LDH.

catalyst processed in organic media with mean platelet size on the order of  $0.2 \mu\text{m}$  with 20 wt% SWCNT additive and enhanced contact between components by additional low power sonication. IPA has deemed itself an extremely useful host for the processing steps presented here due to its ability to hold NiFe LDH in suspension and put little stress on the titanium-containing tip during sonication, allowing for prolonged treatment times if necessary.

### 3.4.2 sr-NiFe LDH Processed in DI Water

Certain aspects of carrying out the size-reduction steps and composite preparation in aqueous conditions make it less appealing than organic solvents like IPA. The first issue concerns long-term tip-sonication which is a technique at the forefront of this study. As touched on above, during sonication the titanium-containing tip will degrade to some extent as a result of the energy being exerted on it as high-power sonic waves pass through. The degradation can cause physical breakdown at the tip releasing small titanium particles ripped from the head. The extent to which this happens depends on the sonication time, frequency, power setting and the choice of solvent. By its nature, DI water will put more pressure on the sonic tip, perhaps due to its high ionic affinity or its viscosity and surface tension properties. In any case, sonication in DI water on the time scales used

thus far can cause large amounts of Ti contamination, to such an extent that mass loading of the active material cannot be accurately achieved. Hence, the transfer step to IPA in section 3.4.1. Acquiring some selected-area EDX spectra to accompany TEM images as in Figure 3.4.12 can help demonstrate  $\leq 100$  nm titanium particles alongside NiFe LDH platelets when similar sonication times are applied in DI water.

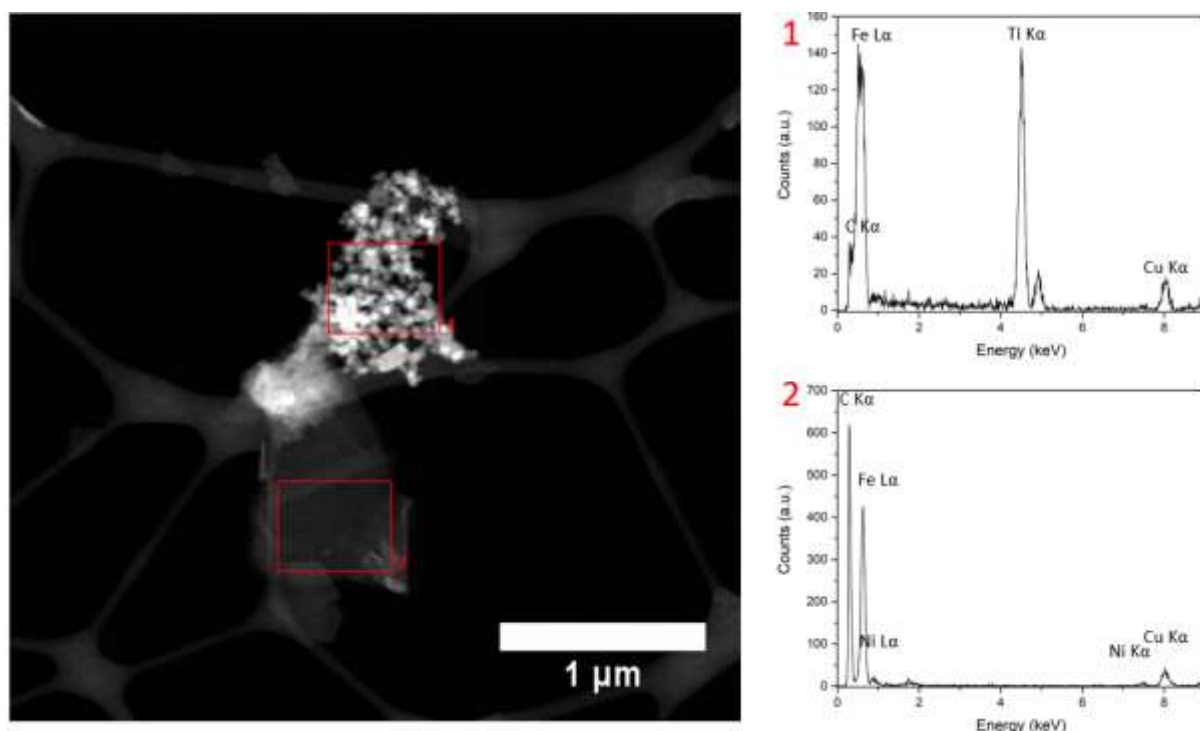


**Figure 3.4.12: TEM image accompanied by EDX maps of the selected areas 1 and 2, suggesting the presence of titanium particles as impurities.**

The effect of such nanoparticles as impurities on the electrochemical capabilities of the sr-NiFe catalyst can be elucidated via simple CV comparison. Figure 3.4.13 illustrates just that. Predictably, going from final centrifugation rate of 500 rpm to 5000 rpm and 10,000 rpm, the platelet size will decrease significantly which should be reflected in the overpotentials. From the SEM images in the figure however, it can be seen that at gradually higher rates, increasing content of Ti contamination is also introduced as the titanium nanoparticles are themselves, selected into the dispersions with the highest concentration for 10,000 rpm (Figure 3.4.13 d). When studying the electrochemistry here there are essentially two competing effects at play when applying centrifugation steps. Namely, platelet size reduction, which will improve the performance, and titanium contamination, which will hinder it. Studying the polarization curves in Figure 3.4.13 (a), a

subtle overpotential drop is observed between platelets of final centrifugation rate 500 rpm and 5000 rpm (mean lateral dimensions 0.54 & 0.17  $\mu\text{m}$ , respectively) along with some minor introduction of titanium contamination (SEM micrographs Figure 3.4.13 b & c). Increasing to 10,000 rpm brings about a substantial jump in contamination. So much so that the mean NiFe platelet size is not quantifiable by observation under SEM. Additionally, the  $\eta$  value worsens for this sample. This is due to the loss of active NiFe LDH material loaded onto the nickel foam substrate during electrode preparation as the titanium begins to represent a more significant mass fraction of the sample. This is quite obviously a significant issue in the electrode preparation scheme and will limit the minimum achievable platelet size for sr-NiFe LDH processed in water. Contamination to this extent is not observed when the same methodology is applied to organic-based NiFe LDH dispersions.

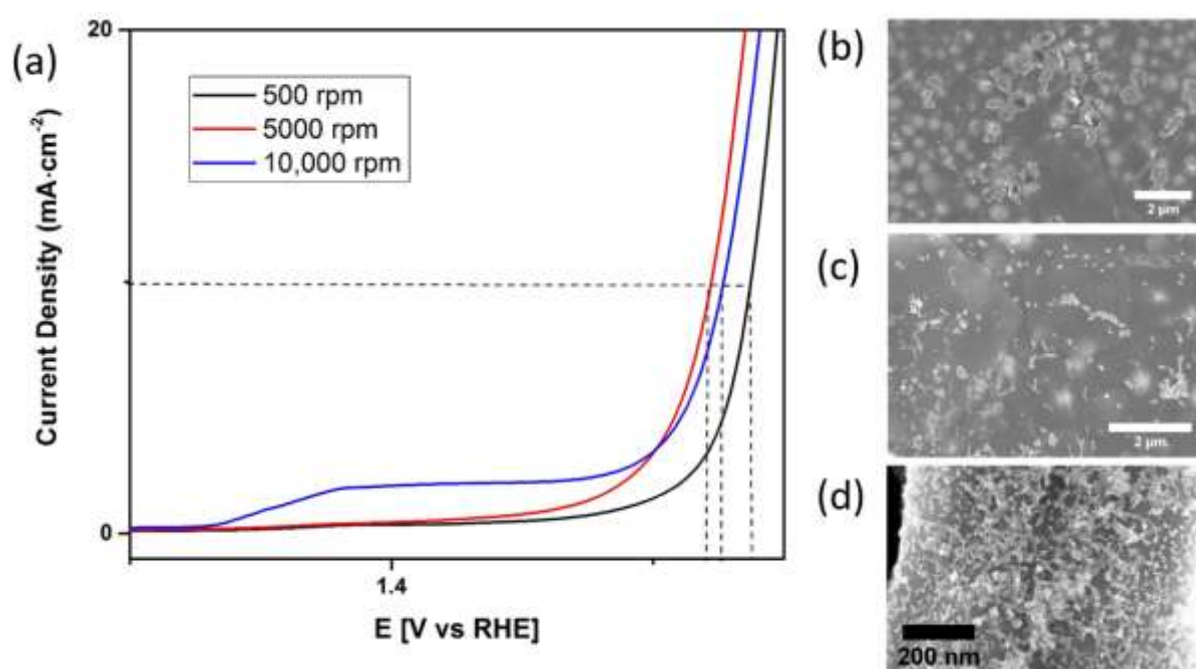


**Figure 3.4.13:** (a) Polarization curves for catalysts of size-selected sr-NiFe LDH processed in water with final centrifugation rates 500, 5000 and 10000, and (b), (c) & (d) SEM images of the respective material.

The second issue to this end concerns composite preparation. In order to repeat the preparation of SWCNT composites with sr-NiFe in water, a relatively stable suspension of nanotubes is necessary. However, SWCNT stability in water is not as good as in IPA and requires a surfactant to assist in dispersing them. Common surfactants for this purpose include polyvinylpyrrolidone (PVP) and carboxymethylcellulose (CMC) and while they are efficient at forming stable suspensions, their presence in the final composite is predicted to inhibit the interfacial connectivity between sr-

NiFe LDH and SWCNT and in doing so impede the gravimetric rate capability and limit the overpotential of the resulting electrolyser cell.

Having said that, it is still desirable to pursue the route of aqueous processing because of the potential for different stability effects of the final catalyst and as we know, the stability of the active NiFe platelets is a key factor in the electrocatalytic performance of the material over long time scales and cycle life. The exact nature of the instability and electrocatalytic degradation over time will be specifically studied in Chapter 4, but for now the goal is to observe the difference in catalytic behaviour of water-processed NiFe LDH compared to IPA and if possible, draw some conclusions as to the dependence of the catalyst' built-in stability on the processing conditions.

Firstly, to help elevate the effect of Ti contamination on fragmented platelets, dispersions beyond final centrifugation rate 5000 rpm are not considered as useable material. Additionally, sonication times are dropped from 7 hours to just 1 hour of pulsed tip-sonication (5 s on, 5 s off) at 60% power under cooling at 5 °C to minimize degradation of the tip head. Water being a superior solvent for NiFe LDH means this is quite enough fragmentation to produce satisfactory size reduction. Figure 3.4.14 nicely illustrates this with platelet size reduction down to  $0.15 \pm 0.01 \mu\text{m}$  in a sample, apparently clean of titanium particles by studying low magnification SEM.

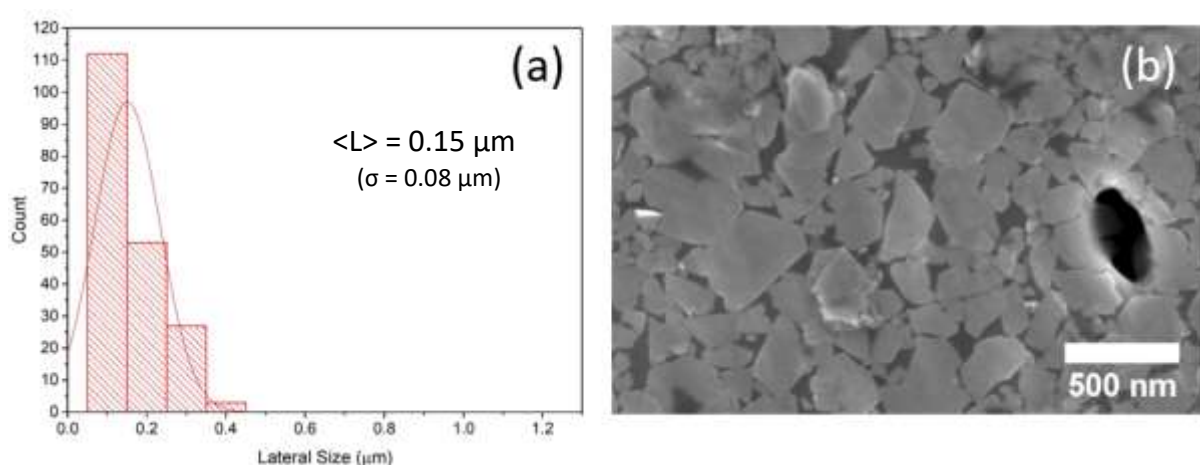


**Figure 3.4.14:** (a) Size distribution histogram (b) SEM image of NiFe LDH fragmented in DI water.

Next, this size-reduced material is to be tested for its electrocatalytic capability in conjunction with SWCNT additive using a PVP surfactant (Tuball™ BATT). Catalysts were

prepared using the optimum 20 wt% carbon additives, as exacted previously, with the mass fraction of PVP being accounted for. Results show some clear instability with cycling of the catalyst 150 times. Figure 3.4.15 (red curve) demonstrates the instability and unpredictability of including non-active components into a catalyst in any appreciable mass fraction. The overpotential values are poor when compared with the equivalent IPA-based electrode and fail to settle towards an equilibrium value, continuing to rise beyond 100 cycles. In order to combat this effect additional steps must be taken to attempt to remove as much PVP as possible.

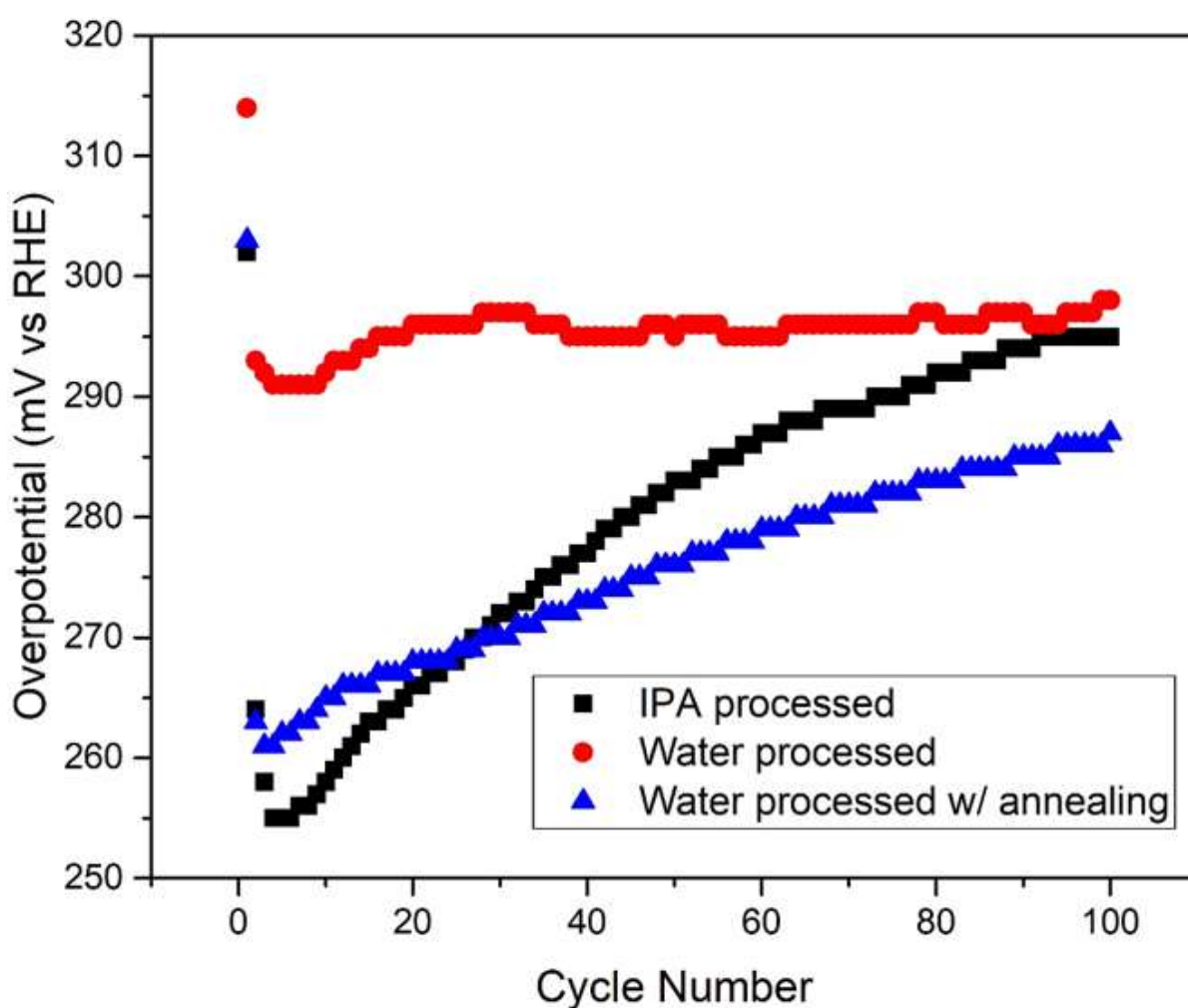


**Figure 3.4.15:** Comparison of overpotential values as a function of cycle number for catalysts of sr-NiFe LDH – SWCNT composites processed in IPA and DI water (with & without annealing).

With a melting point of 177 °C,<sup>134</sup> it may be possible to remove some of the PVP from the composite electrode after spraying onto the nickel substrate by evaporation without denaturing the active material. A study carried out by Hobbs *et al.*<sup>135</sup> investigated the effects of heating on the

structure, morphology and composition of NiFe LDH platelets by way of *in-situ* TEM heating with SAED and EDX mapping. Above 250 °C an initial amorphization is observed followed by various phase changes to oxide and spinel compounds at elevated temperatures of 850 °C. Importantly, based on these results, one can confidently heat the sr-NiFe LDH – SWCNT composite to 200 °C which will give a good chance of removal of some unwanted PVP without destabilization or any change of phase in the active material. The only concern of heating to this degree is the removal of water molecules from intercalation sites which has been demonstrated at temperatures below 200 °C using TGA analysis (Figure 3.2.5). This may in turn have an effect on the interlayer spacing of the annealed material if rehydration doesn't occur fully upon cooling.

So, 2 hours of heating at 200 °C was applied to electrodes after spraying in the hope of demonstrating some improvement in the OER cycling. Figure 3.4.15 illustrates the effect of the 'annealing' step on the cycling performance. Compared to the data for the catalyst where annealing was carried out as part of the processing, the curve suggests substantially lower overpotential values with a minimum as low as 261 mV as well as showing a more regular shape. Also comparing with IPA-processed composites the curve shows notable differences. The most significant difference is the slope of the curve from cycle number four onward. The flatter slope in the water case says something about the stability of the active material through the course of 100 cycles. It is difficult to tell based on this data alone whether or not there is a significant removal of water affecting the performance here. However, an improved stability of cycling is observable for aqueous processed NiFe LDH catalysts with and without carbon additives or any annealing steps. So, these results can be considered conclusive in that the processing conditions reflect on the long-term performance for sr-NiFe LDH composite catalyst systems.

Additionally, CP curves reflect the same consensus. While the examples in Figure 3.4.16 suggest lower overpotential capabilities for the water-processed material, what is most important is the general slope observed after  $\eta$  reaches its minimum value after around 10 minutes in each case. The relative steepness once again is indicative of the stability of the active sr-NiFe LDH platelets with more stability being shown from water processing and hence, a flatter curve is observed. This is more

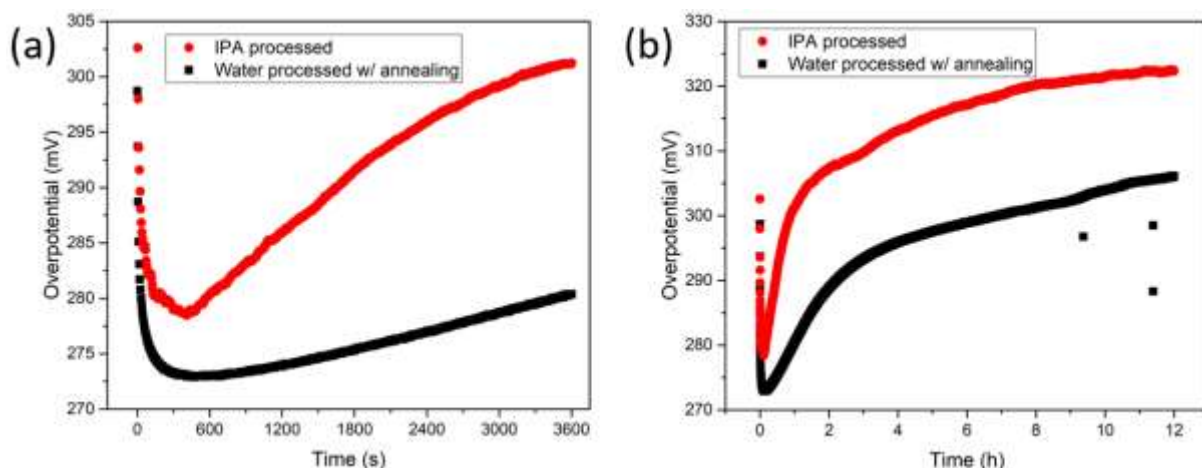


**Figure 3.4.16:** (a) Chronopotentiometry through 12 hours curves for catalysts of fully optimized sr-NiFe LDH – SWCNT composites processed in IPA and DI water, respectively. (b) Close-up image of the first hour.

obvious over short time scales (Figure 3.4.16 a). The effect means that overpotential can level off at a lower equilibrium value in the long term. This is clearly observable in Figure 3.4.16 (b) which measures the overpotential over 12 hours. This tells us in no uncertain terms that while there may be a number of difficulties involved when carrying out size reduction processing in water in a practical sense, the fact is that exchanging to an organic solvent will hinder the long-term electrocatalytic capability and so it is worth implementing certain additional measures to carry out the entire scheme in DI water.

### 3.5 Conclusions

In overall conclusion to this chapter, it can be said that combined post-synthesis processing techniques of fragmentation, size-selection and composite preparation have been combined to improve the electrocatalytic outlook for NiFe LDH material as a highly active nonprecious metal-based anode in alkaline electrolyser cells. This presents a low-cost, low-energy and scalable process from chemical synthesis to device preparation. Electrodes were tested with the aim of determining their practical viability in operating conditions by predominantly studying cycle life rather than conventional polarization curves to understand the processes which dominate the catalytic output in the early cycle life of an electrolyser cell. Both IPA and water present promising capabilities as solvents for processing, with the latter, when annealed, giving better long-term stability in terms of electrolyser cell overpotential as a function of time, despite the perceived difficulties involved in

dealing with aqueous media e.g. the addition of surfactants, post-annealing procedures and issues with tip-sonication. Additionally, this work so far suggests, from an electrochemical perspective, the existence of a majority of catalytically active sites around platelet edges with a minority along the planar surface based on the effect observed of controlling the mean platelet sizes  $\langle L \rangle$  on overpotentials achieved. Overall, this study aimed to utilize this effect to offer a simple yet effective set of steps which allow notable improvements in catalytic behaviour of electrochemically active platelet-like materials which is not limited to the combination of metals considered here.

### 3.6 Experimental

**Materials:** Nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , extra pure, Fisher Scientific), Iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , purity <98%, Sigma Aldrich), urea ( $\text{CH}_4\text{N}_2\text{O}_2$ , purity  $\geq 99.3\%$ , Alfa Aesar) and TEA ( $\text{C}_6\text{H}_{15}\text{NO}_3$ , purity  $\geq 99\%$ , Sigma Aldrich) were used as received without further purification.

**NiFe LDH Synthesis:**  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , urea,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and TEA were made into a 200 ml solution using DI water such that their respective concentrations were 7.5 mM, 2.5 mM, 17.5 mM and 10 mM. The resulting solution was stirred using a magnetic stirring bar at 150 rpm at room temperature for 24 h, after which a brown precipitate was observed. Next, the reaction mixture was split into two 100 ml round bottom flasks and heated with magnetic stirring (150 rpm) under reflux to 100 °C in a mineral oil bath for 48 h. Afterwards the system was allowed to cool naturally to room temperature. The entire dispersion was placed in four 50 ml centrifuge tubes and centrifuged at 3000 rpm for 10 minutes to separate the desired precipitate from the solvent. The material was then washed three times by dispersing sediments in DI water (roughly 40 ml in each tube) by shaking, and then centrifuging to separate. The clean material was then either re-dispersed in DI water and characterized or dispersed in IPA with an additional two washing steps.

**Anion Exchange:** To perform anion exchange, 100 mg of the as-prepared platelets were added to 100 ml solution of either 1 M NaCl + 3.3 mM HCl (for  $\text{Cl}^-$  anion exchange) or 1M  $\text{NaNO}_3$

+ 3.3 mM  $\text{HNO}_3$  (for  $\text{NO}_3^-$  anion exchange). In each case the resulting solution was bubbled under  $\text{N}_2$  gas for 2 h and stirred for a further 24 h (150 rpm), before being centrifuged at 3000 rpm for 5 min and the sediments collected and washed three times with DI water by centrifugation, as before.

**Centrifugal Size-Selection:** Sample dispersion of NiFe LDH in IPA or DI water were size-selected by initially centrifuging at 500 rpm using a Heraeus Multifuge X1 Centrifuge with a F15-6x100y carbon fibre rotor.

**Electrode Manufacturing:** Electrodes for OER testing were prepared by spraying NiFe LDH component onto a nickel foam substrate using a USI Prism Ultracoat 300 spray tool with the substrate kept at 100 °C. A flow rate of 0.5 mL/min was used and mass loading was monitored using a Sartorius SE2 ultra-microbalance.

**CNT Dispersions Preparation:** Dispersions of SWCNTs in IPA were prepared by adding 10 mg of SWCNT powder (P3-SWNT, Carbon Solutions Inc.) to 100 ml of solvent and applying ultrasonication by way of sonic tip (Fischer Scientific Sonic Dismembrator Ultrasonic Processor) at 40% power for 45 min assisted by a cooling system maintaining the dispersion at 5 °C. Following that, bath sonication at 37 kHz was applied to the dispersion for 1 hour using a Fisherbrand 112xx Series Advanced Ultrasonic Cleaner at 60% power. Water dispersions were prepared by diluting Tuball SWCNT dispersions (with PVP surfactant) to appropriate concentrations using Millipore DI water.

**Composite preparation:** Composites were prepared using known concentrations of SWCNT and NiFe LDH suspensions in organic/aqueous solvents. Appropriate volumes of each were measured out using glass pipettes in order to achieve 10 mL samples of 10, 15 and 20 wt% SWCNT with respect to NiFe LDH. In order to achieve good contact between the components, further tip sonication at 40% power for 10 minutes was applied.

**Electrochemistry:** Electrodes were placed in a three-electrode setup with a platinum wire acting as the counter and Ag/AgCl reference electrode. The electrolyte used was 1 M KOH (Lennox)

solution in DI water. Cyclic voltammetry, linear voltammetry and chronopotentiometry were utilized as the principle characterization tools in terms of electrochemistry. The potentiostat used was a BioLogic VMP 300. Voltage sweep rates were kept at  $5 \text{ mV} \cdot \text{s}^{-1}$  in a potential window  $0 - 0.6 \text{ V}$  (vs Ag/AgCl) for all voltammograms. The potential measured vs Ag/AgCl is mathematically converted to potential vs reversible hydrogen electrode (RHE) according to  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^0$  where  $E_{\text{Ag/AgCl}}^0$  is the saturated Ag/AgCl electrode potential equal to  $0.197 \text{ V}$  at  $25^\circ\text{C}$ . All chronopotentiometry measurements were carried out by holding the cell at  $10 \text{ mA} \cdot \text{cm}^{-2}$ .

## 4 Characterising the Principle Degradation Effects During NiFe LDH Catalyst Lifetime

It is well known and has been comprehensively reported that NiFe LDH has impressive electrocatalytic capabilities for the OER half-reaction in alkaline water splitting with low overpotentials and Tafel slope values compared with other candidates being researched for this purpose. In the NiFe LDH work presented in Chapter 3 it was possible to reach overpotential values as low as  $237 \pm 7$  mV vs RHE and a  $32 \text{ mV} \cdot \text{dec}^{-1}$  Tafel slope. Additionally, the material brings with it a cost effectiveness when compared to traditionally competitive OER catalysts such as those based on Raney Nickel and precious ruthenium/iridium metals.<sup>27, 39, 106</sup> However, in order for materials such as LDHs or others like it to become high performance catalysts in line with the practical requirements associated with commercial applications, there are a number of considerations aside from the standard (overpotential, Tafel slope etc.) which must be faced. One important factor is the stability of the catalyst in operating conditions. In this case, the stability of NiFe LDH and its composites in OER operating conditions. Namely, in alkaline media at constant current (at least  $10 \text{ mA} \cdot \text{cm}^{-2}$ ) or in a cyclic manner, depending on applications.

CV and CP experiments in Chapter 3 heavily suggest an intrinsic instability of NiFe LDH in such conditions. This was addressed and improved upon to an extent by way of composite preparation with SWCNTs with good interfacial connectivity between the components, induced by sonication. Despite that, the composite study and subsequent electrochemistry provided little in the way of direct insight into the nature of the active material's degradation. In this chapter the aim will be to complement the electrochemical data with additional analytical and characterization tools which will be used to examine active material before and at various points during and after long-term OER catalysis. While active, it is thought that perhaps a combination of changes of crystal phase, chemical composition and perhaps morphology occur which ultimately govern the performance of the catalyst with time. In an attempt to probe these effects, a combination of techniques will be

implemented including HRTEM, STEM-EDX (with mapping), FT-IR, powder XRD, Raman spectroscopy, XPS and ICP-MS.

Before moving on with the study it is useful to outline what exactly was learned to this end from the experiments in Chapter 3. One important result was that composite materials allowed the catalyst to cycle with a much less steep drop off in overpotential in early cycle life (i.e. up to fifty cycles) meaning the potentials approach a lower stable value of  $\eta$ . The attraction of using CNTs as performance-enhancing additives in electrical systems are well known. They provide a highly conductive network with large contact area and robust mechanical properties which can allow improved performance for materials in a wide variety of areas. If conductivity enhancement was the only effect then with time the overpotential would reach a similar equilibrium value even with SWCNTs, regardless of the shape of the cycling curve. As it is, what is evident in the results in Chapter 3 (Figure 3.4.11 a) is the equilibrium overpotential value after cycling is reduced upon addition of SWCNTs meaning not only is there improving in conductivity and connectivity within the matrix but the platelets are protected from degradation to some extent compared to bare sr-NiFe LDH. Because the SWCNTs can have no effect on the chemistry or phase of the active NiFe LDH, this hints at some type of mechanical degradation as being a contributing factor.

Another clear observation was made relating LDH stability to the choice of solvent used to disperse the platelets during fragmentation and composite preparation. Catalysts displayed unique cycling behaviour when made using active material processed in aqueous and organic solvent (IPA in this case). Specifically, the water-processed material displayed a slower rate of increase in overpotentials during approximately fifty cycles compared to the IPA-processed material. At the point of testing, the material is dried on the surface of a nickel substrate but there is clearly some residual effect. The stability is not the same and during catalysis this manifests itself in the electrocatalytic performance. This may suggest some change in the material during this time.

As well as attempting to define the source of degradation, the phase of the crystalline material will be attempted to be monitored during catalysis as it is known that metal hydroxide catalysts can

demonstrate subtle changes in crystalline phase which can affect the catalytic performance in a positive way. Dionigi *et al.*<sup>107</sup> suggest evidence of an undeniable change in the structure during the anodic potential sweep which may also be induced by the oxygen evolution reaction itself. The authors use the direct analogy of the  $\text{Ni(OH)}_2/\text{NiOOH}$  redox system and its OER catalysis. In this system there is direct evidence of phase transformation from water-intercalated  $\alpha\text{-Ni(OH)}_2/\gamma\text{-NiOOH}$  phases to more densely packed  $\beta\text{-Ni(OH)}_2/\text{NiOOH}$  states, known to be a more efficient system for OER catalysis. While a direct phase allocation has not been presented as of yet for an Fe-containing  $\text{Ni(OH)}_2/\text{NiOOH}$  system, it is expected to follow a similar path. XRD and a variety of spectroscopic experiments are intended to attempt to elucidate some subtle phase information to this end along with additional crystallographic information. For example, Chen *et al.*<sup>103</sup> propose that multi-layered NiFe LDH platelets swell upon ageing in alkaline media as  $\text{OH}^-$  groups are allowed time to intercalate between layers. The author concludes that this is the source of early performance enhancement and should be crystallographically detectable.

## 4.1 Crystallographic Phase Characterization

Along with chemical composition, the most significant factor during the LDH catalysts' lifetime is thought to be its crystalline phase and whether or not this changes. This stems from findings in various reports which prove subtle phase changes in single metal hydroxide catalysts under various electrochemical conditions.<sup>40, 107, 136</sup> In this section these phase changes will be outlined and compared with any detectable phase changes in the case of a multi-metal hydroxide with the available characterization techniques.

Lyons and Brandon<sup>137</sup> provide details of the redox behaviour of single-metal  $\text{Ni(OH)}_2$  and how it relates to the crystal phase with reference to the Bode diagram,<sup>136</sup> a widely accepted and well defined scheme of four unique phases (limiting cases) defined by the oxidation state of Ni, interlayer distance, water content and stacking sequences.<sup>137</sup> The transition of  $\alpha \rightarrow \beta$ , and to a lesser extent  $\alpha \rightarrow \gamma$ , represents a structural shift to a more highly ordered and densely packed phase which can support electrocatalysis at possibly lower overpotentials. The main factors governing the phase of

$\text{Ni}(\text{OH})_2$  are alkaline ageing as well as the application of electric potentials.<sup>25, 136, 138</sup>  $\alpha\text{-Ni}(\text{OH})_2$  and  $\gamma\text{-NiOOH}$  are hydrated cases with intercalated water molecules causing swelling, and average oxidation states for Ni of roughly 2 and 3.5 respectively. Conversely,  $\beta\text{-Ni}(\text{OH})_2$  and  $\beta\text{-NiOOH}$  represent the dehydrated cases after ageing in alkaline media. The oxidized  $\beta\text{-NiOOH}$  case exists as far as Ni oxidation state 3 and differs only from the  $\beta\text{-Ni}(\text{OH})_2$  phase in the orientation of surface oxygen atoms between layers, which manifests as a slight swell in d-spacing. Figure 4.1.1 is clear in stating that both the  $\alpha/\gamma$  and the  $\beta/\beta$  redox couples are sensitive to both ageing and overcharging.<sup>139</sup> Dionigi and Strasser<sup>107</sup> more recently built on this knowledge by taking what is known of  $\text{Ni}(\text{OH})_2$  and suggesting the behaviour will be vitally important in understanding the electrochemistry of NiFe LDH in that the latter is expected to exhibit similar reliance of crystal phase on the redox activity.

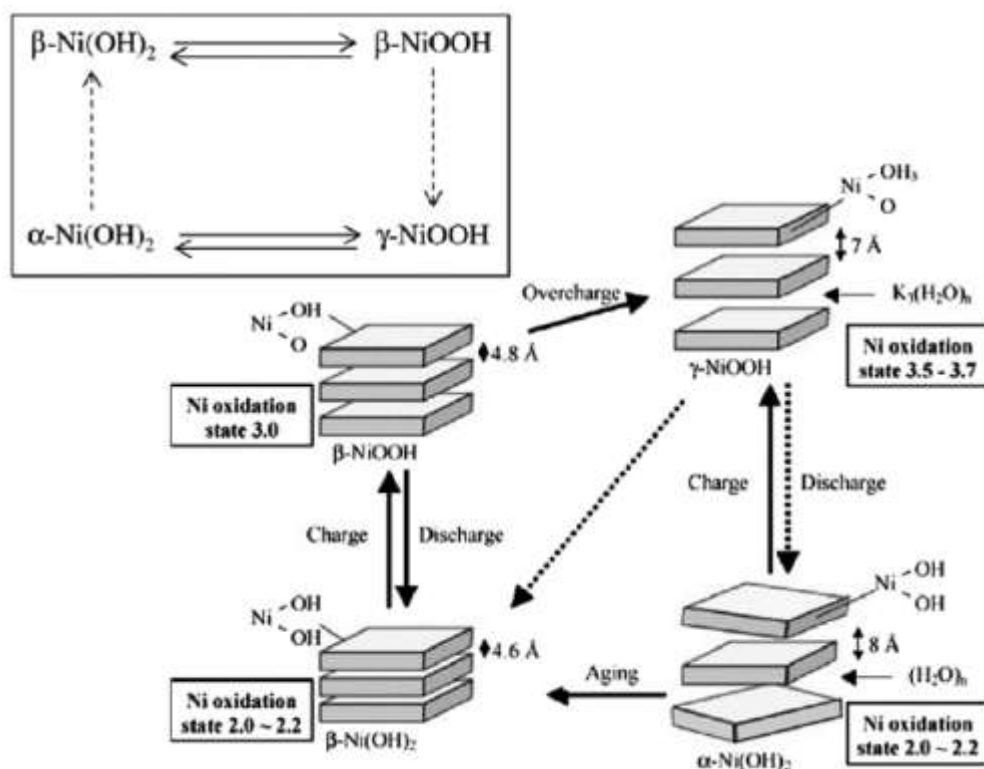


**Figure 4.1.1: The Bode diagram, a schematic representation of the established phase transitions for a nickel hydroxide OER catalyst.**<sup>136</sup>

An additional, perhaps counteractive effect comes from a study by Chen *et al.*<sup>103</sup> who propose the layered nature of NiFe LDH to be a key factor in its OER activity in alkaline conditions. They say that the unexposed interlayer basal planes are OER active along with those sites at platelet edges. While not immediately available in the alkaline media, these basal plane sites become

activated over time due to gradual intercalation by  $\text{OH}^-$  ions. However, this slow diffusion of proton acceptors causes dissolution of the LDH structure with time, ultimately denaturing the catalyst. Importantly, they report an XRD detectable interlayer swelling of basal planes upon ageing in KOH. This would mean that the LDH compound behaves quite the opposite to what the Bode scheme would suggest based on  $\text{Ni}(\text{OH})_2$ . In this section the aim is to challenge both trains of thought and develop a sensible conclusion as to what the governing mechanism is during exposure to alkaline conditions and cycling, based on any phase changes that can be observed.

Conventional powder XRD will be implemented as a prime characterization method in this section. For observing phase information in the NiFe LDH crystal, it is expected that upon the return to open circuit potentials the phase will relapse to its original state in the presence of water and relevant ions. So, without *in-situ* capabilities, there is a necessity to perform crystal diffraction measurements relatively soon after. This, in turn, means it will be difficult to detect phase changes with something like STEM-SAED characterization which requires extensive drying and pumping down of the material after catalysis to uphold vacuum conditions (around  $10^{-8}$  mbar requirement for the FEI Titan instrument). In order to observe crystallographic phase information via SAED without complete drying one would require a higher scope of TEM analysis involving either *in-situ* liquid cell capabilities. Hence, for the scope of this work we will rely on direct powder XRD analysis of dried and semi-dried samples.

#### **4.1.1 X-Ray Diffraction**

Before carrying out any crystallographic characterization, a sensible first step would be to address any potential additional catalytically active components (i.e. aside from NiFe LDH) which may be contributing to the OER catalysis in the presented electrochemical setup for this work. As mentioned before, the Bode phase cycle (Figure 4.1.1) has been demonstrated for  $\text{Ni}(\text{OH})_2$  but not yet determinately for a mixed-metal case. So, there exists some ambiguity when one attempts to address the early cycle life overpotential drop as we see in data like Figure 3.4.7 b in the previous section. On this evidence alone, one cannot rule out the possibility that this overpotential shift is the

result of some residual  $\text{Ni(OH)}_2$  from coprecipitation as well as maybe some oxidized nickel from exposed areas of the substrate after deposition of the active material. So, in order to remove any discrepancy in our theory, some simple CV experiments will first be carried out on an alternative, non-active substrate. The substrate of choice is glassy carbon (GC) which will be used sporadically in this chapter for a variety of reasons. It is used at this point for its electrical conductivity as well as its high chemical stability and relative catalytic inertness which should mean that there will be no change in the substrate during alkaline cycling. So, unlike the Ni foam case, with GC based electrodes it will be possible to look exclusively at the intrinsic NiFe LDH cycling behaviour.

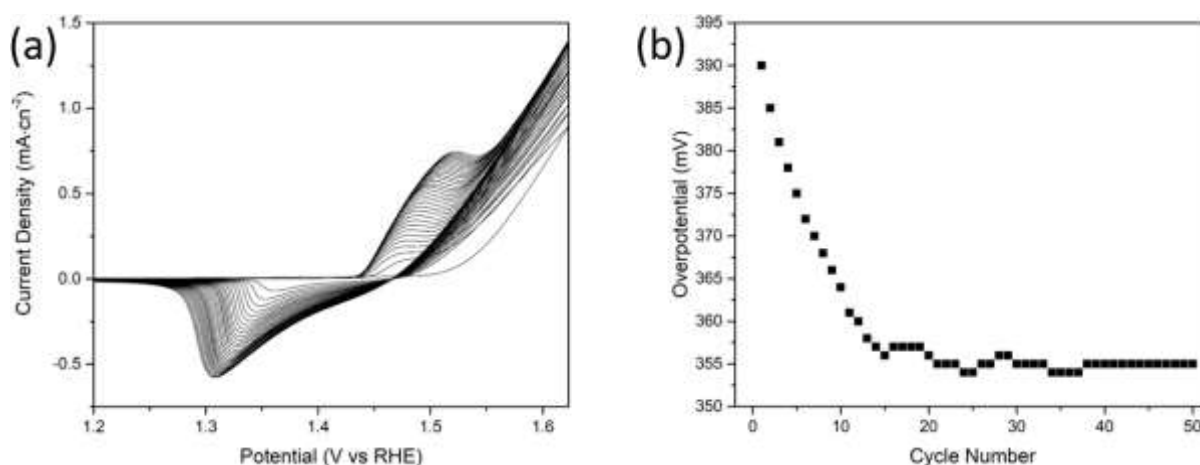


**Figure 4.1.2: (a) CV and (b) overpotential cycling curve of NiFe LDH catalyst on GC through 50 cycles.**

The method of preparation is outlined in section 4.4 with platelet dispersions being sprayed directly onto the heated, polished GC surface. Figure 4.1.2 above displays the results of cycling the NiFe LDH - GC electrode fifty times in an identical manner to the testing carried out in Chapter 3. At this current density scale, the peak growth of the  $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}$  redox couple is quite obvious, suggesting substantial hydrous oxide layer growth on the surface of the mixed-metal catalyst during this time, a phenomenon well documented for nickel and iron catalysts.<sup>139-141</sup> Regarding catalysis, the first note to make looking at the CV data for the electrode is that the average current density reached in the fifty cycles is considerably lower than those reached for nickel foam electrodes. This is despite the relatively high mass loading of  $0.82 \text{ mg} \cdot \text{cm}^{-2}$  for the sample. Most likely an important factor here is the significantly limited surface area of the flat, pristine GC and from Chapter 3, we are aware that beyond a critical loading value which exceeds complete coverage of the surface,

further mass loading fails to improve the performance. Additionally, with such low currents, it is a possibility that the interfacial contact between GC and NiFe components is not good. One can see also from Figure 4.1.2 (a) that the common threshold of  $10 \text{ mA} \cdot \text{cm}^{-2}$  is not reached. Instead, here a  $1 \text{ mA} \cdot \text{cm}^{-2}$  threshold will be used to characterize the overpotential of the catalyst. Figure 4.1.2 (b) illustrates that overpotential through fifty cycles. This graph appears to be a different shape when compared to those for nickel foam – deposited electrodes (with  $\eta$  at  $10 \text{ mA} \cdot \text{cm}^{-2}$ ). What is most important at this point however is the clear drop in overpotential in early cycle life. With no ambiguity from a possible nickel foam contribution, it can be deduced here that the active NiFe LDH material is going through some changes, crystallographic and/or compositional or otherwise, during this period to alter the electrocatalytic performance. Beyond that initial drop, the cycling remains steady to an extent for the remainder of the experiment. One does not see the same ‘U’ shape as before (e.g. Figure 3.4.8). This is perhaps because of the low current density passing through the electrode, as a result of poor activity, meaning the material is unlikely to degrade at the same rate as previous cases.

In the knowledge that the NiFe LDH – GC system is effective in so far as a similar trend is observed in the early cycle-life performance, the setup will be continued for use in this section as it presents a favourable base for XRD analysis. Not only is the GC surface flat but contains no overlapping diffraction signals which may obscure the clarity of the NiFe LDH data, as would be the case with the thus far used nickel foam substrate. An x-ray diffraction pattern for one such electrode is presented in Figure 4.1.3 in which the characteristic (003) and (006) basal plane diffraction peaks are immediately obvious for the NiFe LDH material, referring back to the previous chapter (Figure 3.2.3 b) when the active material’s crystal structure was defined as hexagonal with lattice parameters  $a = 3.08 \text{ \AA}$ ,  $b = 23.55 \text{ \AA}$ . As the  $2\theta$  angle is increased to higher values (smaller d-spacing) the definition of the LDH signals is notably low. In this region, the spectrum is dominated by broad background signals attributed to the GC substrate.<sup>142</sup> Based on what we know from the established  $\text{Ni}(\text{OH})_2$  phase scheme, swelling and contraction of the basal planes will be a key insight into the state of the material throughout the cycling lifetime. So, tracking the values of these d-spacings for

the active catalyst will be of utmost importance, crystallographically. The value of the principle (003) peak is 7.8 Å and the second order (006) peak expectably half that, 3.9 Å. This is in good agreement with reported interlayer d-spacing of as-produced LDH crystals with the Ni-Fe metals combination intercalated with carbonate counter anions and water molecules.<sup>43, 143</sup> As touched on already, the material will be analysed in close comparison with the crystallographic phases of Ni(OH)<sub>2</sub>. At this point it is noted that the  $\alpha$ -Ni(OH)<sub>2</sub> crystal in it resting state has a d-spacing value of around 8 Å, so the pattern in Figure 4.1.3 may be labelled as a corresponding  $\alpha$ -NiFe LDH phase, which will be our starting point in terms of structure.

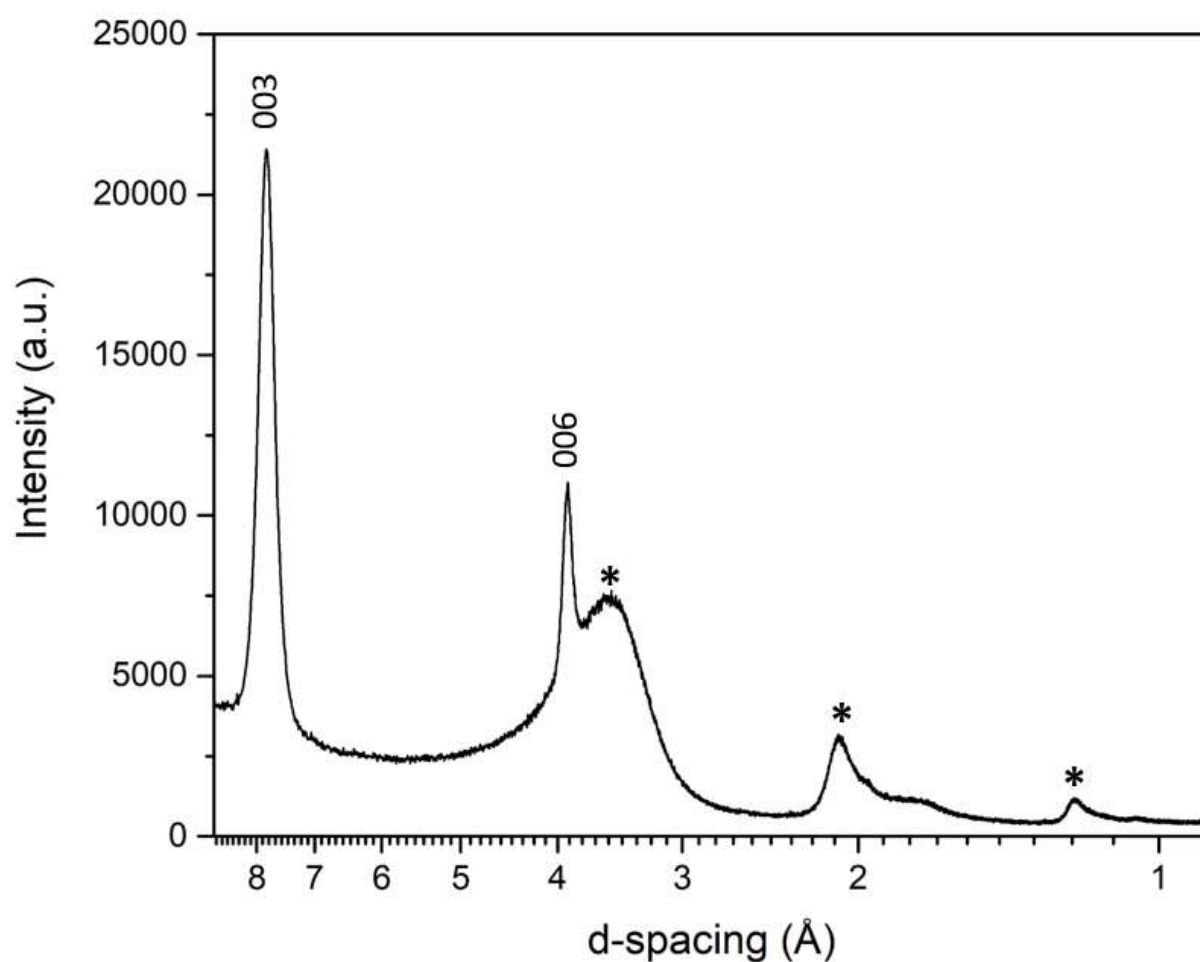


**Figure 4.1.3:** XRD pattern for sr-NiFe LDH on polished GC (peaks labelled \* represent GC crystal diffraction), using a Cu K $\alpha$  source.

Firstly, an ageing experiment was performed as a control. The catalyst was left to age in the active alkaline medium with no applied potential in order to either prove or dispel that the high pH environment alone may affect the nature of the LDH structure. Figure 4.1.4 represents the data for

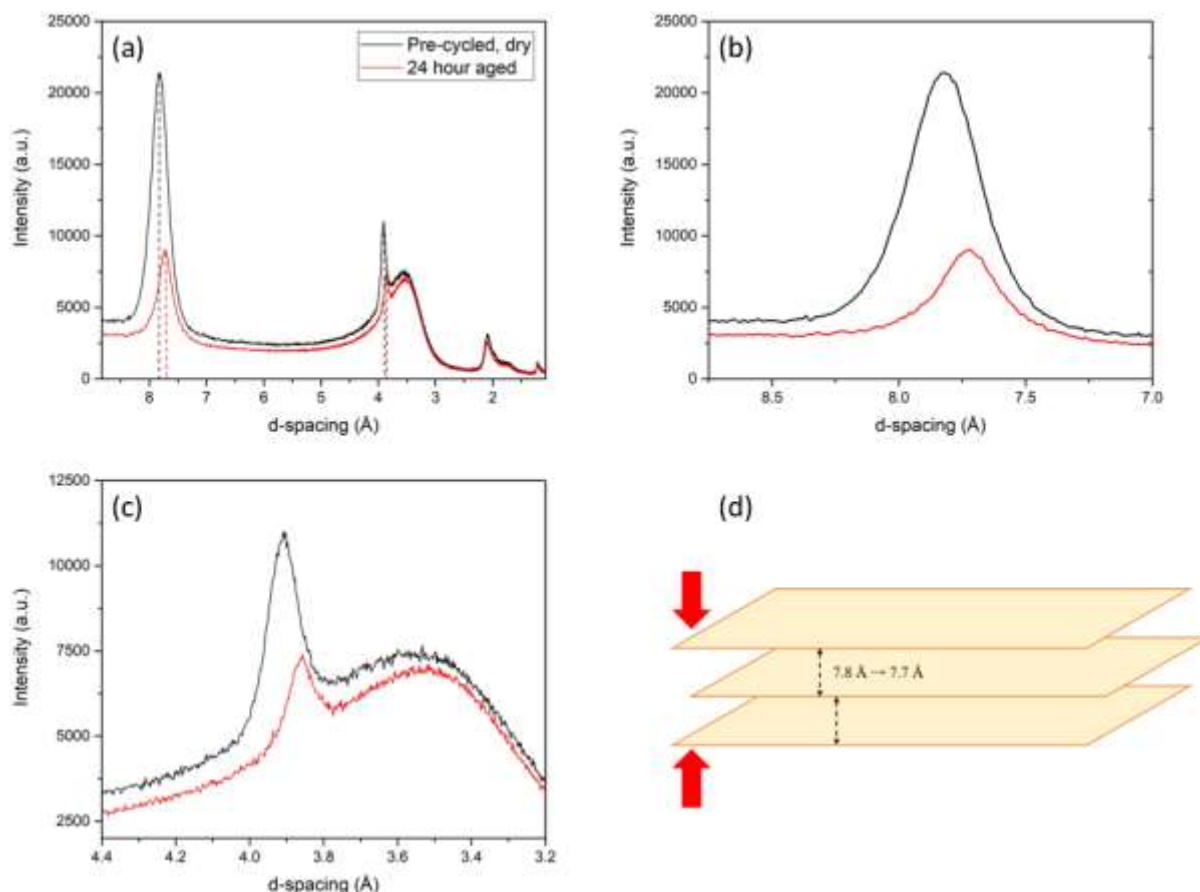


**Figure 4.1.4:** (a) XRD pattern for sr-NiFe LDH on GC before and after ageing in 1 M KOH for 24 hours. (b) & (c) Close up views of the principle (003) and (006) peaks respectively. (d) Schematic representation of basal plane contraction.

the aged catalyst which was allowed to sit in 1 M KOH for 24 hours before removing, rinsing with DI water and finally re-measuring the XRD pattern. There are clearly no additional phases formed at this point. The diffractograms are almost identical apart from slight shifts in the principle (003) and (006) peaks, indicating a contraction of layers during this period. This observation may seem minor, but it is an important indication that this is not a passive time for the catalyst. Changes are taking place already within the crystal and the observation here is in contrast to what has been observed in similar experiments in the literature. For example, in the introduction to this chapter, the study by Chen *et al.*<sup>103</sup> was touched on which demonstrates the early onset intercalation of hydroxyl ions from the alkaline environment in similar ageing experiments (1 M KOH at open circuit voltage). This effect results in a noticeable swelling of the interlayer spacing before becoming catalytically active, which is manifested as a negative shift in  $2\theta$  of the (003) peak. Additionally, Dionigi *et al.*<sup>43</sup> present swelling behaviour of a similar scale upon electrode ‘wetting’ during *in-situ*

characterization. So, why the unique behaviour here? One thought is that during this 24 h period the hydroxide structure is accepting iron impurities from the KOH electrolyte. Iron uptake of hydroxide OER catalysts is well reported in alkaline media.<sup>88, 138</sup> While there is no way to show this directly, using just crystallographic approaches, it can be hypothesized that this may be taking place. If this is the case then the additional trivalent  $\text{Fe}^{3+}$  presence within the LDH layers may be the dominant factor in causing the layers to contract, with a greater Coulombic attraction between layer and counter anion,  $\text{CO}_3^{2-}$ . Another thought is that the phase change, the specifics of which will be outlined in the coming discussion, is being onset to some extent at this early stage. This would be quite significant if proven as it removes the necessity of voltage application (and hence electrocatalysis) in order to observe a change of phase for the mixed metal catalyst.

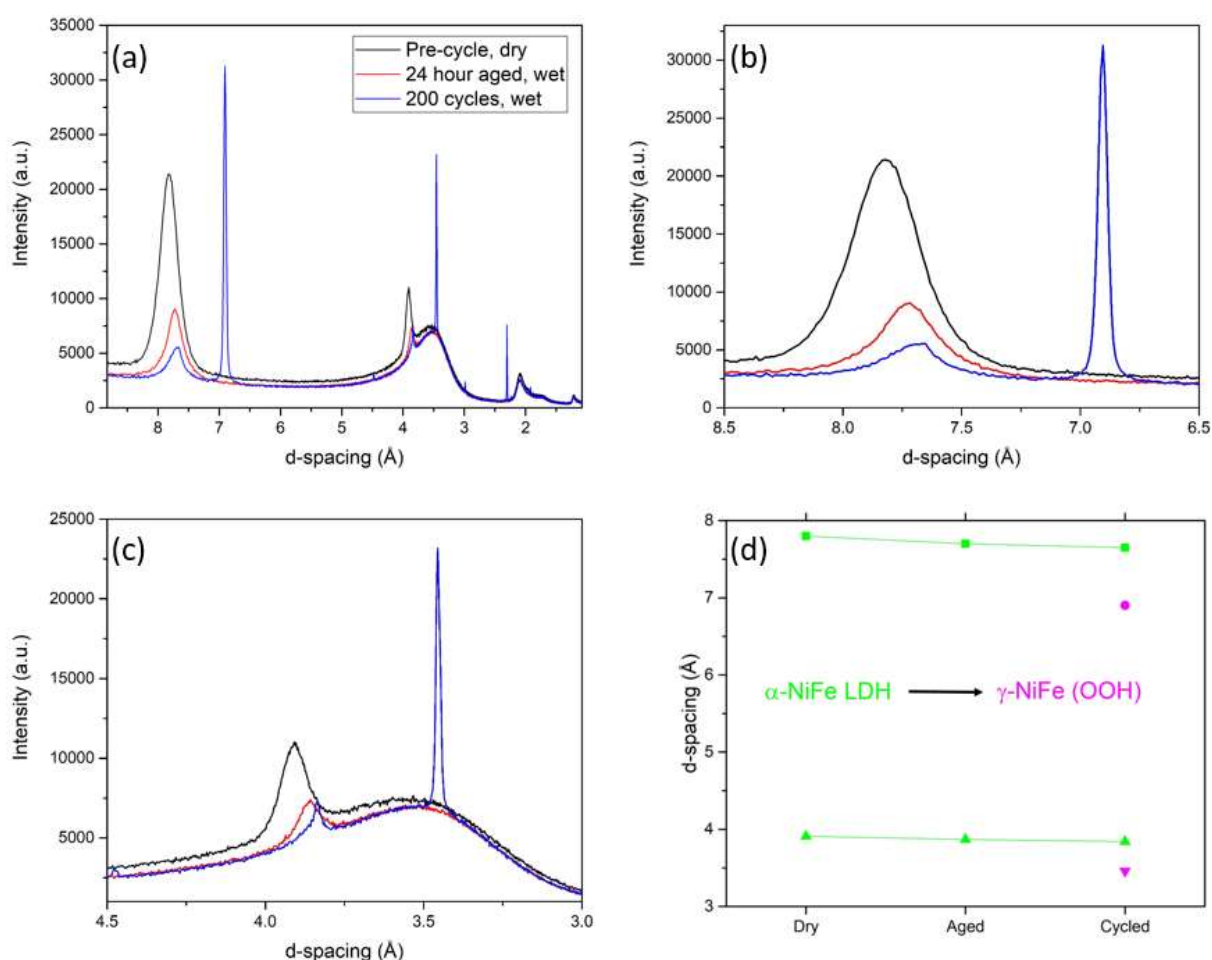


**Figure 4.1.5:** (a) XRD pattern for sr-NiFe LDH on GC cycled 200 time between 0 – 0.6 V vs Ag/AgCl at  $5 \text{ mV}\cdot\text{s}^{-1}$  compared with previous patterns. (b) & (c) Close-up regions near the principle (003) and (006) peaks. (d) Graphical representation of d-spacings from multiple phases.

The NiFe LDH – GC electrode was then taken and placed in a three electrode setup in 1 M KOH where it was cycled between 0 – 0.6 V vs Ag/AgCl at a scan rate of 5 mV·s<sup>-1</sup> two hundred times, before re-measuring the diffraction pattern. The result is displayed and compared with previous scans in Figure 4.1.5. We see at this point further shifting of principle the (003) and (006) d-spacing to lower values meaning more slight contractions of the  $\alpha$  phase basal planes. Figure 4.1.5 (b) & (d) present this shift quite clearly. It is known that subtle shifts like this one are likely to be accompanied by a more significant crystallographic shift at elevated potentials.<sup>43</sup> Indeed, this holds through here as we can see from Figure 4.1.5 (a) that there are clear, sharp peaks in the spectrum of the cycled catalyst (blue line) which suggest the formation of an additional phase. The three major peaks appear at 6.9, 3.5 and 2.3 Å. The peak positions here align well with the first, second and third order diffractions for what has been reported as the abrupt contraction of the hydroxide layers at a point during OER cycling when the  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$  oxidation takes place.<sup>43, 139</sup> Comparing with the Bode cycle<sup>136</sup> for nickel hydroxide catalysts,  $\alpha\text{-Ni(OH)}_2 \rightarrow \gamma\text{-NiOOH}$  phase transition occurs at respective d-spacing values of 8 Å to 7 Å, which fits closely with what is observed for the mixed-metal case here (7.8  $\rightarrow$  6.9 Å). For that reason, this phase transition is labelled as an  $\alpha/\gamma$  equivalent phase transition, which is displayed more clearly in Figure 4.1.5 (d) along with corresponding interlay d-spacings.

Additional diffraction signals in the cycled pattern at low d-spacings presented in Figure 4.1.5 (a) hint at some side product forming during the period of catalytic activity. The peaks are visible at roughly 4.5, 3, 2.25, 1.9, 1.7 and 1.4 Å which aligns almost directly with the signal for 6-line ferrihydrite.<sup>144</sup> If this is the case, the observation gives rise to the possibility of some ferrihydrite forming in response to catalyst degradation. If this is true that a ferrihydrite phase is forming, there must be a source of iron manifesting during catalysis. It is proposed in this work that iron leaching from the active structure takes at OER active potentials. This may be a considerable degradation affect in the catalyst in terms of performance and is a point which will be built on in detail in the following sections. If iron is leaching however, this would surely also result in an equal degree of leftover mixed-phase  $\text{Ni(OH)}_2$ . This hydroxide phase would be extremely difficult to detect in the

diffraction pattern as its XRD signal is known to align within  $\pm 0.2 \text{ \AA}$  of the respective NiFe phases and with low relative intensity. Regardless, the diffraction information in Figure 4.1.5 is possibly the first direct evidence for this work the catalyst does in fact degrade during activity and it is an observation which will be built on later in this chapter.

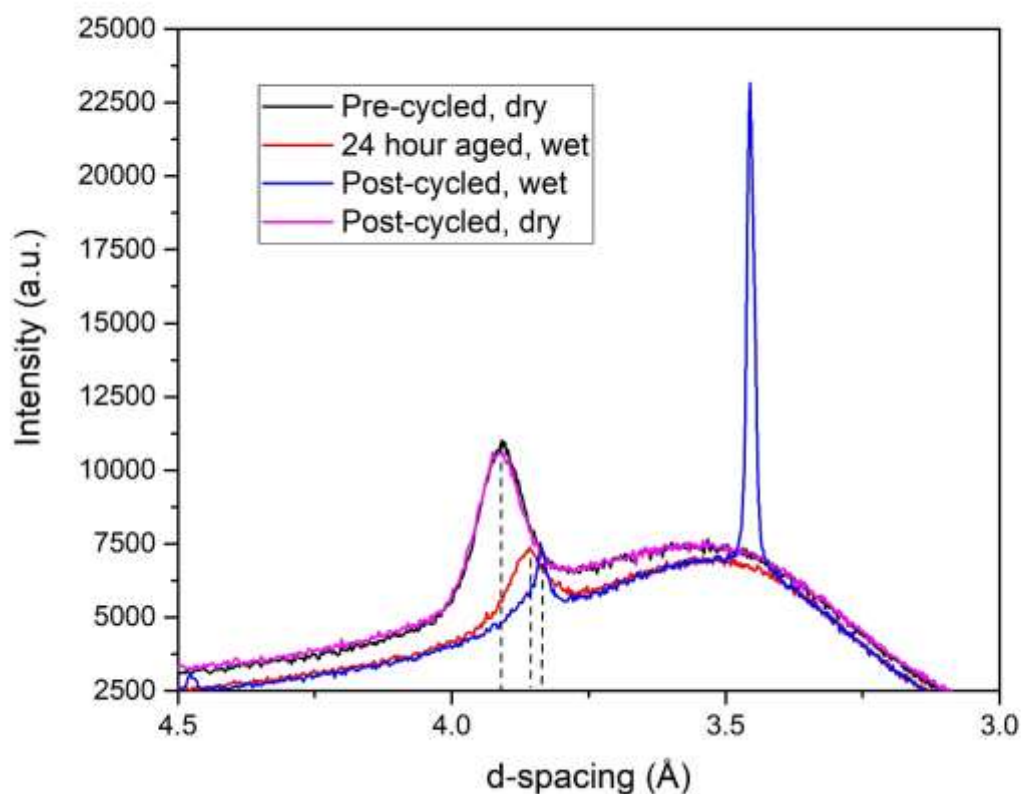


**Figure 4.1.6:** Close-up area of XRD pattern near the (006) diffraction peak for the cycled sr-NiFe LDH catalyst on GC after allowing to dry completely in air, compared with all previous diffraction patterns.

We have not seen to this point the same degree of reversibility which is suggested in other *in-situ* studies. As long as wet, alkaline conditions are maintained to some extent after electrochemical activity (as is the case in Figures 4.1.4 & 4.1.5 where electrodes were not allowed to dry completely before running XRD measurements) there appears to be a memory effect to some extent in the phases. This is especially apparent after cycling, where there remain sharp peaks relating to the secondary phase after voltammetry was stopped as well as the (006) and (003) peak shifts. What's even more intriguing is that the crystal will return seemingly completely to its original structure when given time to dry. This point suggests that the rehydration and  $\text{CO}_3^{2-}$  intercalation

after reduction of nickel back to  $\text{Ni}^{2+}$  is a gradual process. Figure 4.1.6 shows that the cycled, fully dried material once again demonstrates no sign of layer swelling or multiple phases. This may prove an important characteristic in terms of the NiFe LDH phase scheme.

Aside from phases, there is an additional point that the (006) peak returns to almost the precise intensity of the pre-cycled case. Given that the peak pertains to the basal planes, this observation may suggest that there is very little, if any exfoliation taking place during catalysis, which was one of the key observations of the work by Chen *et al.*<sup>103</sup> who reported delamination of NiFe LDH as a result of OER catalysis. Results from this section suggest against the idea that, in the case of the NiFe catalyst presented here, exfoliation has any considerable effect on the OER performance during this cycling window.

The diffraction results observed in this section first and foremost stand as a proof-of-concept demonstration of the validity *ex-situ* analysis can have in studies like this one in a field which is dominated in the literature with mostly *in-situ* analysis. With simple methodology involving CV cycling followed by standard powder XRD data acquisition, it is possible to convincingly demonstrate a crystal phase transition within the LDH during OER cycling in alkaline conditions which proves to have a direct consequence in this study, where the goal is to gain insight into how the LDH structure and composition may change and affect the material's active lifetime.

The findings in this section, which are mirrored in both experimental and DFT calculation-based studies in the literature, are known to improve upon some of the material properties which pertain to a high level of activity for an electrocatalyst. It is now known that the layer contraction which mostly defines the phase transition is accompanied by metal cation intercalation, mostly  $\text{K}^+$  in this case, from the aqueous potassium hydroxide solution electrolyte.<sup>40, 43, 138</sup> It is thought that an increase in the order of the crystal, as well as the observed contraction of the structure, will improve the conductivity and hence, the catalytic rate capability of the system. However, from Chapter 3, within the NiFe LDH OER lifetime not only can we observe a catalytic improvement but also a significant degradation afterwards in the performance with time, both in terms of cycling and constant-current modes of electrocatalysis. The identification of some apparent ferrihydrite by-

product in the cycle material (Figure 4.1.5 a) is an early hint to the nature of this degradation. This observation will be built on in later sections when it can be coupled with spectroscopic data. So, in this sense, understanding phase behaviour is only half the battle. In order to paint a complete picture of the catalyst lifetime, it is necessary to identify and observe those counteractive phenomena, perhaps as a first step towards rectifying the issues so we can move towards realising a more practical, commercially viable OER catalyst based on NiFe LDH. Going forward, the goal will be to build on this data and determine, with the use of a number of spectroscopic approaches, what other factors may be present that could work to diminish the catalyst's performance during long-term alkaline water splitting.

### 4.1.2 Additional Electrochemistry

Before moving on to spectroscopy, some final steps can be taken to complement the findings of the XRD analysis in this section. The point which I would like to be clarified is whether ageing, or the electrocatalytic activity itself, play the main role in the onset of LDH phase transformation. Using CV and CP methodology can help shed some light on this. It can be seen from the diffraction data, Figure 4.1.4 in particular, that alkaline ageing influences the crystal structure. There is a reduction in the interlayer spacing which, although seemingly subtle, has been shown to be a complementary effect of the phase shifts both in this work and in literature.<sup>43</sup> Additionally, Trotochaud *et al.*<sup>40</sup> report for pure Ni(OH)<sub>2</sub> and with low levels of iron incorporation, an increase in crystallinity with ageing, driven by a shift from the  $\alpha$  to  $\beta$  hydroxide phase. If true for the mixed metal case, this change may be noticeable in the early onset performance of the catalyst. So, 1 hour and 24 hour ageing experiments were carried out for the sr-NiFe LDH to clarify this point.

First of all, Figure 4.1.7 gives the OER overpotential cycling and constant-current behaviour for the aged sr-NiFe electrodes as compared with an electrode which was not given time to age. What we want to be able to tell here is whether or not any change can be noticed in the very early-life overpotential transitions for the catalyst (first 10 cycles or so). If ageing can have the phase effect here similar to the one described by Trotochaud for Ni(OH)<sub>2</sub>, then perhaps there will be a change in

the catalytic ‘starting point’. Based on the figure, the answer to such a proposal is unfortunately no on all counts. No matter if the material is aged for one or twelve hours there appears to be no observable change to the characteristic shape of the catalysis curves acquired with both CV and CP.

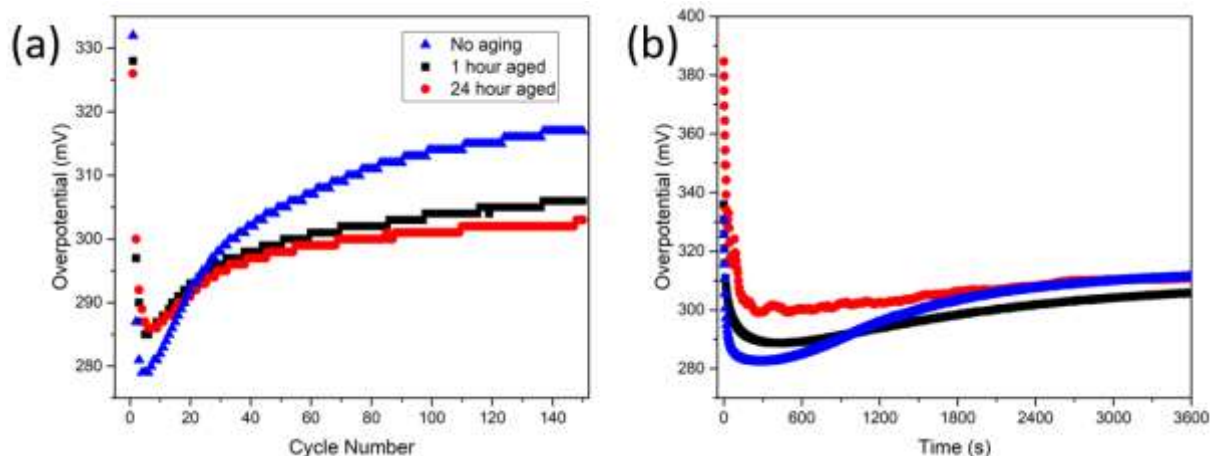


**Figure 4.1.7: (a) Overpotential cycling curve through 150 CV cycles and (b) CP data for 1 hour at  $10 \text{ mA}\cdot\text{cm}^{-2}$  for sr-NiFe LDH catalysts with no ageing, 1 hour and 24 hour of ageing in 1 M KOH.**

More intricately, one can look at the oxidation and reduction peak potentials for nickel in the NiFe LDH system to determine phase activity.<sup>40, 139</sup> Compared with  $\alpha/\gamma$  nickel redox activity, the  $\beta/\beta$  system will have a higher potential redox couple, which should be detectable either as a shifted set of redox peaks or simply as an additional set of peaks in the voltammogram if both  $\alpha$  and  $\beta$  phases are present in significant quantities. Figure 4.1.8 gives first cycle CV data for the aged and non-aged cases. At this point, the oxidation peak has not yet been established but the reduction peaks are clearly visible. As we move through ageing in KOH, there appear to be no additional peaks formed nor any considerable shifting of peak potentials. There is simply no onset of an  $\alpha \rightarrow \beta$  transition by ageing alone, not to say the transition doesn't take place at some point during OER activity, although it is not detected in this work. In fact, Trotocahaud *et al.*<sup>40</sup> encountered a similar phenomenon for their heavily iron-doped  $\text{Ni}(\text{OH})_2$  catalyst. Although observing clear evidence of an  $\alpha \rightarrow \beta$  phase for the pure nickel cases in highly pure KOH electrolytes (i.e. with no Fe contamination) and even with low levels of Fe incorporation, increasing iron levels up to 25% with respect to nickel, the phase transition appears to be blocked. This observation alone is highly suggestive that the superb activity of NiFe LDH for OER does not appear to be reliant on long range order or crystallinity so much, but rather derives its ability from the intrinsic Ni-Fe electron density push-pull balance within the layers which

allows for favourable intermediate formation free energies.<sup>42, 43</sup> Another very important point for this work which can be suggested here is that for this material, any phase behaviour is onset by OER catalytic activity alone and not a knock-on effect of the alkaline environment.

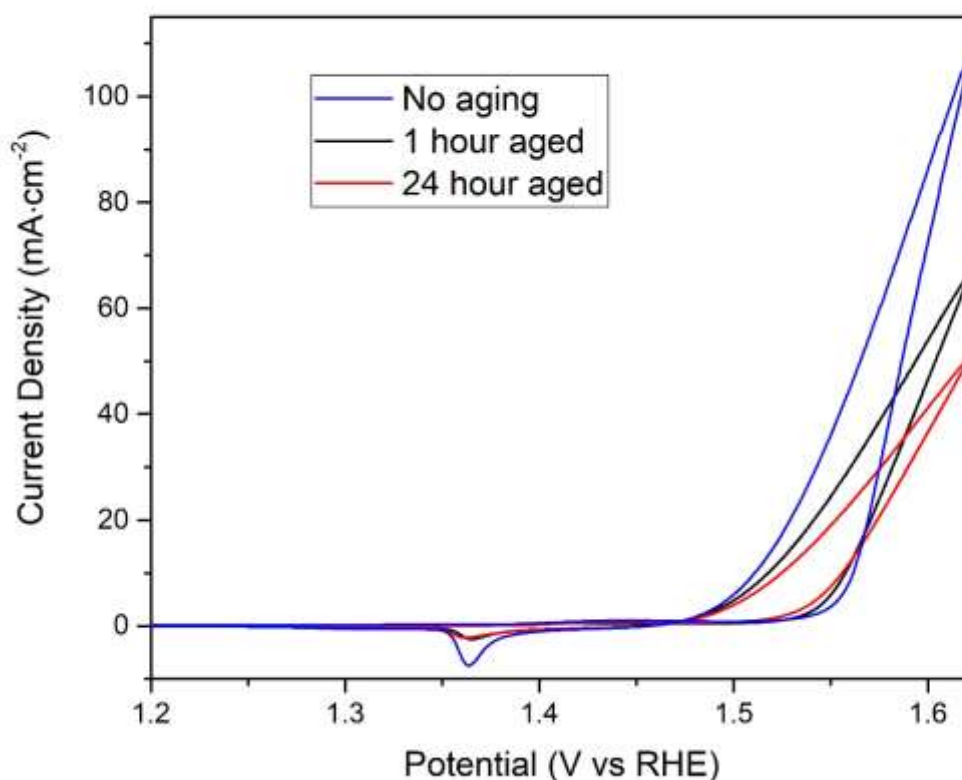


**Figure 4.1.8:** Initial CV curves for sr-NiFe LDH catalysts with no ageing, 1 hour and 24 hours of ageing in 1 M KOH.

With this point we can go one step further with this and track the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox couple as the electrode is cycled. Once again, a shift to higher potentials would be expected if some  $\beta$  phase was being induced by cycling, but it cannot be seen. The CV in Figure 4.1.9 represents a non-aged sr-NiFe LDH catalyst. In fact, the redox peaks in this CV and in all NiFe LDH CVs in this work are slightly shifted the opposite direction to lower potentials. The exact reason for this shift is unclear but we can theorize at this point that there is potentially a compositional change happening to alter the appearance of the voltammogram. We know that relative to the pure nickel case, mixed Ni and Fe hydroxides exhibit a delayed onset potential for Ni oxidation. This was reported in Chapter 3 where we can clearly see more than one  $\text{Ni}^{2+}/\text{Ni}^{3+}$  redox couple, one deriving from pure nickel (lower

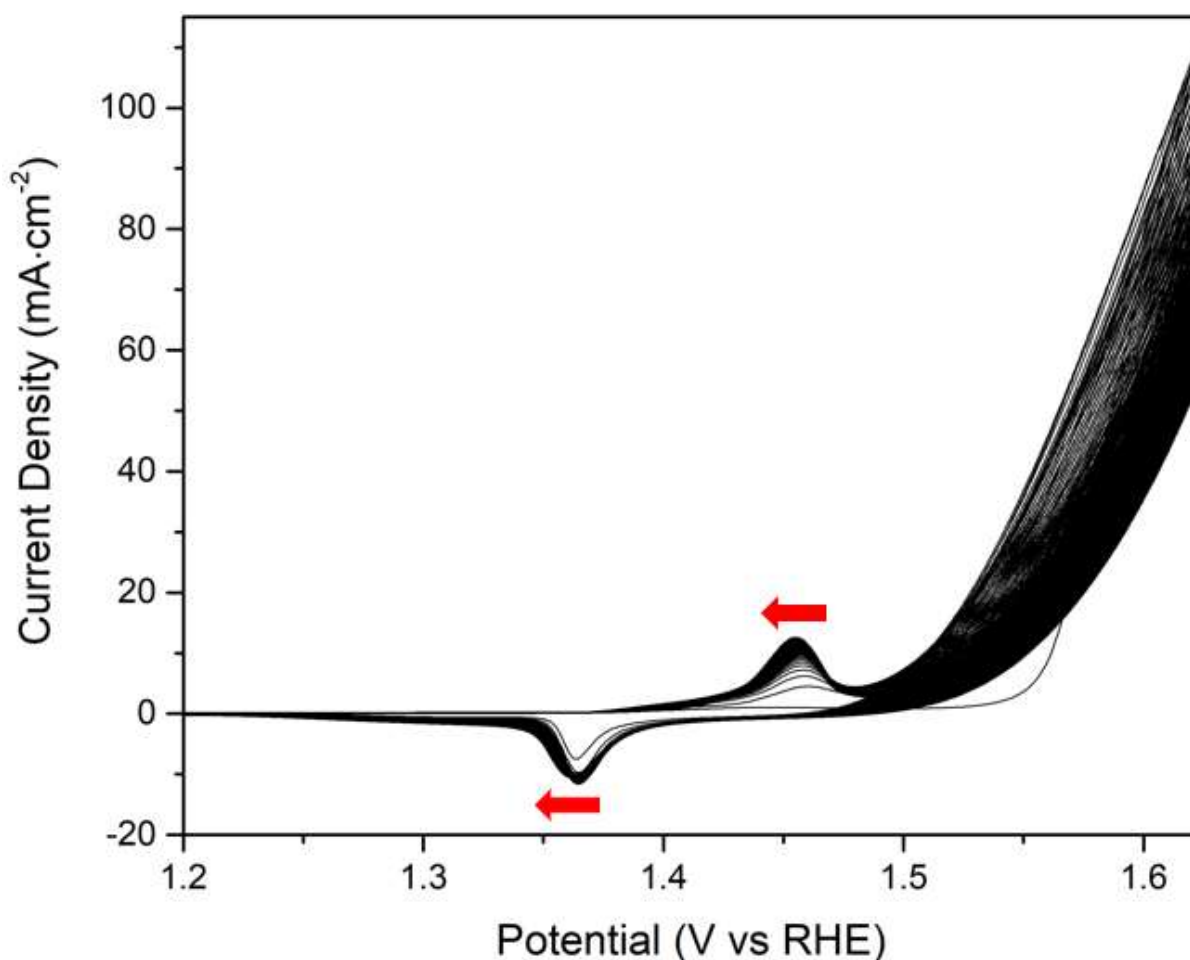


*Figure 4.1.9: CV cycling of a sr-NiFe LDH catalyst through 200 cycles.*

V) and the other from NiFe LDH (higher V). With that given and acknowledging the ferrihydrite contamination detected by XRD in the cycled material, there is a chance that the shift in the potential to lower voltages here is another indication of a loss of Fe from the active structure during cycling. If true, this may be considered a principle counteractive effect in the catalyst's lifetime. Perhaps leached iron is responsible for the observed ferrihydrite in the cycled diffraction pattern. This is a speculation which will be analysed further.

## 4.2 Chemical Composition & Morphological Characterization

Moving on from crystallographic phase identification, this section aims to recognise any additional phenomena during the NiFe LDH catalyst lifetime which counterbalance the phase effects in terms of long-term OER performance. A variety of spectroscopic techniques are used here to

achieve a well-rounded idea of the extent to which the catalyst degrades during this time and the nature of the degradation.

### 4.2.1 STEM-EDX

EDX mapping was carried out via (S)TEM analysis. Preparing a sample for TEM usually involves drop casting a liquid suspension of the material on to a copper grid with lacey carbon with drying under vacuum or in air. The IPA or aqueous LDH suspensions are drop cast directly at low concentrations. However, *ex-situ* analysis means the material needs to be removed from the substrate by physically scraping the adhered powder and re-dispersing. Nickel foam is not the most compatible substrate for this method because of the inaccessibility of the majority of surface area for scraping. Moreover, the intense Ni background (from Ni foam) in EDX elemental analysis may overlap with other signals and make the results unreliable. As such, the sample preparation for this section is relatively unique. The appropriate substrate needs to have a flat, pristine surface and be conductive, allow adhesion of active flakes and not contain any of the major active elements which may cause ambiguity in the elemental data. Once again, GC is proposed to this end as it adheres to all of these requirements, is readily available and in fact commonly used as a high performance OER substrate.<sup>38, 77, 122</sup> An additional advantage of using GC substrates for NiFe LDH catalysts is that the active material is quite visible on the surface with a distinctive yellow/orange colour. The first thing which is noticed after prolonged catalysis is a change in the colour to a dark brown, almost black when dried, suggesting chemical or compositional changes may be occurring during this time. Interestingly, iron hydroxide (ferrihydrite) is known to have a brown colour.<sup>44</sup> The digital photographs in Figure 4.2.1 display such an observation. Figure 4.2.1 (a) shows the pristine, ‘shiny’ surface which is achieved by thorough polishing (outlined in section 4.4), in (b) one can see the clear contrast in colour upon spray deposition of active sr-NiFe platelets and (c) presents the clear change in coloration after cycling. This image also displays what appear to be white fractals on the surface. These structures are visible under SEM and have been characterized as KOH salt crystals formed after drying in air on the GC surface. This has been proven with *in-situ* EDX prior to further analysis (Figure A7 in Appendix A). The salt composition will not hinder the EDX analysis as there is no

overlap of elements (i.e. Ni, Fe) so it isn't necessary to attempt to remove KOH at this point. The salt coverage does however hinder SEM analysis directly on the GC substrate. Having said that, it is still possible to observe clear physical degradation of the platelets under TEM after scraping onto a copper grid (inset images, Figure 4.2.3 and Figure A9 in Appendix A).

As a control experiment before looking at the cycled material, TEM samples were prepared and tested of the pre-cycled sr-NiFe LDH particles on a copper grid. Statistical EDX analysis was performed section-by-section over a large area of the sample surface with STEM. For this qualitative study, fifteen sections were analysed. Their EDX spectra in each case (Figure A8 in Appendix A) give the atomic ratios presented in Figure 4.2.2, each of which is measured against a reference Cu background. It is clear that the ratios here for the untouched material are quite consistent with each other and amount to an average of 0.75 Ni to 0.25 Fe, or 3:1, for this batch of LDH. It is stressed that this is not a quantitative study and the compositional values measured do not accurately reflect the material. This study only aims to detect any change in the observable metal ratio using EDX, as an indication of some possible change in composition. With that said, the ability to measure consistent results thus far over a large number of sites validates the analytical approach.

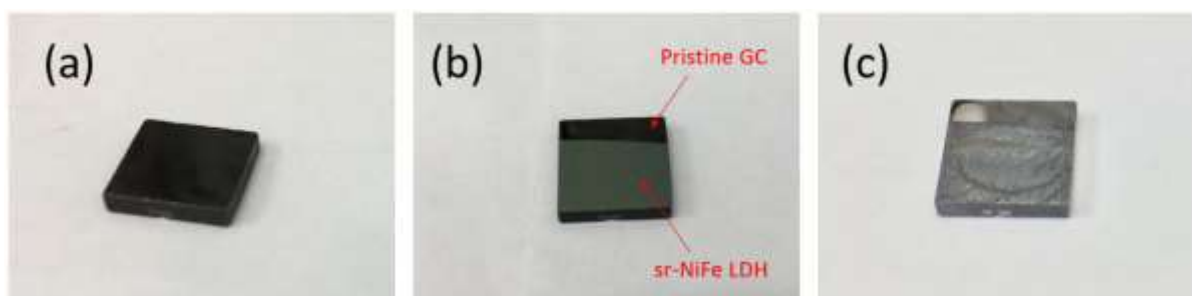
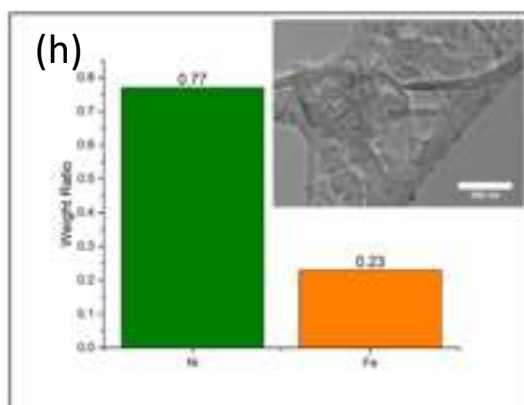
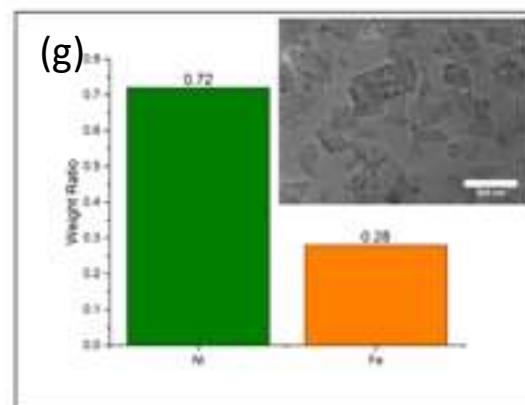
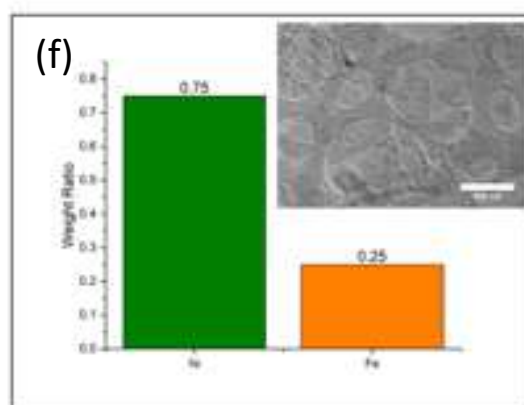
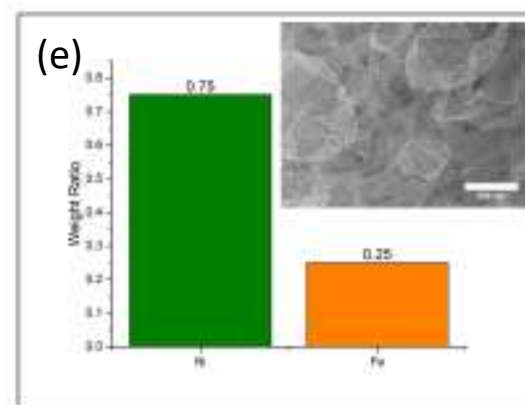
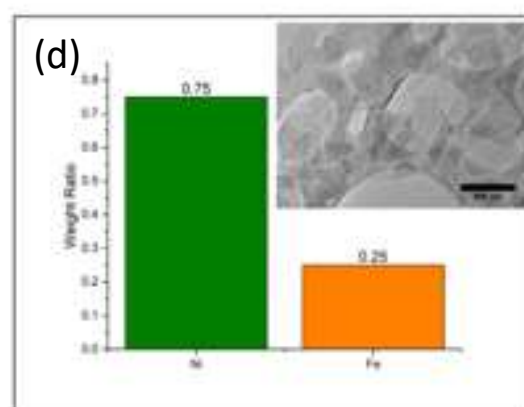
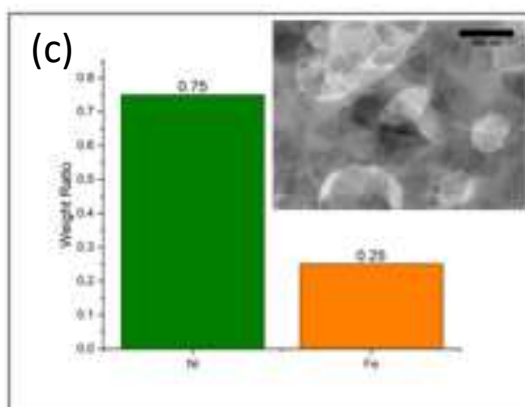
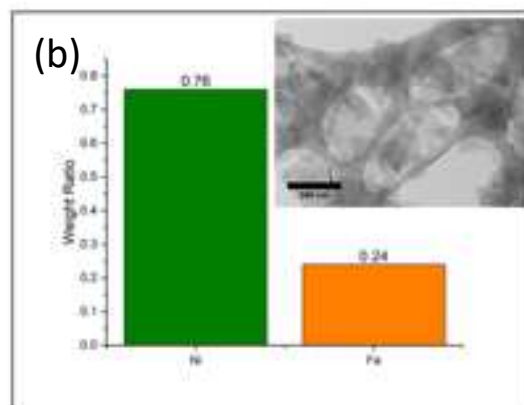
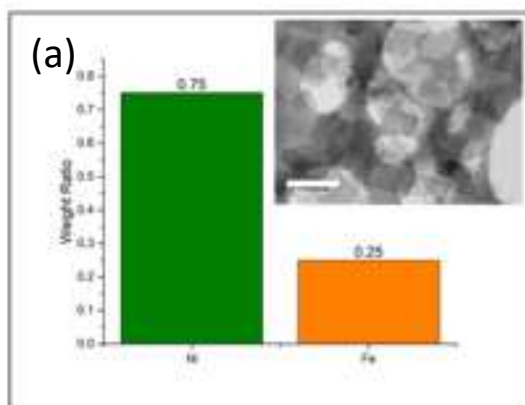


**Figure 4.2.1: Digital photographs of (a) pristine, polished GC substrate, (b) ultrasonic spray deposited sr-NiFe LDH and (c) post-cycled case.**

After OER cycling and scraping of the cycled material from the GC surface using a polymer tweezers, the material was dispersed in IPA by vigorously shaking, vortexing and bath-sonicating before drop casting on a copper TEM grid with lacey carbon as before. A summary of the atomic ratio of the metal centres (from EDX spectra, Figure A9 in Appendix A) are summarized in Figure 4.2.3. What is first noted is that one cannot see the same consistency in the results. Ratios range from 3:1 to values as high as 7.3:1, the latter potentially suggesting considerable leaching of iron from



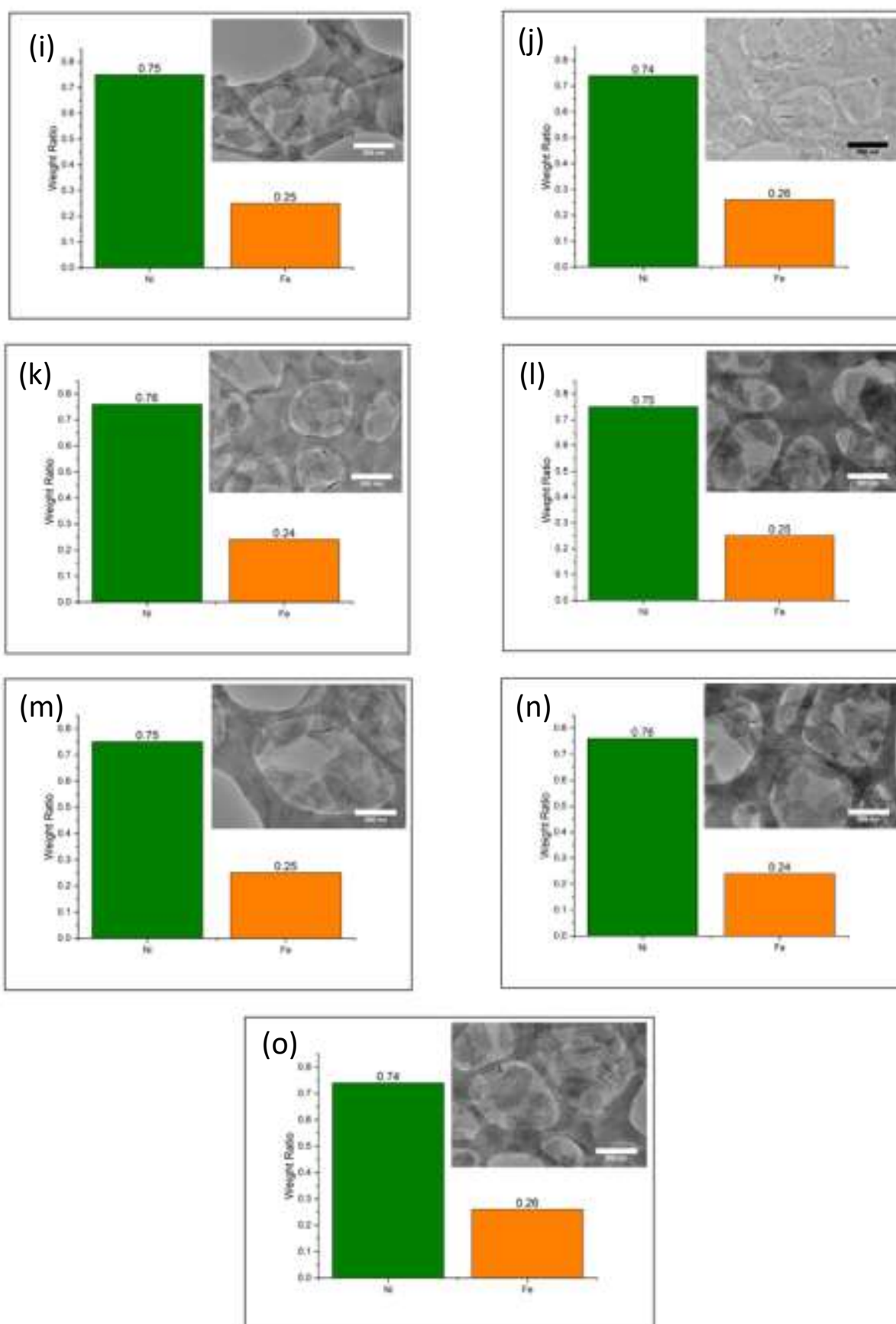
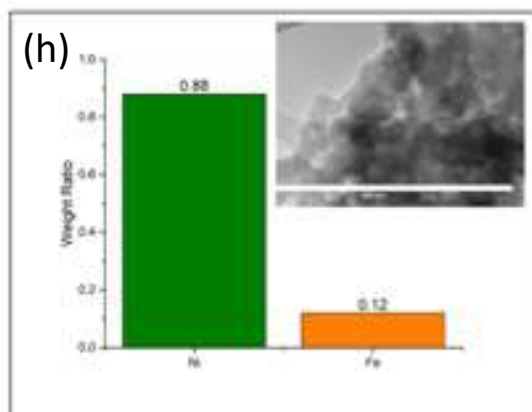
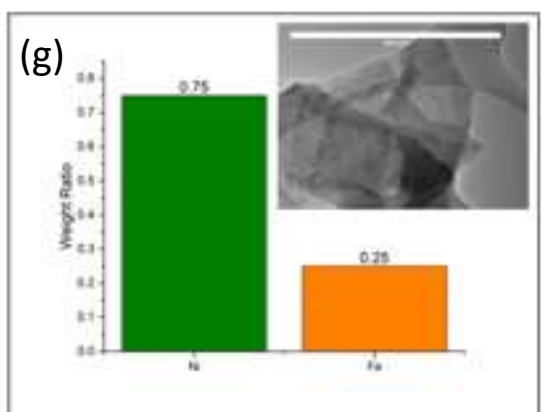
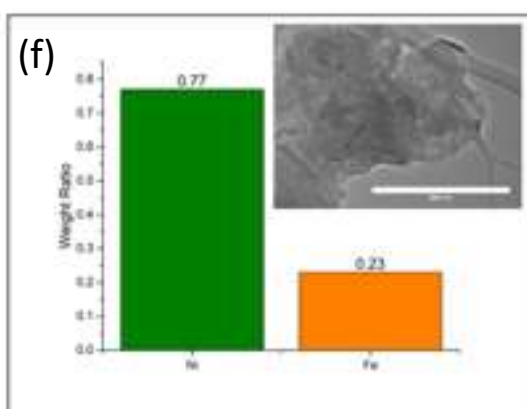
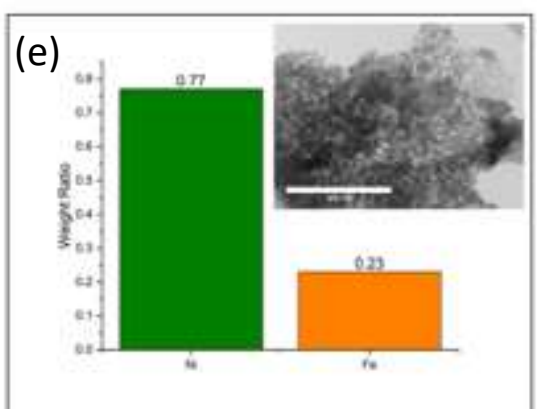
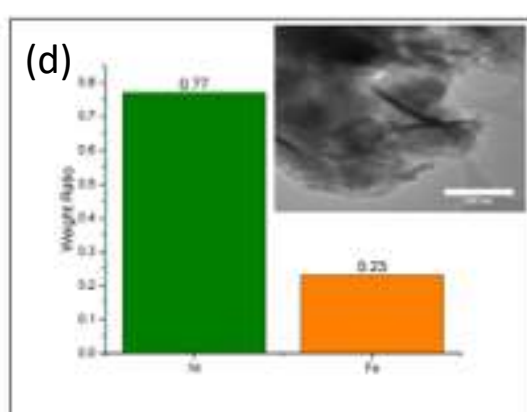
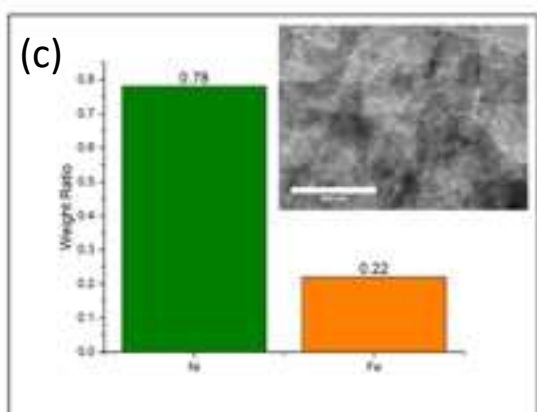
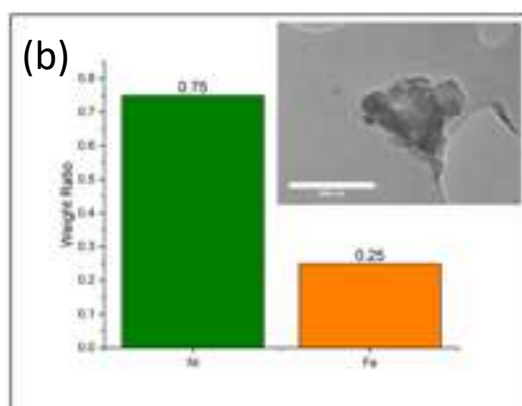
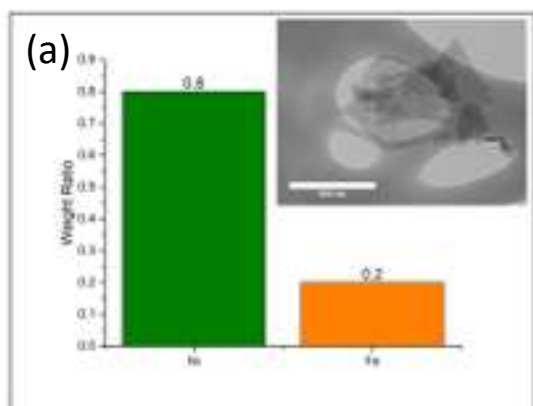


Figure 4.2.2: Bar charts representing ratios of Ni to Fe across a range of areas for pre-cycled sr-NiFe LDH, along with HRTEM images of the associated areas (inset, all scale bars are 500 nm).

octahedral sites within the mixed-metal crystal structure. On average, a ratio of 0.79 Ni to 0.21 Fe, or 3.8:1, is determined from the fifteen randomly selected areas. But this value alone does not describe the nature of activity across the active material. The discrepancy in values from one area to another for this study suggests that the entire mass of active material on the GC-anchored catalyst was not subjected to the same degree of degradation. Some areas seem to have undergone considerable leaching of Fe with respect to Ni while others appear unaffected. The reason for this is most likely that surface-layer platelets on the sprayed NiFe LDH - GC electrode are more exposed to electrolyte ions and hence experience higher activity.

Focusing on the TEM images inset in Figures 4.2.2 & 4.2.3 (see Figure A8 & A9 in Appendix A) one can notice a change in the appearance of the material at these magnifications, particularly in those areas most affected by leaching after catalysis. The appearance of those areas particularly affected show some apparent porosity forming, in stark contrast to other areas where the as-synthesized platelet morphology remains. Some examples of this are visible in particular in Figure 4.2.3 e, h and k with pore diameters scaling in the range of tens of nanometres and all of which display increased Ni:Fe ratios, a probable indication of Fe leaching. If this observation does in fact point to a direct correlation between cation leaching and morphological alteration, then it can be considered as a likely degradation effect, consequence of alkaline OER activity.

Having observed apparent leaching of Fe from the host structure, the next question which should be answered is, what happens to the cations after being removed? They would likely combine with local available anions to form stable hydroxides or oxyhydroxides. Based on numerous reports in the literature<sup>44, 145</sup>, some iron oxyhydroxide, perhaps a ferrihydrite, is likely to form, whose nature is dependent on factors like pH and temperature. This is consistent with the apparent detection of oxyhydroxide, seemingly 6-line ferrihydrite, in the cycled NiFe LDH – GC catalyst during XRD analysis. This will be built on later with further analysis. In any case, it is a strong possibility that such iron (III) compounds could be detectable as clusters, visible alongside the LDH crystals within the cycled material. The best initial approach to detecting this was EDX mapping via STEM. So, both pre- and post-cycling samples were loaded similarly, this time into a microscope with STEM



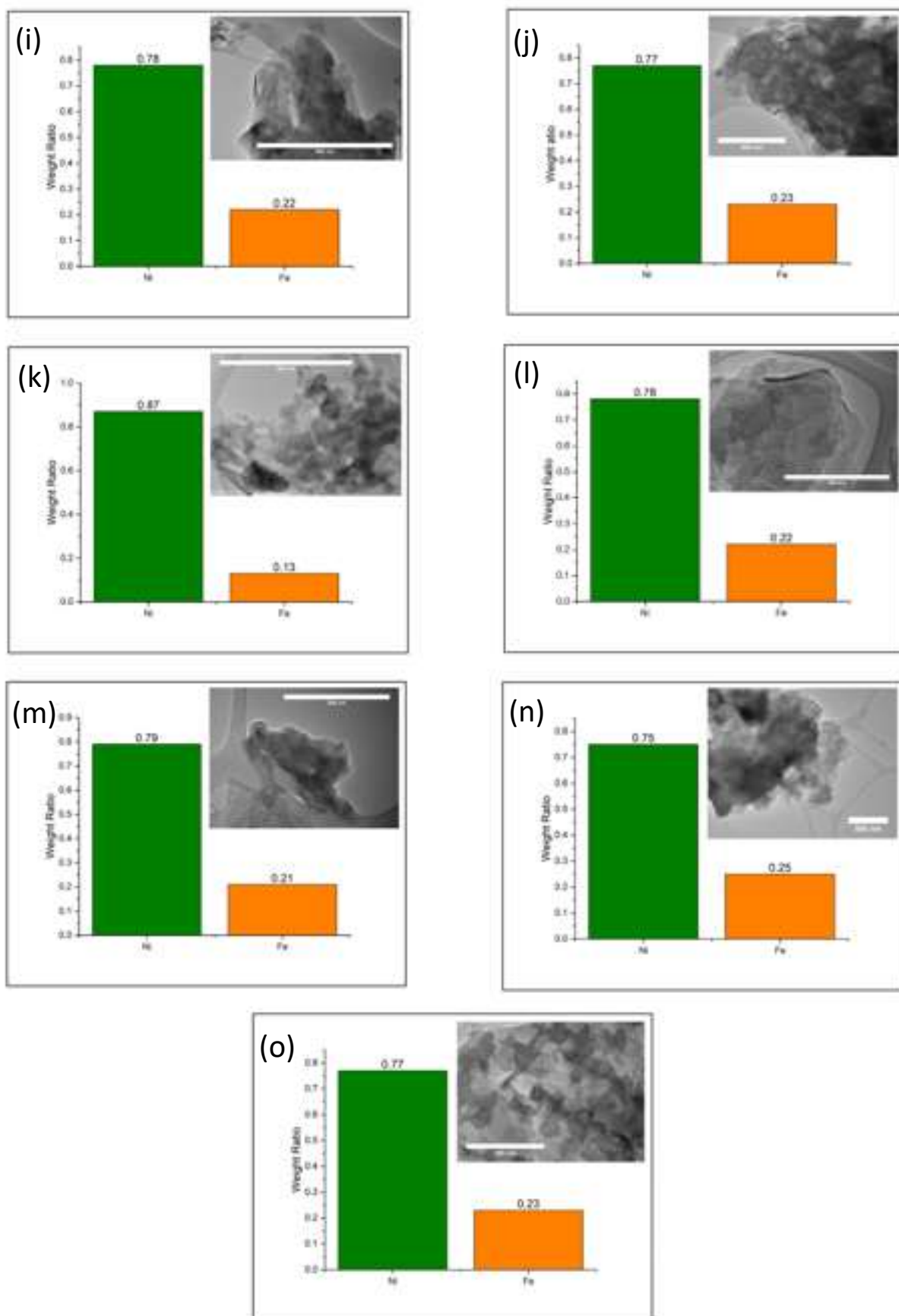


**Figure 4.2.3:** Bar charts representing ratios of Ni to Fe across a range of areas for OER cycled sr-NiFe LDH, along with HRTEM images of the associated areas (inset, all scale bars are 500 nm).

capabilities, namely an FEI Titan 80 – 300 kV FEG S/TEM instrument. As before, a control study was carried out on the pre-cycled sr-NiFe LDH to demonstrate homogeneous inclusion of the metal centres across the platelet (Figure 4.2.4), similar to the case of the as-synthesized material back in Figure 3.2.4, as it should be (note that L-line data is omitted here due to weak signals in both Ni and Fe cases). The data at this point once again gives elemental maps of homogeneous inclusion of the Ni and Fe metals.

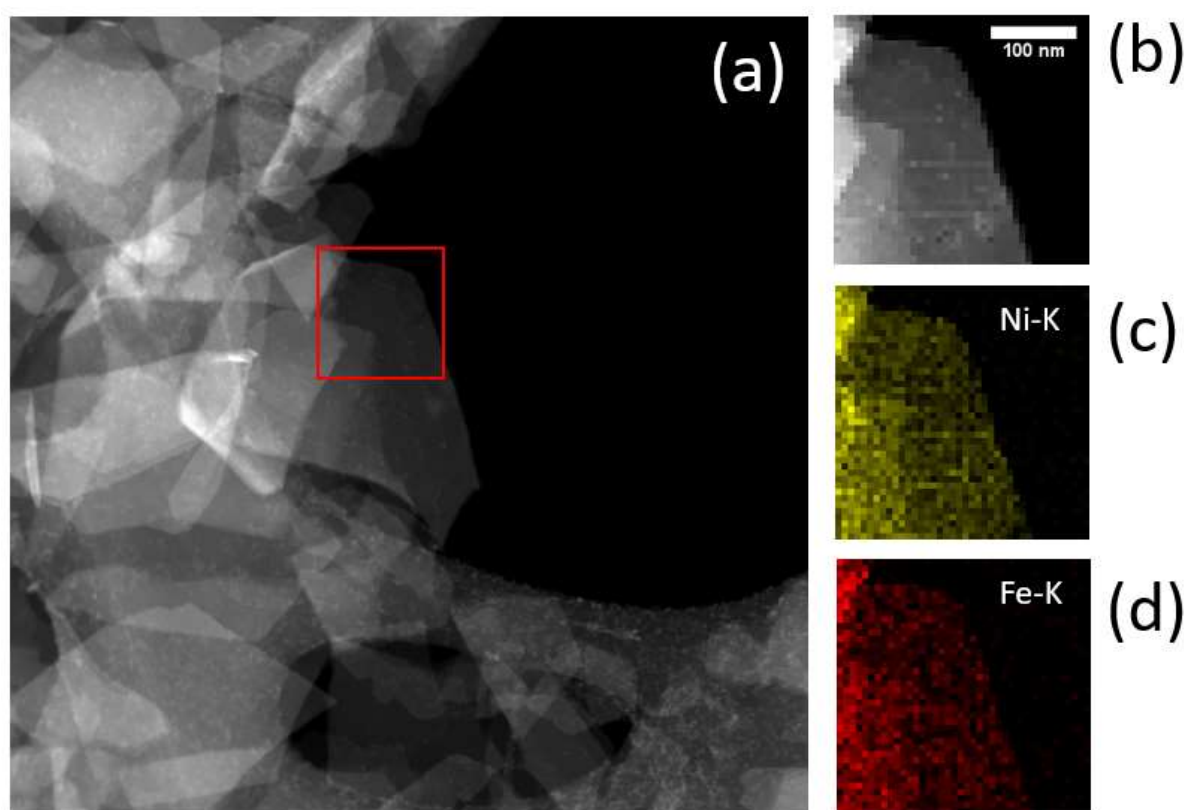


**Figure 4.2.4:** (a) STEM image of pre-cycled sr-NiFe LDH with selected area of interest and (b) close-up image. (c) & (d) Ni and Fe K-line mapping of this area respectively.

Next, the EDX mapping was observed for the material after extensive OER catalysis cycling. Finding an appropriate area to detect additional iron structures or clusters meant first finding a site whose morphology was blatantly different to that of the crystalline, planar LDH. Figure 4.2.5 (a) is an example of just that type of area with a pristine phase visible and some seemingly amorphous material sitting on top. To look at the composition of the object, EDX mapping was carried out on the exact area, with interest in Ni and Fe atoms via signals from both K and L lines (Figure 4.2.5). Concentrating on the position where the object is found in the EDX maps, it is clear that no great

contrast can be seen for Ni mapping, whereas in the case of Fe one can notice clear contrast in the position of the cluster. This must mean that clusters like this one, visible across the cycled catalyst, must be iron-based and possibly formed in part from leached  $\text{Fe}^{3+}$  cations (although trace amounts of iron are often present in the starting KOH solution which may contribute the formation of such clusters). Further spectroscopic analysis in following sections will attempt to help elucidate the exact nature of the compound. The high pH conditions will likely be an important factor here as to whether a stable hydroxide is formed<sup>92, 146</sup> or a ferrihydrite of some description.<sup>44, 147</sup> In either case, the nature of the ferric (oxy)hydroxide formed could yet be important in terms of catalysis. As Bandal *et al.*<sup>106</sup> summarize, Fe is active for OER in many different forms each with unique capabilities depending on which structure can facilitate a higher degree of charge and mass transfer kinetics. So, the nature of the compound formed here will govern the catalytic contribution of the leached iron, subtle as it may be.

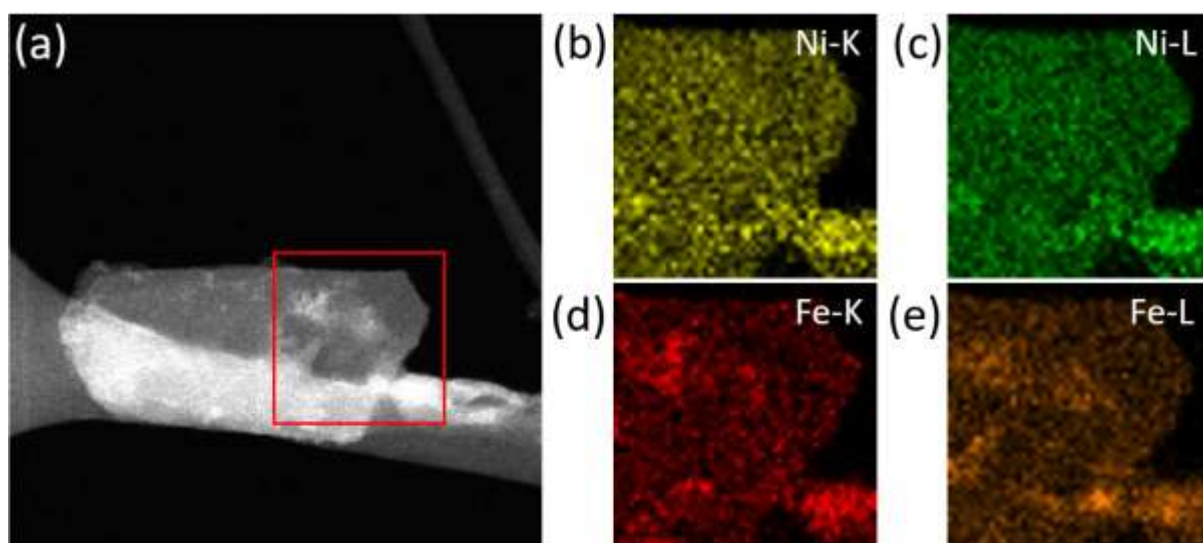


**Figure 4.2.5:** (a) STEM image of the area of interest with K and L line EDX maps of (b) & (c) nickel and (d) & (e) iron respectively.

To conclude the progress in this section so far, there have been steps taking toward beginning to understand one possible source of NiFe LDH material degradation after OER catalysis i.e. the removal of metal ions from octahedral sites within the hydrotalcite-like structure. There was a clear preference in terms of removal of metal ions with  $\text{Fe}^{3+}$  seeing greater leaching compared to  $\text{Ni}^{2+}$ . This is perhaps sensible as the stability of nickel is expected to be greater in the crystal as it is the only coordinated metal in the host mineral hydrotalcite itself. Conversely, iron is the ‘guest’ component

whose stability would intuitively not match that of nickel. The leaching of cations was accompanied by apparent dysmorphia of the catalyst at active sites to such an extent that the two effects are thought to be mutually inclusive and point at the likelihood of inhomogeneous activity through the sprayed material thickness. Most probably, it is the material on the outer surface of the electrode which becomes active and degrades to a greater extent. If the material below the surface is not effectively contributing to the performance, then this reinforces the importance of efficient mass loading when preparing electrodes. Once the point of complete coverage of the substrate is achieved, further mass loading should not improve its performance and would be wasteful. This point is reflected in the electrochemistry as we see optimum mass-loading values for catalysis, after which electrocatalysis ceases to improve any further.

Building on the results from this section, the intention moving forward will be to discover further details in both the exact cause of metal leaching and the exact form the cations take after the fact. Addressing the question of what causes the leaching will pit two trains of thought against one another. The first being that leaching is an inevitable result of the LDH material ageing in high pH alkaline media and the second being that the act of electrochemical activity in those conditions is essential. It has already been demonstrated in this work that phase transitions require the latter, but it is as of yet unknown if the case is the same here. Also, addressing the questions surrounding the nature of leached metal ions, a combination of techniques involving Raman spectroscopy, FT-IR and XPS will be specifically employed to complete the understanding of the leaching process as a contributor to the OER catalytic degradation.

#### **4.2.2 Raman Spectroscopy**

In order to get more information about the intricate changes which may go on within a crystal catalyst during its active lifetime, one must consider Raman spectroscopy as an essential method of characterization. Raman analysis has the potential to uncover information regarding the relative metals composition of a mixed metal catalyst as well as the degree of crystallographic order within the system, with the ability also of detecting phase changes which may occur. The expectation here

is that such analysis will allow for a less ambiguous look at how the electrocatalytic activity of a multi-metal catalyst like NiFe LDH can affect such properties of the material. In order to carry out clear, direct *ex-situ* analysis of the material during different stages of its catalytic lifetime, Raman spectroscopy was carried out for the active material directly on the surface of the thus far used nickel foam because it adds no problematic background signal to the Raman spectra and additionally, there are no requirements for removal of the LDH from the surface for sample preparation. The electrode was simply removed for the electrochemical three-electrode setup during cycling lifetime at points of high interest based on the known behaviour of the NiFe LDH catalysts and how the overpotentials evolve, as outlined in Chapter 3. The relationship between catalyst performance and stability of the active component are mutually dependant. For example, if one was to deposit the active NiFe LDH on a substrate which is more compatible with Raman (e.g. glassy carbon or silicon with some conductive coating) the OER performance which has been established in this work will be different. For reference, compare the overpotential cycling behaviour for the material on GC in Figure 4.1.2 with any of those presented in Chapter 3 for the NiFe or sr-NiFe LDH on nickel foam. In the case of the GC catalyst where the performance is much lower, the overpotential reaches a minimum value and stays around that point beyond fifty cycles, presumably due to the low current being pulled during each cycle. This means the inflexion points (i.e. points of interest) will be reached at different cycle numbers, and not to the same extent. So, the decision was made to continue to use nickel foam support for Raman experiments, despite the surface roughness, which may cause difficulty in terms of signal-to-noise ratio. This is evident in the Raman spectra presented in this section. The Ni foam alone does not give any peaks here but rather produces a broad background/photoluminescence signal (Figure A10 in Appendix A). However, the noisy background does not inhibit the reading of the spectra and the key Raman bands remain clear.

To begin we designate the characteristic Raman shifts for pre-cycled sr-NiFe LDH material on Ni foam in order to build an understanding of the changes which may take place within the crystal when operating conditions are applied. As in the case of crystallographic analysis previously, here the relatively well known and understood structural phases of  $\text{Ni(OH)}_2$  will be utilized as a model of

understanding against which the mixed-metal NiFe material will be compared and contrasted. Figure 4.2.6 shows the narrow wavenumber ( $0 - 1000 \text{ cm}^{-1}$ ) range Raman shifts for the active material before catalysis. One can notice two significant peaks in the figure at wavenumbers 462 and  $527 \text{ cm}^{-1}$ , which are indicative of the Raman peaks for NiFe LDH.<sup>39</sup> The former can be attributed to Ni-O band which is usually present in the range  $445 - 465 \text{ cm}^{-1}$  for  $\text{Ni(OH)}_2$  crystals.<sup>148, 149</sup> This band gives no phase information as of yet because it is present in both the  $\alpha$  and  $\beta$  phases of the host  $\text{Ni(OH)}_2$  structure. On the other hand, the higher wavenumber band ( $527 \text{ cm}^{-1}$ ) is commonly allocated to correspond with Ni-O vibrations within a disordered or defective system.<sup>150</sup> This points toward the sample at this stage being largely  $\alpha$  phase hydroxide as opposed to the more ordered  $\beta$  phase. A  $\text{Ni(OH)}_2$  study by Trzesniewski *et al.*<sup>149</sup> also allocates the higher band as a Ni-O vibration and the lower, Ni-OH. According to the authors, by elevating the cell potential, one can use the change in relative peak intensities for the bands in question to indicate the phase of the material, as will be touched on later in this section. Another study by Louie & Bell<sup>151</sup> looks at the effect on the principle  $\text{Ni(OH)}_2$  bands from iron inclusion in the structure. They demonstrate that for Fe incorporation up to 32% and with no applied potential, these two bands can be assigned as they are in the pure  $\text{Ni(OH)}_2$  environment (i.e. Ni-O, Ni-OH), albeit shifted to higher wavenumbers. The NiFe LDH material in the work presented in this thesis does not exceed iron inclusion of 25% relative to nickel, so the peaks may be labelled as such. Beyond 32% Fe incorporation, Louie & Bell report that the 462 and  $527 \text{ cm}^{-1}$  peaks will quickly fade in intensity and disappear.

Beyond the wavenumber range displayed in Figure 4.2.6 there is very little information to be seen. Upon very close examination of the spectrum higher wavenumbers (Figure A11 in Appendix A) one may allocate a weak, broad band at  $3665 \text{ cm}^{-1}$ . This feature might be the remanence of a band found in pure  $\text{Ni(OH)}_2$  relating to the highly ordered  $\beta$  phase and whose peak sharpness and intensity is significantly affected by appreciable amounts of Fe within the crystal, as is the case here. This band can be rationalized as some minor  $\text{Ni(OH)}_2$  phase in the synthesized material. What is clear at this point is that there appears to be limited evidence of multiple phases present in the initial dry sr-NiFe material with no applied potential, equivalent to the  $\alpha$  and  $\beta$  phases one would observe in a pure

Ni system. The  $\alpha$  phase appears to have a considerable majority with only a minor, weak signal giving evidence of any  $\beta$  phase. This aligns with the lack of any  $\beta$  phase electrochemical signal from voltammetry (section 4.1.3).

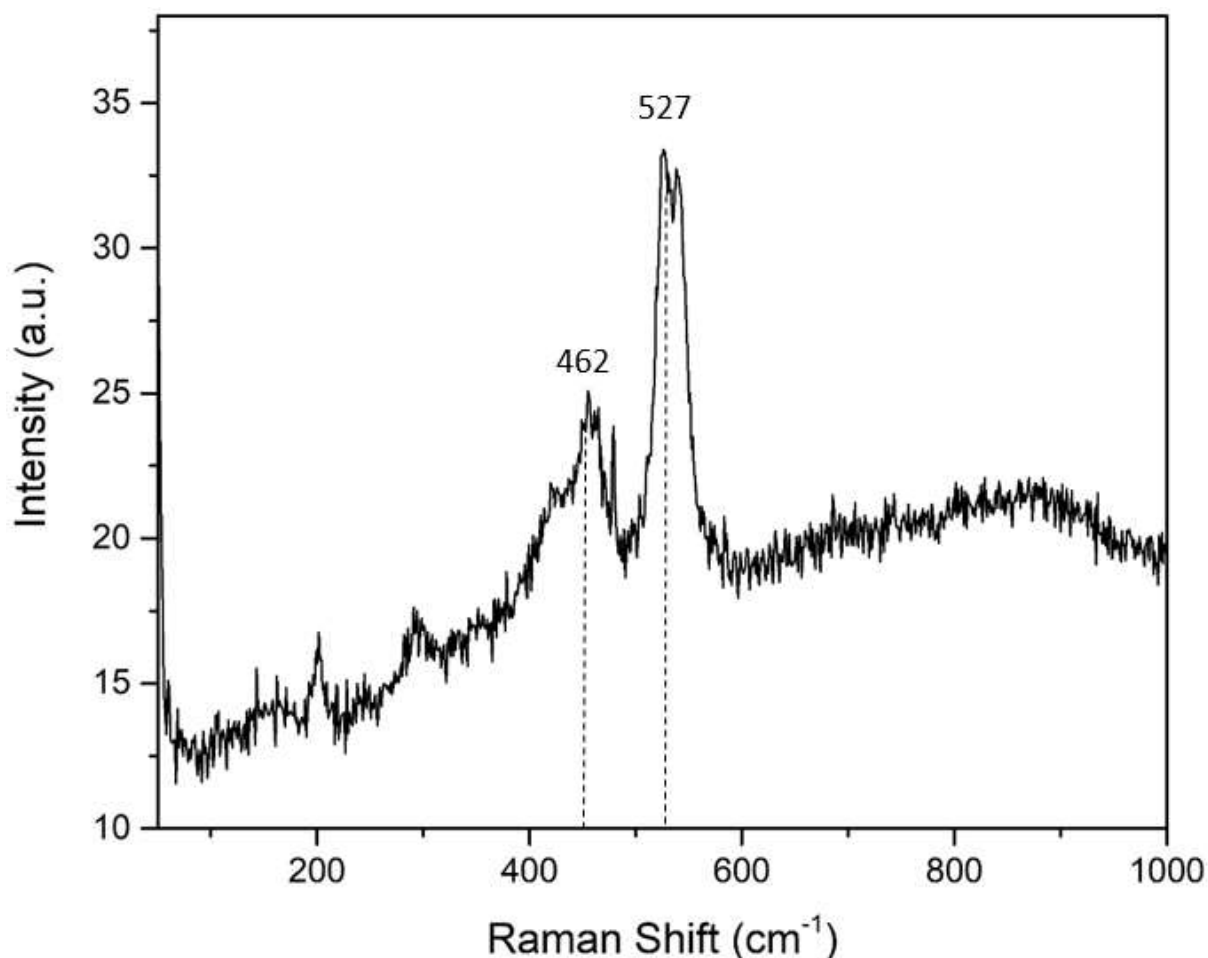


**Figure 4.2.6:** Raman fingerprint spectrum acquired for pre-cycled sr-NiFe LDH on Ni foam using a 532 nm excitation source at 1 mW with 1800 lines/mm spectral gratings.

Ageing the active material in 1 M KOH for 24 hours serves as a control experiment to check for any observable changes in the spectrum which may occur as a result of the alkaline environment rather than an effect of the potential application. What often takes place in the early lifetime of an alkaline OER catalyst is an uptake of  $\text{Fe}^{3+}$  ions from the electrolyte. Iron impurities are often present in trace amounts in electrolytes like KOH. These ions can be taken up by the LDH structure prior to OER catalysis. Even in small amounts, iron uptake in the active material can have a substantial effect on the initial catalyst performance, before phase and leaching effects take place with cycling. According to Louie & Bell<sup>151</sup>, for NiFe catalysts in alkaline media with no applied potential, iron

uptake may cause a positive shift in relative peak intensities  $I_{464}/I_{527}$  (Figure 4.2.7) relative to that value for the dry material  $I_{457}/I_{527}$  (Figure 4.2.6). Here the value of the former is judged to be roughly 0.96 and the latter 0.75. This demonstrates a considerable positive shift in the ratio which may suggest some additional  $\text{Fe}^{3+}$  ions are incorporated into the NiFe LDH system at this time. Uptake of additional trivalent cations at this point would be consistent with the contraction of layers detected by XRD in response to ageing (Figure 4.1.4). However, it has also been reported the slight loss of intensity for the higher wavenumber peak upon wetting as it is a band closely connected to the existence of surface defects.<sup>150</sup> The decrease in signal to noise ratio for the spectrum in Figure 4.2.7 is likely an effect of residual dried surface KOH on the catalyst. Future experiments would perhaps benefit from a cleaning step after ageing using DI water, although not entirely necessary in this case, as the relevant peaks are still visible.

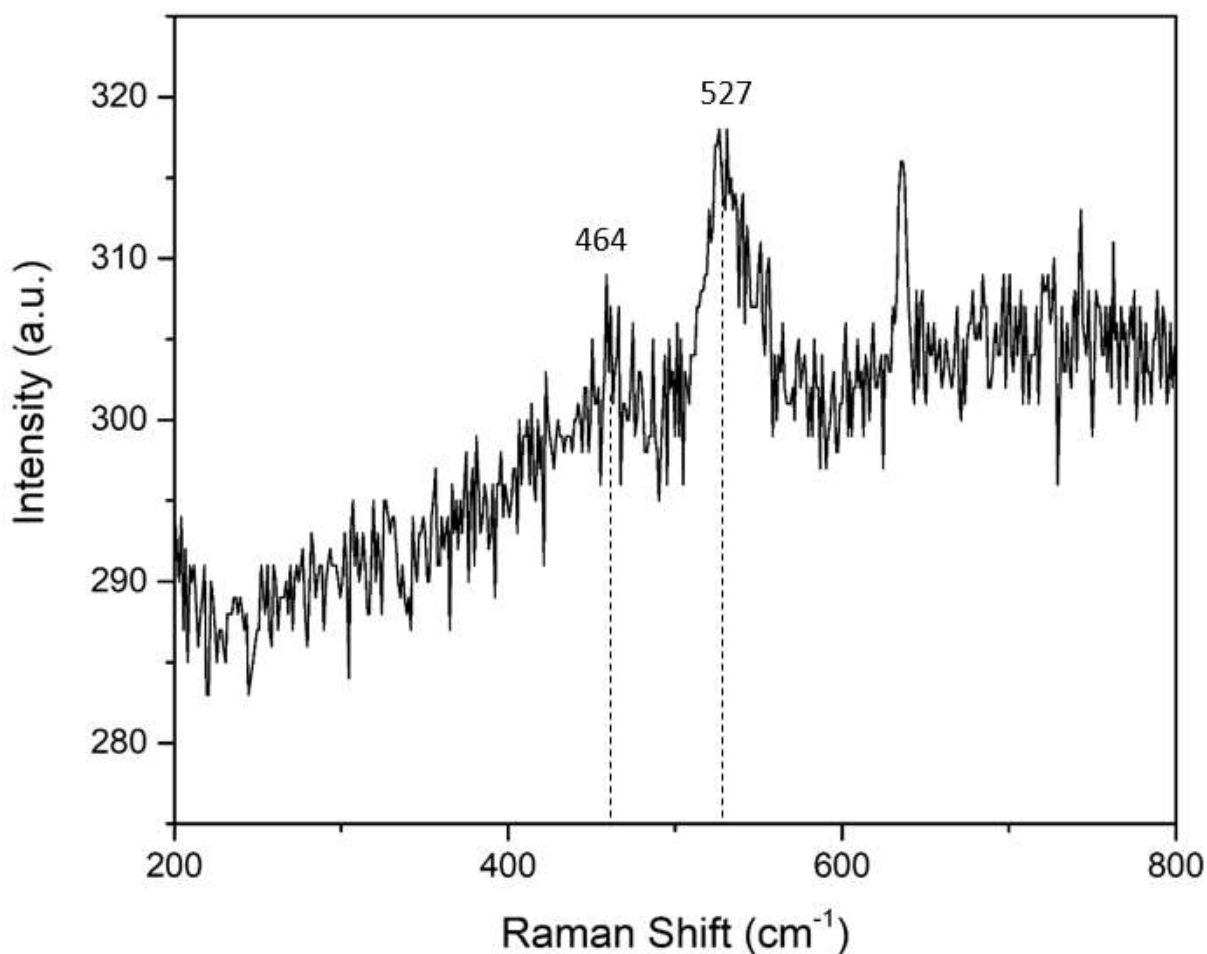


**Figure 4.2.7:** Raman spectrum acquired for aged sr-NiFe LDH on Ni foam in 1 M KOH for 24 hours using a 532 nm excitation source at 1 mW with 1800 spectral grating.

The evolution of the two principle peaks within OER active hydroxides in alkaline media is well documented. Various *in-situ* studies have demonstrated how the host structure reacts to the onset of potentials across voltage windows typically associated with alkaline water electrolysis (i.e. around 1 – 1.9 V vs RHE). Trześniewski *et al.*<sup>149</sup> describes the activity of a majority  $\alpha$  phase crystal (similar to the material under review here) during a voltage sweep 1 – 1.9 V (vs RHE) with 0.1 V steps. At low potentials, the hydrated  $\alpha$  phase will readily deprotonate, which is accompanied by an increase in intensity of the Ni-O band ( $I_{527}$  in this case). Beyond that, the  $\alpha \rightarrow \gamma$  phase transition dominates, bringing with it a shift in the two peaks to higher wavenumbers, which are now allocated as the Ni-O bending vibration ( $e_g$ ) and stretching vibration ( $A_{1g}$ ) for NiOOH, where nickel has been oxidized from  $Ni^{2+}$  to  $Ni^{3+}$ .<sup>152</sup> These bands are known to have high Raman cross section and should be clearly visible when the phase transition occurs.

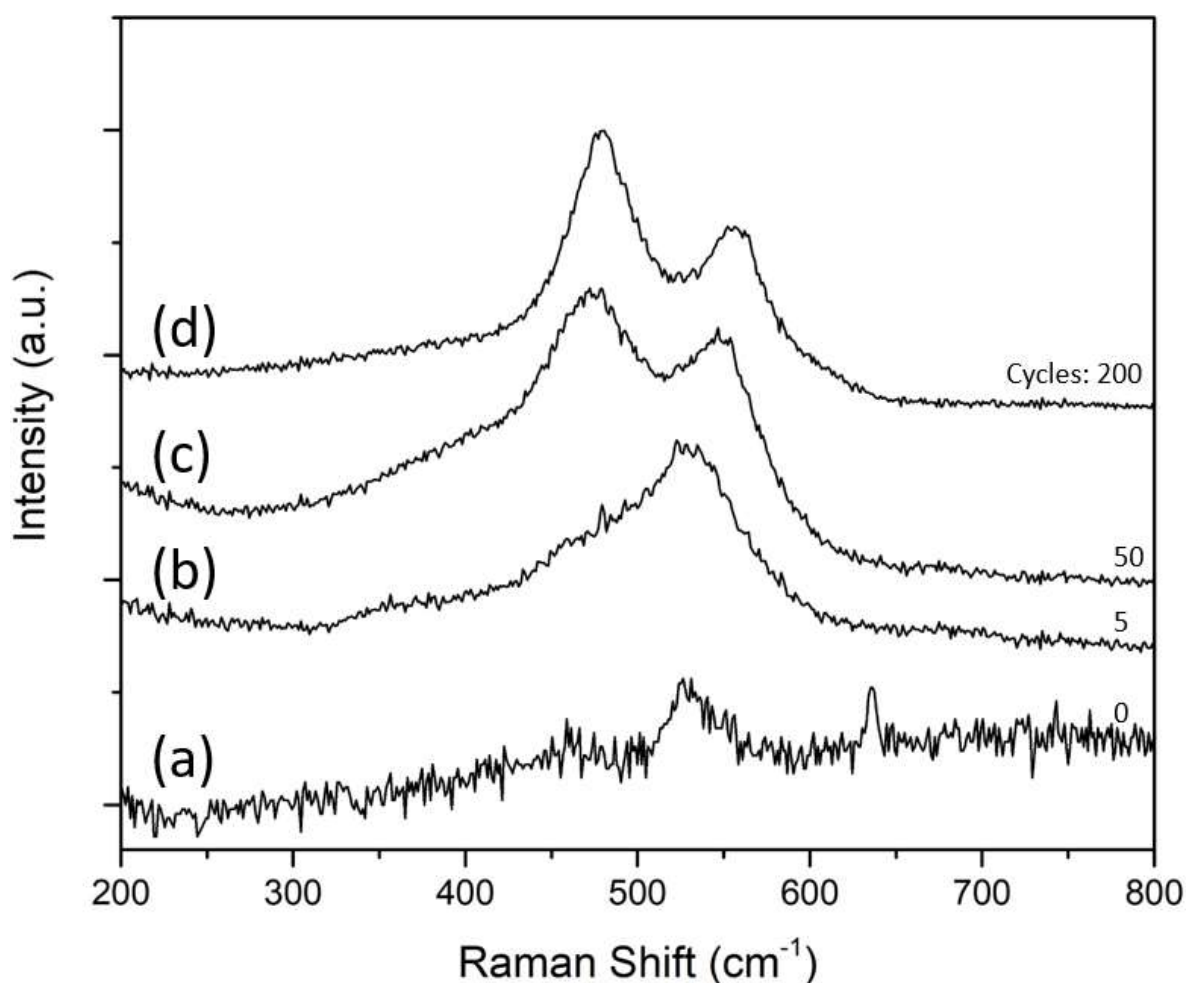


**Figure 4.2.8:** Raman spectra (1800 lines/mm) in the selected wavenumber range 200 – 800  $cm^{-1}$  for sr-NiFe LDH on Ni foam in 1 M KOH after (a) ageing (b) 5, (c) 50 and (d) 200 CV cycles between 0 – 0.6 V vs Ag/AgCl at 5  $mV \cdot s^{-1}$ .

The data displayed in Figure 4.2.8 represents a set of experiments carried out to *ex-situ* analyze NiFe LDH catalyst samples at various critical points during the OER active lifetime (all data acquired *ex-situ*). The points of interest for each Raman spectrum to be measured were decided by studying the repeated behaviour of sr-NiFe LDH flakes on Ni foam (see various examples of overpotential cycling curves in Chapter 3). They were chosen as cycle number 5, at which the minimum value of  $\eta$  was generally reached, cycle number 50, before which a significant inflexion point occurs, and finally after 200 cycles when the overpotentials begin to finally stabilize. Figure 4.2.8 compares all three cases with the 24 h aged material in KOH before cycling. What is immediately obvious from the figure is that the transition of peak intensities and wavenumbers of the bands are very much gradual processes, taking place throughout the catalyst lifetime rather than immediately. This is a unique perspective of Raman analysis and could reveal key information regarding the nature of how the active hydroxide catalyst changes with time during long term cycling, as opposed to within a singular voltage sweep.

After 5 cycles (Figure 4.2.8 b), one can see a slight wavenumber shift, with little to no change in peak intensity ratio. However, multiple *in-situ* studies report a shift in peak intensity ratio  $I_{457}/I_{527}$  from less than 1 to greater than 1 within each and every CV cycle, associated with the  $\alpha \rightarrow \gamma$ , hydroxide to oxyhydroxide phase change for each voltage sweep of 1 to 1.6 V (vs RHE). This single-cycle transition is reflected in CV analysis from this work which suggests that during the early cycling, phase changes must have occurred, yet the Raman data after 5 cycles displays no evidence as such. Therefore, there must be, to a high extent, a memory effect for the phase transition. In early cycle life, the reversible phase transition appears to occur as regularly as the oxidation/reduction of nickel. As the catalyst continues its cycling lifetime through 50 and 200 cycles however (Figure 4.2.8 c & d),  $I_{457}/I_{527}$  reaches values greater than 1 with a slight further shift of the peaks to higher wavenumber and additionally, an apparent improvement in the Raman cross-section for the species, meaning a secondary phase is now being detected.

There are two immediate hypotheses for this trend. One is that the phase change is not completely reversible and that each cycle leaves behind it some residual oxidised  $\gamma$ -NiOOH which

will accumulate over time. However, we are concerned only with the state of the material when it is active at elevated potentials. So if the data in Figure 4.2.8 simply reflects the residual  $\gamma$  phase it says nothing about the LDH at active potentials and therefore cannot conclusively allow for any comment to be made about the catalyst cycling performance. On the other hand, if we can exclude the possibility of residual  $\gamma$ -NiOOH phase then it may be possible to relate the peak shifts to a change in metals ratio for the long-term active NiFe LDH. As touched on already, Louie & Bell<sup>151</sup> carry out a thorough compositional Raman study for Ni-Fe based OER catalysts in alkaline media (1 M KOH), varying the Fe wt% from 0 to 100. They find that at elevated potentials (0.6 V vs Hg/HgO), removal of Fe from the system can cause a substantial increase in the  $I_{457}/I_{527}$  ratio and Raman cross section as the signal begins to move more towards the characteristic NiOOH signal (i.e. the case where all iron is removed). If this effect is to have any contribution to what is observed over the NiFe LDH catalyst lifetime in Figure 4.2.8, then this would align quite well with the degradation we see in catalyst performance over this period. In all likelihood, the peak transition results from a combination of effects.

### 4.2.3 Fourier Transform Infrared Spectroscopy

FT-IR is often considered a complementary technique to Raman spectroscopy. It is a tool which has already been utilized in this work for material characterization, looking at the as-produced NiFe LDH and highlighting the ability of the material to undergo ion exchange with simple etching (Figure 3.2.6). At this point of the research, we approach the FT-IR analysis with a different objective. Similar to before we want to perform a basic fingerprint characterization of the material on a suitable substrate, but unlike in Chapter 3, the main goal now is to try and determine what effects, if any, can be observed in the sample's FT-IR spectrum in response to the undergoing of relatively long-term ageing in alkaline media and electrocatalytic cycling, rather than picking specific points. While XRD and Raman analysis have allowed for the elucidation to some extent of the crystal phase behaviour of the catalyst, the search for solid evidence of iron leaching to complement previous observations, goes on. Given what is hoped to be achieved for the FT-IR analysis (i.e. less emphasis on phase behaviour and more on metal leaching), only three stages will be considered: the initial dry material,

aged for 24 hours on 1 M KOH and finally the cycled material which has been cycled with CV between 0 – 0.6 V vs RHE for fifty cycles. Not relying on the precise cycling behaviour as was necessary in section 4.2.2, it is possible to return to preparing sample electrodes by spraying directly onto a polished glassy carbon substrate. The acquired spectrum for the sr-NiFe LDH before testing is given in Figure 4.2.9. As was the case in the previous chapter, we once again assign the principle peaks for the as-produced sample. Water molecules principally give rise to the broad peak at 3424  $\text{cm}^{-1}$  as well as the lesser peak at 1616  $\text{cm}^{-1}$  ( $\nu_{\text{O-H}}$  vibrational and rotational modes respectively).<sup>85</sup> This immediately suggests a well-hydrated, mostly  $\alpha$  phase LDH to begin with. Hydroxyl groups at octahedral sites within the crystal also contribute to these signals, perhaps accounting for their broad appearance. At 1354  $\text{cm}^{-1}$  there is a sharp peak which coincides with the principle vibrational mode for a carbonate anion,  $\text{CO}_3^{2-}$ .<sup>33, 153</sup> The layered crystal is well intercalated with the expected counter anion. The highly intense peak centred around 720  $\text{cm}^{-1}$  is attributed to the Fe-O and Ni-O vibrations in various configurations (i.e. M-O, O-M-O, M-O-M etc. where M = Fe or Fe and O = oxygen).<sup>33</sup> The sharpness of this peak, along with the high intensity suggest high quality and bonding homogeneity across the sample at this point, a standard against which later spectra may be compared. Faint peaks located in the region of 1150 – 1210  $\text{cm}^{-1}$  are characteristic of C-N vibrational modes for tertiary amines, which is evidence of some residual TEA from synthesis.<sup>44, 85</sup> As for the peaks which are visible at 519  $\text{cm}^{-1}$ , according to a study by Saiah *et al.*<sup>153</sup> on NiFe LDH, peaks in this area represent the transitional modes of hydroxyl groups under the influence of a coordinated trivalent metal. In the case of as-produced, dry sr-NiFe LDH only iron exists in the more oxidised 3+ state with nickel in a divalent state. Looking at Figure 4.2.9, there appears to be more than one peak packed closely in this area, likely because of the multiple coordination possibilities of this vibration (i.e. Fe-OH, Fe-O-Ni etc.).<sup>154</sup> Experiments were performed in ambient conditions, which is why a peak at around 2200  $\text{cm}^{-1}$  will appear from  $\text{CO}_2$  stretching in all of the FT-IR spectra here.

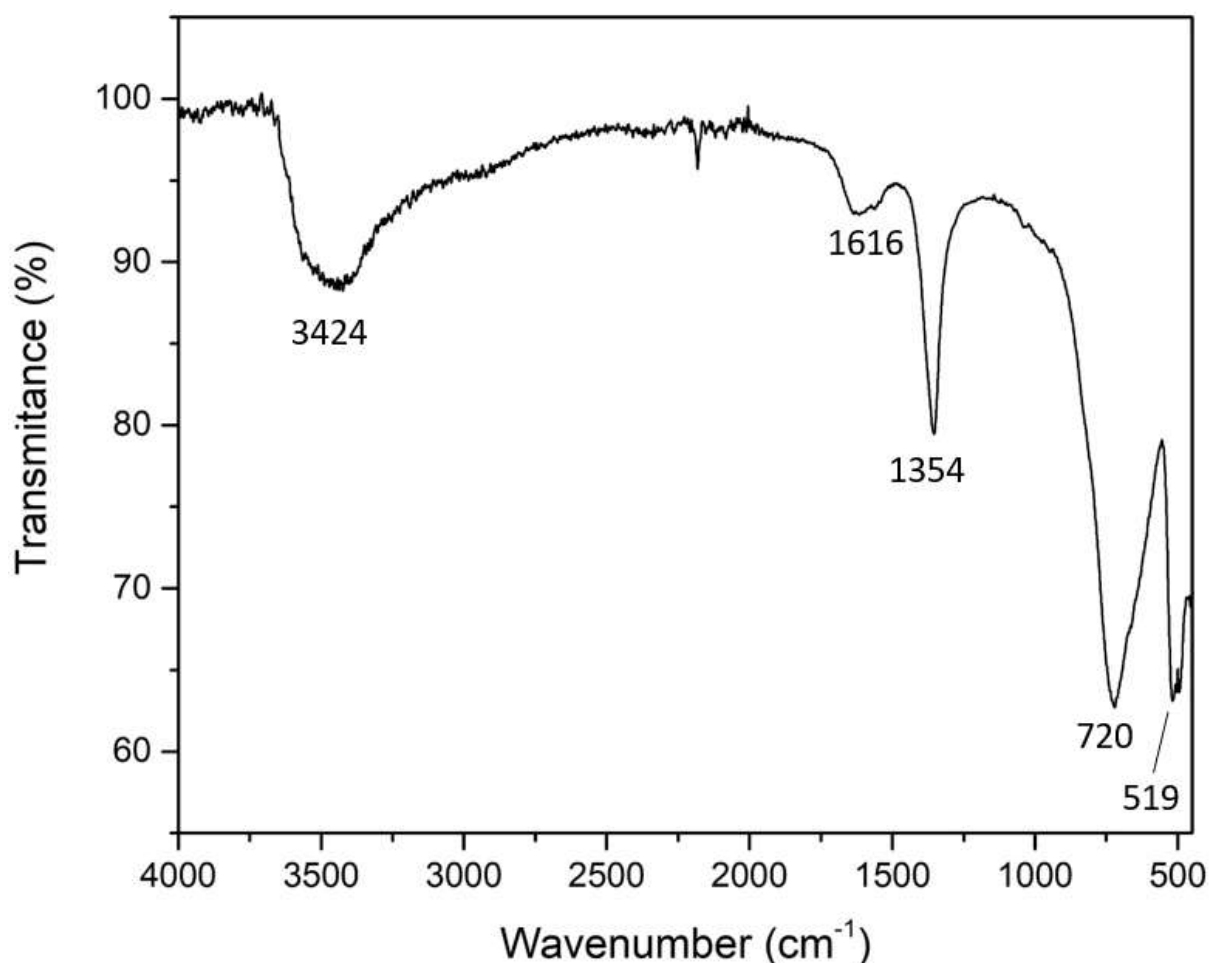


**Figure 4.2.9:** FT-IR 'fingerprint' spectrum for sr-NiFe LDH on GC.

The FT-IR spectrum shows that the sample at this stage is of satisfactory quality and is seemingly phase pure. From here, the material was sprayed directly onto a polished GC substrate as before for electrochemical testing. As a control, the sprayed electrode was allowed to age in 1 M KOH for 24 hours and analysed. This was done to ensure any effects which may be observed can be attributed to degradation caused by catalytic activity rather than the alkaline environment. The result (Figure 4.2.10) shows no observable changes in the characteristic IR spectrum. If anything, one can observe a slight intensity reduction in all of the characteristic peaks at 3437, 1630, 1356 and 719  $\text{cm}^{-1}$  with respect to the 516  $\text{cm}^{-1}$  peak. One may rationalize this by first considering that the peaks at 3437, 1630 and 1356  $\text{cm}^{-1}$  represent, for the most part, intercalation components (i.e.  $\text{H}_2\text{O}$  and  $\text{CO}_3^{2-}$ ). Chen *et al.*<sup>103</sup> report early onset intercalation of hydroxyl groups at interstitial sites during the ageing process and early catalysis. If this is the case then the partial removal of the intercalants from the as-produced crystal is to be expected, hence the loss of intensity for the respective peaks.

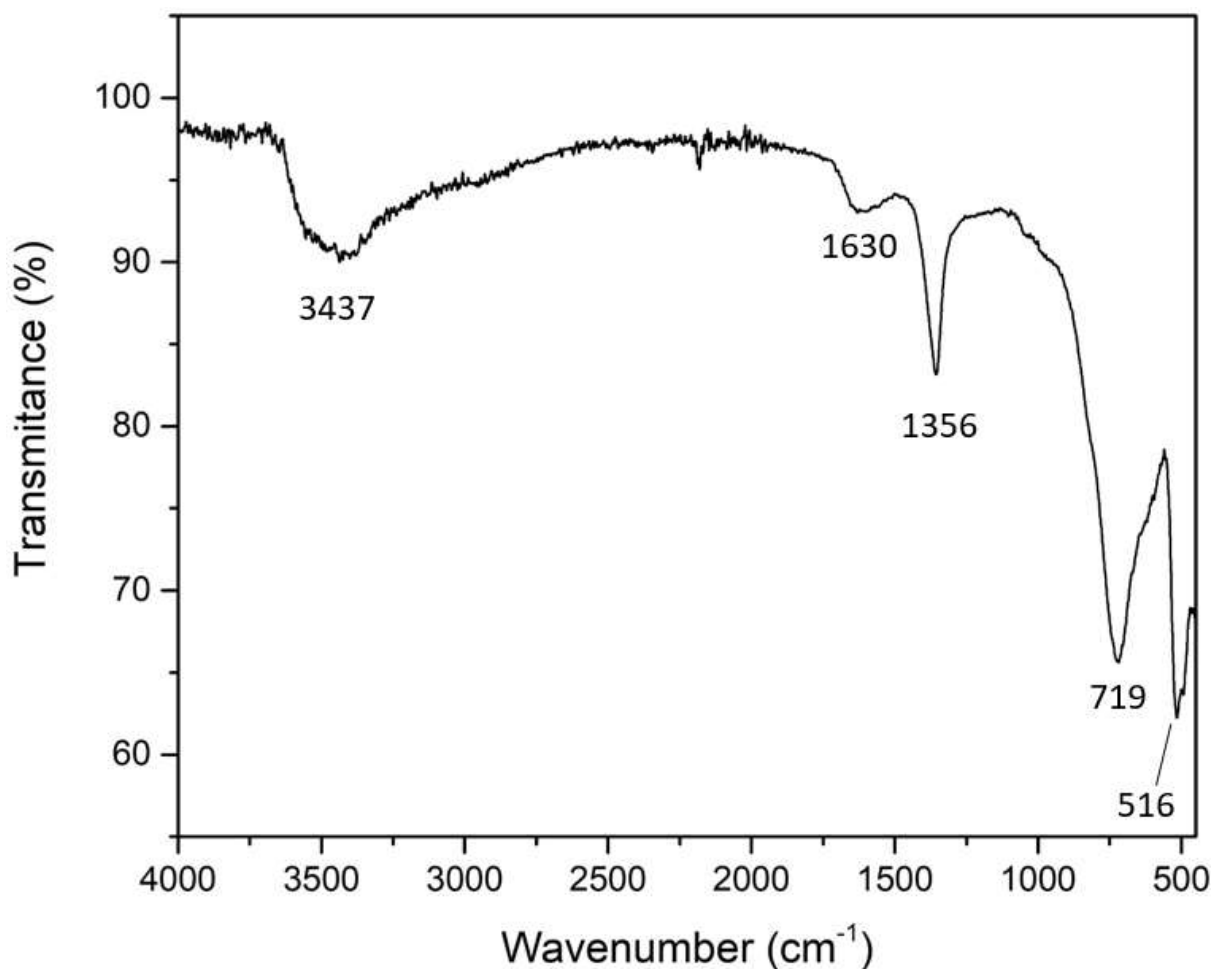


**Figure 4.2.10:** FT-IR spectrum for sr-NiFe LDH on GC after 24 h of ageing in 1 M KOH.

Taking the sprayed, aged electrode, CV sweeps were then performed over 50 cycles. Cycling was not performed to the same extent as before (standard cycle number has been 200 for nickel foam - deposited electrodes) in an attempt to minimize the likelihood of active material dethatching from the pristine GC surface, which was an issue when the material is subjected to more strenuous electrochemical conditions. However, one can see from the CV output for the cycles that the performance, although relatively poor to begin with, is significantly affected during this time and hence, some degradation of the active component is likely to have taken place. Figure 4.2.11 displays a typical spectrum for the post-catalysis sample. The first and most notable feature of the spectrum is the further flattening of the broad O-H vibrational stretching band centred around  $3431\text{ cm}^{-1}$ . This is unsurprising because one would expect repeated deprotonation to be accompanied by the loss of

water from interlayer positions. This may be considered somewhat consistent with the findings in the previous section where Raman spectra of the cycled electrodes demonstrate an apparent gradual phase change during the cycling lifetime with an increasing amount of residual secondary phase. However, the additional significant point here which Raman analysis could not show is the loss of water molecules. This suggests that the residual oxyhydroxide phase may partially contain  $\beta$ -NiOOH, rather than purely  $\gamma$ -NiOOH.

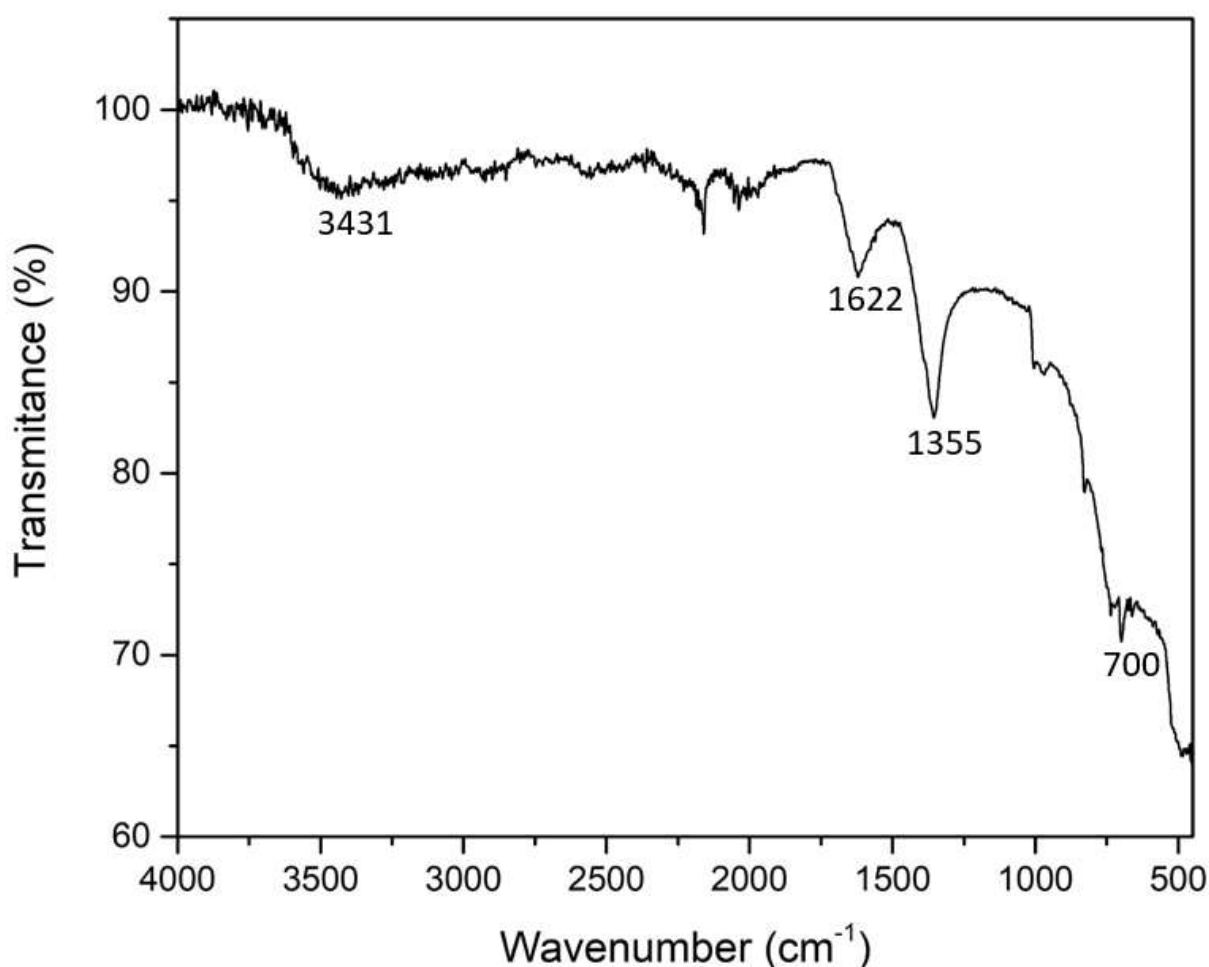


**Figure 4.2.11:** FT-IR spectrum for sr-NiFe LDH on GC after 50 CV cycles, 0 – 0.6 V vs Ag/AgCl at 5 mV·s<sup>-1</sup>, in 1 M KOH.

With a gradual  $\alpha \rightarrow \beta$  phase transition one would expect an improvement in catalytic performance during the transition but what appears from the voltammetry is a steady worsening of the performance (generally from cycle number four onward). So, we search for indications at this point that may explain this behaviour. Firstly, the significant loss of intensity for the prominent peak around 700 cm<sup>-1</sup>. It is known that this peak represents the various coordinations of M-O for Ni and

Fe within the hydroxide structure. The loss of this signal in Figure 4.2.11 may suggest a partial breakdown of the structure, which is anchored by metal-oxy bonds in the as-produced LDH. Another possibility is that this is another consequence of the gradual transition from hydroxide to oxyhydroxide, which comes as a result of long term cycling, whereby the majority of the  $\text{Ni}^{2+}$  (LDH) now exists as oxidised  $\text{Ni}^{3+}$  in the residual oxyhydroxide species which would bring about a shift in intensities from the  $700\text{ cm}^{-1}$  peak to the  $510\text{ cm}^{-1}$  peak which represents trivalent metal coordinated hydroxyl vibrations.<sup>153</sup> The loss of the large peak around  $700\text{ cm}^{-1}$  reveals a number of peaks not previously visible, at  $828\text{ cm}^{-1}$  and a double peak around  $1000\text{ cm}^{-1}$ . The former is assigned to the carbonate in the sample while the latter is slightly more puzzling. Features in this region for LDH spectra are generally assigned to hydroxyl groups. This can account well for the multiple signals around  $970\text{ cm}^{-1}$  but not for the second feature at  $1007\text{ cm}^{-1}$ . This will be revisited later in the section.

A more stringent observation of catalyst degradation would be to prove the leaching of metal centres from the crystal, as suggested based on the evidence of the statistical STEM-EDX findings in section 4.2.1. If iron is the preferential leaching component because of its lower stability within the LDH, then it should be detectable as some oxide or hydroxide compound after release into the alkaline medium. It is known that at high pH and low concentration,  $\text{Fe}^{3+}$  will manifest as some suspended hydroxide species of the form  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}(\text{OH})_4^-$  or somewhere in between (Figure 4.2.12). Regardless of the form in aqueous suspension, the dried iron hydroxide would likely form  $\text{Fe}(\text{OH})_3$  whose FT-IR signal should be detectable. So, here we principally aim to detect an Fe-OH vibration feature in the cycled infrared spectrum. Such a feature is expected to show up around  $1360\text{ cm}^{-1}$  for various ferric oxyhydroxide species.<sup>44, 155</sup> An unfortunate circumstance here is that this area is dominated by a strong C-O vibrational band deriving from  $\text{CO}_3^{2-}$  intercalation ions. Despite that, a subtle shoulder is visible in the spectrum at  $1360\text{ cm}^{-1}$  which has not been visible in previous spectra for dry and aged pre-cycled material. This feature may be evidence of leached  $\text{Fe}^{3+}$  component if it can be clearly shown.

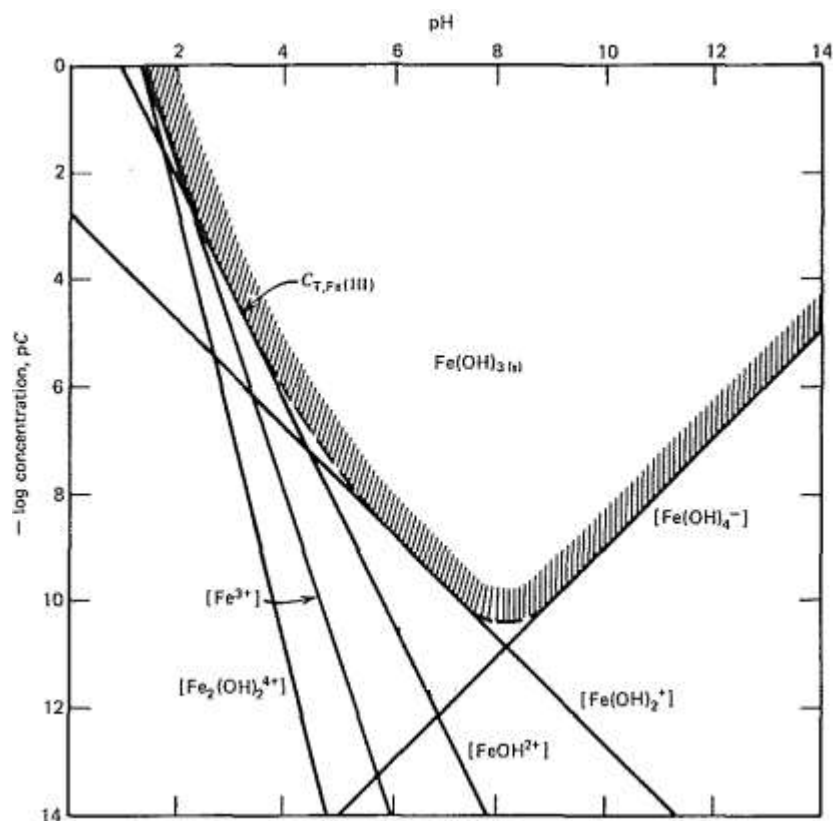


Figure 4.2.12: Room-temperature equilibrium concentrations of Fe(III)-hydroxo species in aqueous  $\text{Fe(OH)}_3$  suspension.<sup>156</sup>

So, an alternative route is required in order to provide clear evidence of some ferric oxyhydroxide compounds in the cycled sample. One way to go about this is to utilize one of the most significant LDH properties, the facile exchangeability of intercalated counter anions. As demonstrated in Chapter 3, simple acid and salt treatment can allow for near-complete anion exchange between NiFe LDH layers. If complete exchange can be carried out from  $\text{CO}_3^{2-}$  to some ion with no infrared signal then it is possible to free up that wavenumber region of the FT-IR spectrum for the pre-cycled material so that any ferric oxide/hydroxide signal may be spotted. The experimental procedure for the ion-exchange process from  $\text{CO}_3^{2-}$  to  $\text{Cl}^-$  is outlined in section 3.6 and involves treatment with NaCl and HCl in water. This was performed on some as-produced NiFe LDH and the result is shown as the black line in Figure 4.2.13. Compared to the previous spectrum for the pre-cycled material (Figure 4.2.9) where one can see a prominent peak at  $1354\text{ cm}^{-1}$ , in this case the peak seems to have all but disappeared. There is some remanence of a signal in this area which can

be designated as some minor carbonate intercalated phase. For the most part though the spectrum represents successful anion exchange to  $\text{Cl}^-$  between the layers.

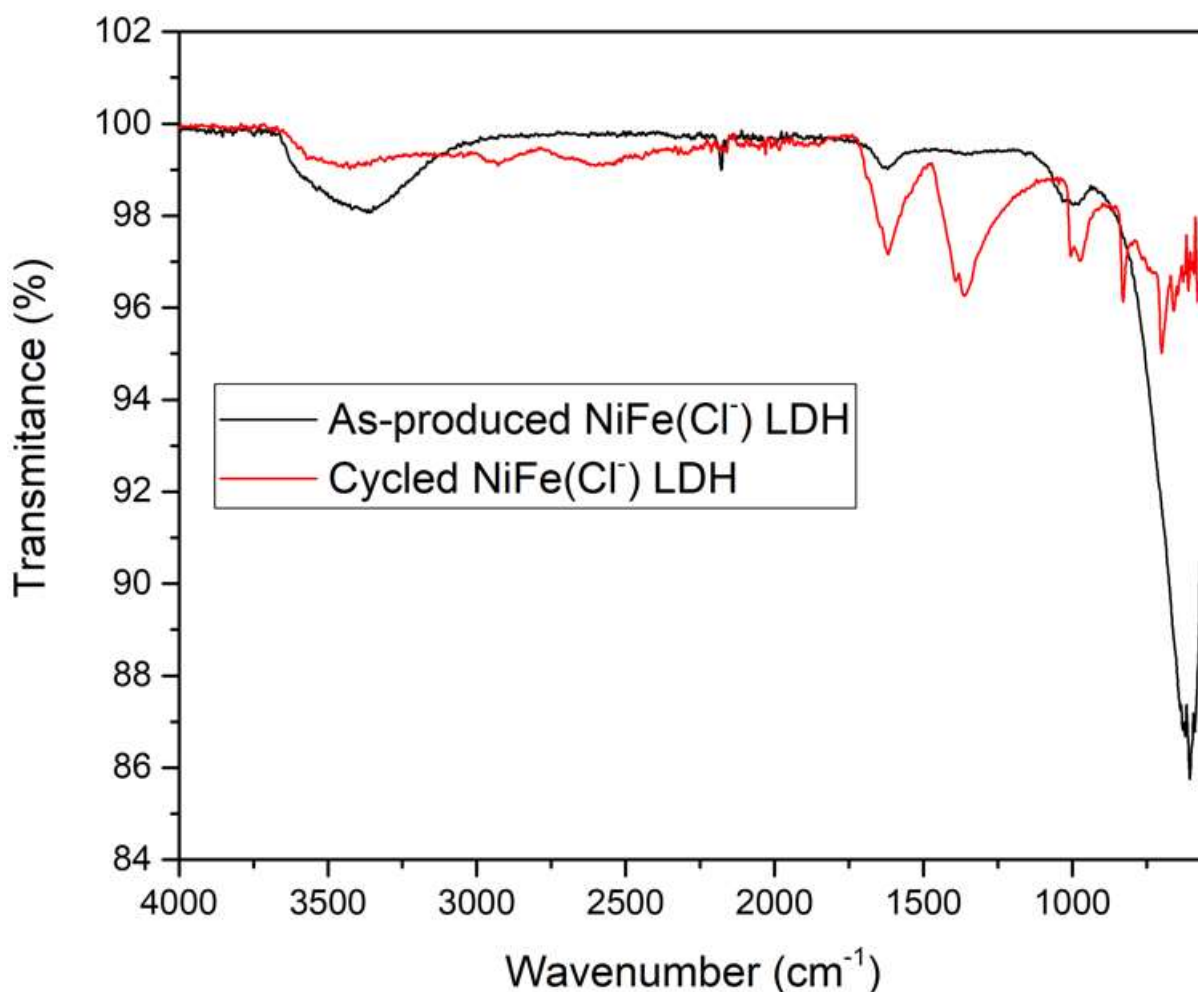


**Figure 4.2.13:** FT-IR spectra of pre-cycled (black line) and post-cycled (red line)  $\text{Cl}^-$ -intercalated NiFe LDH.

An identical process was applied to the chloride intercalated material as before i.e. spraying directly onto a polished GC substrate followed by OER cycling in KOH. The repeated FT-IR for the post-cycled catalyst is represented as the red line in Figure 4.2.13. Within the cycled spectrum we now see a doublet peak with considerable intensity relative to before. There appears a principle peak at  $1363\text{ cm}^{-1}$  with a shoulder at  $1391\text{ cm}^{-1}$ . Knowing that the vibrational spectrum for KOH (electrolyte) has no signal in this region, one can deduce that these peaks are somehow formed in response to activity in the LDH.<sup>157</sup> Additionally, according to the literature there are no signals which one could relate to a  $\text{NiOOH}$  or  $\text{FeOOH}$  compound, or indeed a combined one where the fingerprint lies mostly below  $800\text{ cm}^{-1}$ .<sup>158, 159</sup> So, there is a distinct possibility that the signal is describing iron

hydroxide/oxyhydroxide which is proposed at this point to be happening in response to gradual leaching of  $\text{Fe}^{3+}$  from the LDH structure in response to the applied potential sweeps, although carbonate anion exchange is swift and may be contributing to the peaks in this area as well.<sup>160</sup> Concerning the classification of complexes potentially formed from leached iron, specific peak assignments are difficult. It is possible that the leached iron takes the form of some ferrihydrite. 2-line ferrihydrite has been reported as a by-product of the alkaline precipitation synthesis, which involved similar conditions. Additionally, the diffraction pattern from the cycled XRD analysis in section 4.1.2 closely resembles the signal for 6-line ferrihydrite. So, one or both of these may be the case here, where leached iron is forming some precipitate of the same nature.<sup>44</sup> Rout *et al.*<sup>161</sup> quote a pair of infrared peaks for 2-line ferrihydrite at 1392 and 1572  $\text{cm}^{-1}$  corresponding to Fe-OH and Fe-O vibrations respectively. This matches well with Figure 4.2.13 as we see the intense peak at 1391  $\text{cm}^{-1}$ , but the Fe-O signal is not obvious. It is possible though to observe a subtle shoulder at this wavenumber, meaning the signal may be weak and mostly shielded by the nearby O-H signal. For one final suggestion of evidence of ferrihydrite, I return to the previously unmatched peak at 1007  $\text{cm}^{-1}$  which makes up one half of the double peak observed in both of the cycled cases (Figure 4.2.11 & 4.2.13). J.D. Russell<sup>155</sup> reports a peak in this region for hydroxyl groups in ferrihydrite species, which is defined as a deformation vibration for surface hydroxyl groups.

While perhaps inconclusive in terms of the exact form of the cycled NiFe catalyst and by-products, the FT-IR data presented here suggests considerable structural and compositional changes in the crystal in response to OER catalytic activity. The spectra suggest a loss of characteristic M-O and M-OH bonding for the mixed-metal structure accompanied by the manifestation of additional compound(s) as by-products of the catalyst degradation. Coupling observations from STEM-EDX and XRD analysis, it is proposed that the compounds are mostly iron based, perhaps a ferrihydrite, although the specification of such compounds cannot be made directly with the available information.

#### 4.2.4 Inductively Coupled Plasma Mass Spectrometry

To this point, there have been no steps taken yet to examine the electrolyte and how it changes in nature during catalysis. If the observations made so far are in fact evidence of iron ions leaching from the LDH then whatever iron compounds are formed as a result should be present in some concentration of the electrolyte after activity. Here ICP-MS is employed as a highly sensitive method of detection for this purpose. The choice of this technique over other compositional analytical approaches like AAS is based on the extremely low concentrations expected. Using previous data acquired in this work, namely the stoichiometric molecular formula  $\text{Ni}_{0.78}\text{Fe}_{0.22}(\text{OH})_2(\text{CO}_3)_{0.11} \cdot 0.5\text{H}_2\text{O}$  estimated based on a combination of TGA and AAS analysis in section 3.2, as well as the quantitative EDX survey from section 4.1 which gives a rough indication of the extent of iron leaching, one can expect trace iron concentrations in parts per billion (ppb) for the analyte. Importantly, the KOH electrolyte to begin with will not be free of trace iron ions, so what is hoped to be achieved here is a detectable *increase* in the Fe signal on the order of that expected based on rough stoichiometric estimations.

The tests experienced some difficulty in acquiring clear elemental signals. The results displayed up to 60% signal suppression even when the analyte was diluted ten times its original concentration. After two repetitions of the data acquisition for each sample (i.e. before and after OER activity) at dilutions 2, 10 and 100 times the original concentration, values of iron concentration were measured at 370 ppb ( $\sigma = 64$ ) and 400 ppb ( $\sigma = 32$  ppb) for the electrolyte before and after catalysis, respectively. Although the data presents an increase in electrolyte iron content once electrocatalysis was applied, the substantial overlapping of standard deviations for each data set creates ambiguity. ICP-MS analysis showed trace amounts of Cu and Ag which may have caused the formation of insoluble complexes with iron over time, and hence lowered the actual iron concentration. There are some steps which will be applied in the future to avoid this possible inaccuracy. Firstly, freshly prepared samples will be measured directly before and after electrocatalysis, so the storage time will be shortened to a minimum (for the presented data, due to long delays between sample preparation and data acquisition because of COVID-19 restrictions, samples were stored for three months in glass

vials, over which time a large impurity content was introduced to the alkaline sample, something which is generally avoidable.). Secondly, extra pure KOH (by purification) will be used in the experiments. Due to time constraints, experiments could not be repeated with these precautions for this thesis.

#### 4.2.5 X-Ray Photoelectron Spectroscopy

The goal remains to produce additional unique perspectives on the degradation mechanism of the active NiFe catalyst, specifically the leaching effect which, if proven to be accurate, would account well for the gradual loss of OER activity from the LDH edge sites with prolonged electrolysis. With this in mind, XPS is used to study surface active platelets for a sr-NiFe LDH catalyst, deposited this time on a Ti/Au/Si/SiO<sub>2</sub> substrate. To prepare the substrate, electron beam evaporation was carried out in a Temescal FC-2000 to deposit titanium to thicknesses of 150 nm on Au/Si/SiO<sub>2</sub> wafers. A 50 nm layer of Au was first deposited onto the Si/SiO<sub>2</sub> wafers in the Temescal before Ti deposition. The choice of substrate in this case was made based on compatibility with the XPS system. The Ti/Au/Si/SiO<sub>2</sub> plates were additionally cleaned via bath sonication before depositing the NiFe LDH for the purpose of degreasing.

The Ni and Fe 2p spectra are measured directly on the substrate before and after catalysis is performed, in order to establish any distinct changes in the composition of the metal centres. Figure 4.2.14 displays the results for the surveys, focusing on the nickel and iron spectral regions of interest. The peaks in Figure 4.2.14 (a) and (c) represent the 2p<sub>1/2</sub> (725 eV) and 2p<sub>3/2</sub> (712 eV) regions for Fe, while those in (b) and (d) represent the 2p<sub>1/2</sub> (875 eV) and 2p<sub>3/2</sub> (855 eV) for Ni<sup>2+</sup>, before and after cycling. The additional satellite peaks in the nickel spectra can be disregarded. Importantly, the atomic % measured at this point for the metals based on the spectra were 38.7% Fe and 61.3% Ni. After cycling, the 2p surveys for the respective metals appear noisier, but with the same principle 2p<sub>1/2</sub> and 2p<sub>3/2</sub> regions. The atomic percentages however, present a clear change in the material. After cycling, the Fe and Ni atomic % are measured at 19 and 81 % respectively, suggesting a clear loss

of iron from the structure. This is consistent with the evidence to this point of the chapter which seems to demonstrate preferential leaching of iron from the catalyst.

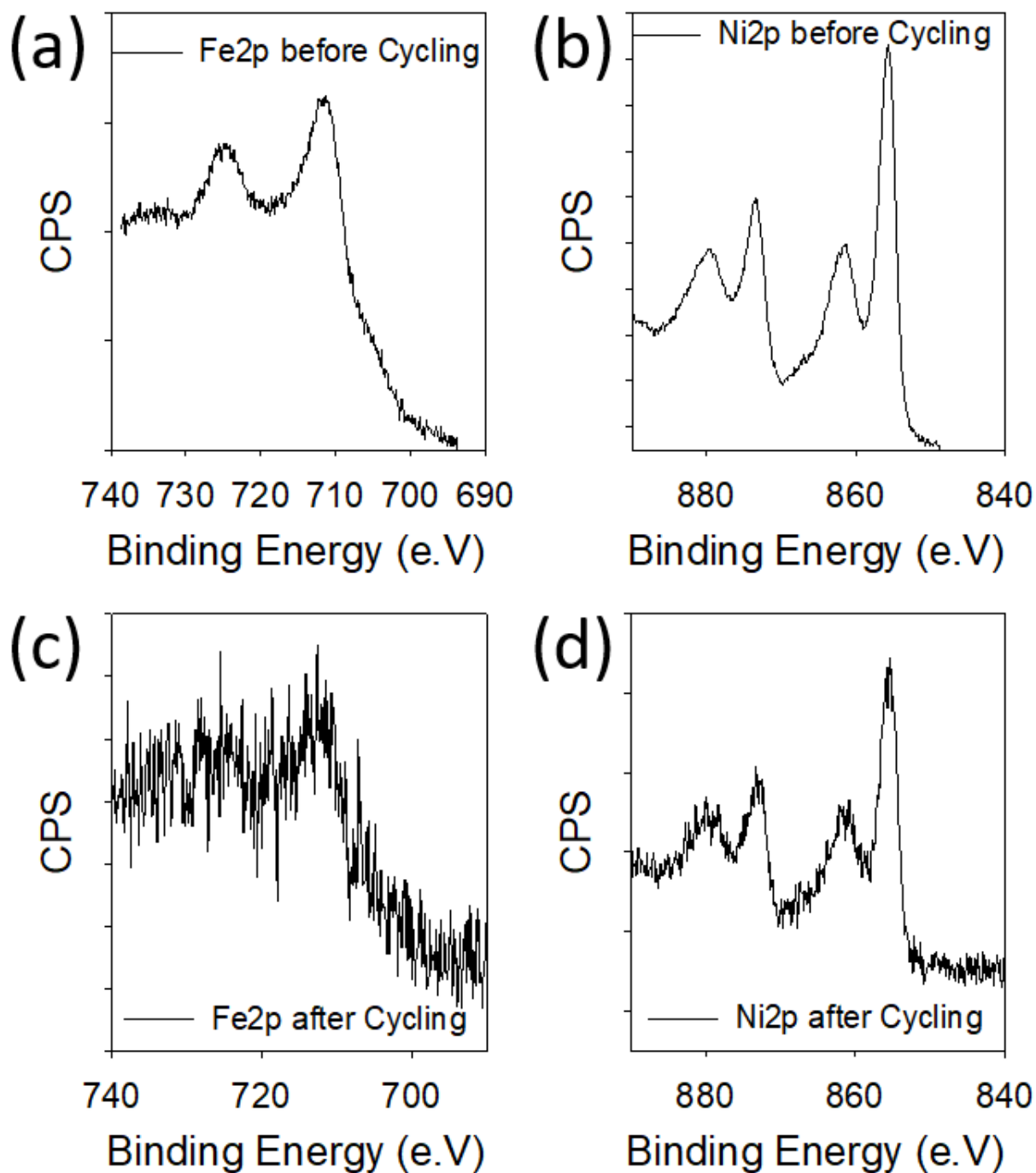


**Figure 4.2.14:** Binding energy XPS spectra for Fe 2p and Ni 2p orbitals before cycling (a, b) and after cycling (c,d) within a sr-NiFe LDH catalyst on Ti/Au/Si/SiO<sub>2</sub>.

## 4.3 Conclusions

Something to be considered based on the evidence of this chapter is the impressive capabilities of *ex-situ* experimentation to give evidence of intricate structural and compositional details within a catalyst during its active lifetime. With a well-established understanding of the behaviour of this NiFe LDH-based catalyst and how its performance changes in different circumstances, experiments were able to be performed at appropriate points during cycled OER catalysis. Perhaps the most successful example of this in the work was the detection of a catalytically induced phase transformation in the LDH structure by performing XRD analysis directly on a GC-supported sr-NiFe LDH catalyst. The results suggest convincing evidence for the formation of a secondary  $\beta$ -phase whose subtle structural shift is believed to improve upon the ability of the material to facilitate the OER mechanism at lower overpotentials. Based on the evidence of *ex-situ* XRD, there are no observable phases for NiFe LDH which correspond to the highly ordered  $\beta$ -phase which has been observed for  $\text{Ni(OH)}_2$  catalysts. The ability of the LDH material without the assistance of such a highly crystalline secondary phase is a testament to the high intrinsic activity of the material.

A number of characterization approaches carried out to compare the active sr-NiFe LDH material before and after OER catalysis seemed to suggest that a principle degradation effect of the material was the preferential leaching of iron from the LDH structure in response to long-term activity. Evidence included the increase in average Ni:Fe ratio from quantitative EDX analysis as well as the identification of some iron hydroxide/oxyhydroxide species from diffraction patterns and FT-IR signals. Electrochemical testing backs up the theory as cathodic shifts of the  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$  oxidation peaks with time suggest a loss of iron from the system. Additionally, ageing experiments fail to demonstrate any changes in the OER catalysis meaning that it is the act of OER catalysis at active edge sites which is triggering the degradation. It is expected that further experimentation will continue to clarify the details of the leaching effect. Methods of approach will include additional AAS and ICP to examine elemental compositions of the NiFe active component and the electrolyte component respectively, before and after cycling.

## 4.4 Experimental

**Glassy-Carbon Electrode Preparation:** Pristine GC substrates were prepared by first sanding and then polishing the surface with progressively finer alumina slurries (1  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$ ) with micro cloth, both sourced from Buehler. First, sanding was performed with 1 $\mu\text{m}$  alumina slurry on 3M™ Wetordry P1200 grade sandpaper. Next, polishing on nylon cloth with 0.3  $\mu\text{m}$  alumina. Finally, polishing on microcloth first with 0.3  $\mu\text{m}$  and then with 0.05  $\mu\text{m}$  alumina slurries. Between each sanding and polishing stage, the surface was rinsed with Millipore water and bath sonicated for 10 minutes, also in Millipore water, before drying in  $\text{N}_2$ . The active material was then deposited by ultrasonic assisted spraying at 100 °C as in Chapter 3 and tested similarly in a three-electrode setup using crocodile clips on a bare contact area of GC (Figure 4.2.1 b).

**STEM-EDX Sample Preparation:** After the sprayed GC electrode was subjected to appropriate electrochemistry, the active NiFe LDH was ‘scraped’ from the flat surface using polymer-based apparatus into a small volume of IPA. The material was then dispersed by bath sonication at 37 kHz, 60% power for 5 mins and drop cast onto a Cu-lacey carbon TEM grid (200 mesh, Ted Pella Inc.) before allowing to dry in air for at least 24 h.

**AFM Sample Preparation:** Samples of as-produced NiFe LDH and sr-NiFe LDH were prepared on a pristine Si wafer substrate for the purpose of AFM analysis. The Si wafer (460 – 530  $\mu\text{m}$  thickness, Ted Pella Inc.) was cleaned by bath sonication in IPA at 37 kHz, 100% power for 10 mins with 3 repetitions before finally rinsing in IPA and drying in  $\text{N}_2$ . The NiFe samples were diluted to low concentrations before drop casting (2 – 3 drops) on the clean Si surface and drying in air.

**XPS Sample Preparation:** The Ti/Au/Si/SiO<sub>2</sub> plates were cleaned by bath sonication at 37 kHz, 100% power for 15 mins before drying under  $\text{N}_2$ . The plates were sprayed as before with ultrasonic assistance and tested in a standard three-electrode setup using an area of bare Ti to contact.

## 5 Improving Capacity Retention in Lead(II) Oxide Nanocomposite LIB Anodes

The landscape of materials technology for anode components of next generation LIBs is broad and competitive. Material families vary from metals and metal oxides to nitrides, sulphides and phosphides. Additionally, many carbon materials and semiconductor compounds exhibit favourable performances in lithium-based energy storage. Nanoscience plays a massive role in synthesizing and developing not only novel materials but novel approaches for processing and combining electrode components to fully realize their optimum performance. With that in mind, there exist a class of materials whose common alloying approach to lithiation gives rise to exceptional theoretical specific capacities. The flagship material of this alloying class is silicon, whose theoretical capacity of roughly  $3600 \text{ mAh}\cdot\text{g}^{-1}$  or more, is at least ten times that of commercially accepted graphite and has drawn worldwide intrigue as to its practical performance and industrial compatibility.<sup>162, 163</sup> However, many other similar materials exist with impressive theoretical capacities, either metallic, like silicon, or additional metal oxides. One such material is lead(II) Oxide, PbO. Lead has played a massive role in the battery industry to this day, being used in 86% of all automobile batteries as of 2015 and boasting a theoretical capacity of  $582 \text{ mAh}\cdot\text{g}^{-1}$  for lithium ion intercalation.<sup>164</sup> Metallic Pb, although the ideal starting component for lead-based LIB anodes, is impractical due to difficulty in storage and transport of the metal, which has a high tendency to oxidize in air at its surface. Metal oxides can, however, be reduced to their metallic form at moderate potentials. This ‘conversion’ is irreversible within the cell conditions, meaning repeated lithiation/delithiation of the metallic Pb can be carried out thereafter. For this reason, oxides are considered an ideal starting component in a practical sense. A significant breakthrough for lead in the field of next generation LIBs remains elusive, however, and in this work the goal will be to systematically clarify the extent to which lead(II) oxide specifically can perform as a high-performance anode in secondary LIB cells compared with other alloying and conversion materials and hence reach some conclusion as to the oxide’s potential as a serious, commercially compatible battery component.

Before beginning, we take a look at the up-to-date research in the field and where the LIB research community is largely placing its efforts for high-performance anodes both in terms of raw materials and composite systems as well as experimental approaches for increasing energy density and cell performance. Once a relatively broad outlook of the field is established, one can see exactly where PbO fits into the picture. The best place to start when reviewing a wide spectrum of materials for a specific application is to establish a small number of key properties which are deemed of the utmost importance when selecting one. To this end, the following have been deemed imperative factors in material selection. Firstly, specific LIB performance factors like reversible gravimetric capacitance, charge and discharge rate capabilities and cycle life and secondly, more practical properties like cost, toughness and/or durability in working conditions and finally sustainability/recyclability. Through years of thorough synthesis and characterization studies, a number of anode material subgroups have emerged with combinations of said properties, with materials from each group being studied intensely in the hope that one candidate, or some combination, will be discovered whose energy density and power output (i.e. rate performance) can rival that of a combustion engine. The three main groups of materials, classified in terms of how they undergo lithiation/delithiation, are classed as 1.) intercalation, 2.) alloy and 3.) conversion anode materials.<sup>165</sup> The former includes graphite which has found considerable commercial success and the latter two have been introduced already and include metallic silicon and the oxide PbO.<sup>165-167</sup> Figure 5.0.1 graphically represents where each class sits in the scale of gravimetric capacity with respect to working potential. The graph clarifies the potential for great improvements on conventional LIBs whose most popular anode component comprises graphite which, as discussed briefly in the introduction to this paper, demonstrates many favourable properties making it a safe, practically viable material but with a relatively modest capacity limit.

Of all the materials in question, none of them represent state-of-the-art LIB anode technology more than silicon and its composites. Silicon's  $\text{Li}^+$  ion storage mechanism as well as subsequent swelling and fracturing issues are outlined in Chapter 1 and closely resemble the issues for PbO and other metal oxide anodes. However, the extremely high theoretical capacity is too much to ignore

and as a result, the material remains the centre of worldwide LIB research despite its considerable setbacks. It also means silicon is the ideal anode to model a study like this on. One point of interest in this work will be to determine what methods have been most successful in optimizing silicon's useable gravimetric capacity and how transferable those techniques are to anode materials like PbO. A study by Park *et al.*<sup>168</sup> have demonstrated the current state-of-the-art full cell *areal* capacities for silicon-based LIBs using segregated carbon nanotube networks, achieving combined electrode areal values of 29 mAh·cm<sup>-2</sup>. The gravimetric, or 'specific' capacity ( $C_{sp}$ ) can be related to this value directly with a proportionality constant described by the mass loading, as described in Equation 5.1 where  $C_A$  is the aerial capacity and  $M/A$  describes the deposition mass per unit area, or mass loading value.

$$C_A = C_{SP} \times \frac{M}{A} \quad \text{Equation 5.1}$$

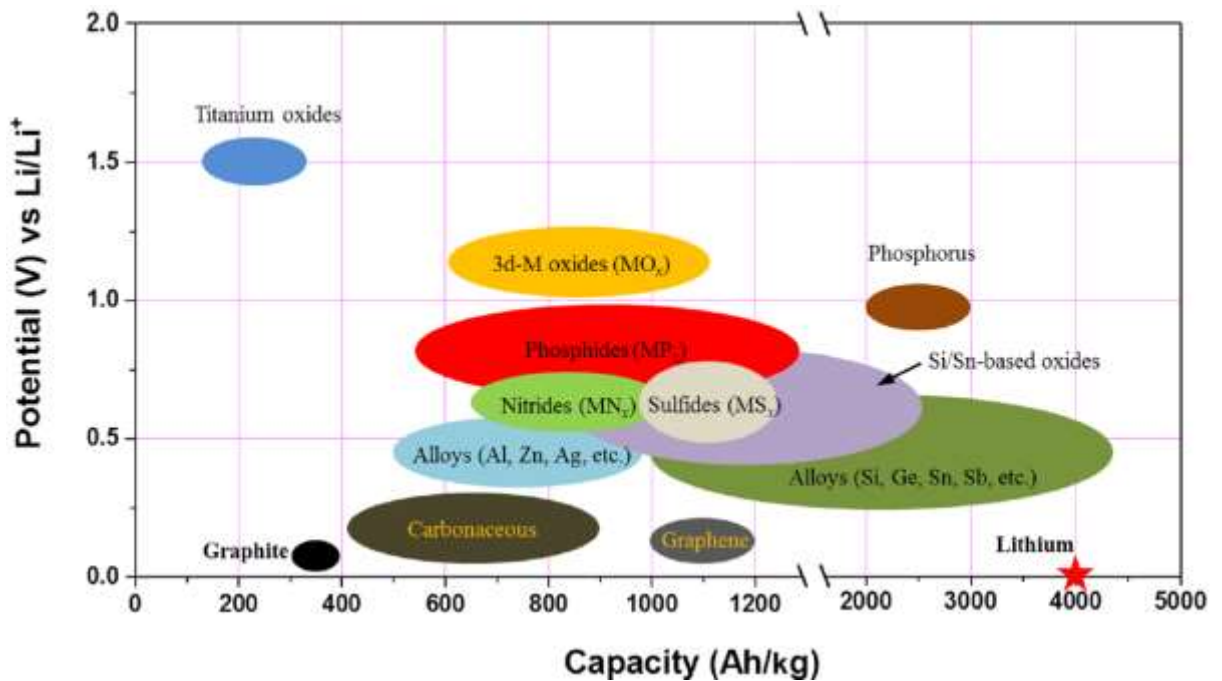


Figure 5.0.1: Graphical comparison of various anode material families in next-generation LIB technology.<sup>165</sup>

The electrodes produced here can achieve enough mechanical stability to allow them to be manufactured in thick films while also exhibiting impressive conductivity and energy density. Studying areal values of key variables like capacity, energy and power is a very useful approach in more practical studies, often coming up when evaluating full-cell devices. However, this work aims

to look at intrinsic capabilities of the PbO material in question and is less concerned about electrodes thickness/density considerations etc. So, we will stick to  $C_{SP}$  characterization in  $\text{mAh}\cdot\text{g}^{-1}$  for this chapter.

Reviewing all of the work being done on silicon and similar materials, the most eye-catching aspect of the research is the simplicity of approach and the seemingly highly reproducible nature of the procedures. For example, the publication by Park *et al.*<sup>168</sup> involves two of the most established processing techniques in nanoscience for battery materials: active material size reduction (using micron-sized Si as the anode component) and the building of controlled CNT nanocomposites. The approach is mirrored across the field of high-performance LIB electrode development, with various active materials<sup>169</sup> and composite additives.<sup>170</sup> With similar pros and cons to silicon, metal oxides like PbO and SnO present an interesting, relatively untouched platform to categorically identify their optimal electrochemical performances based on similar techniques to the cutting edge work presented in the literature for alloy/conversion anodes.

In this chapter the aim is to electrochemically characterize PbO within carbon composites in lithium ion half cells. Firstly, commercially acquired material will be studied, then in-house synthesized material, where attempts will be made to control the phase of the oxide. In order to allow the material to perform to the best of the ability which can be offered by simple processing techniques, the PbO particles will be attempted to undergo size reduction and exfoliation as well as a thorough composite study, all with the aim of reducing diffusion pathways, minimising long-range stress from lithiation and improving the electrical and ionic conductivity within the anode system.

## 5.1 Commercial PbO

Lead(II) Oxide is readily commercially available at low cost. Additionally, it can be synthesized relatively easily via procedures involving heat treatment of some Pb precursor, such as lead carbonate ( $\text{PbCO}_3$ ), lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ), lead benzoate ( $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Pb}$ ) and lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) to name a few.<sup>171-174</sup> The choice of synthesis route can be geared towards certain

applications. For example, spray pyrolysis of lead acetate onto a lead substrate can be used as an approach to produce well-crystallized PbO with a high built-in lithium ion storage capacity. Additionally, controlled synthesis can allow for the highly selective production of either one or the other of the PbO polymorphs i.e. the tetragonal ‘litharge’ phase or the orthorhombic ‘massicot’ phase (the common abbreviations used across the literature are, unfortunately, once again  $\alpha$  and  $\beta$  respectively). Methods for this phase control include hydrothermal treatment as well as dry controlled thermal decomposition approaches.<sup>174, 175</sup>

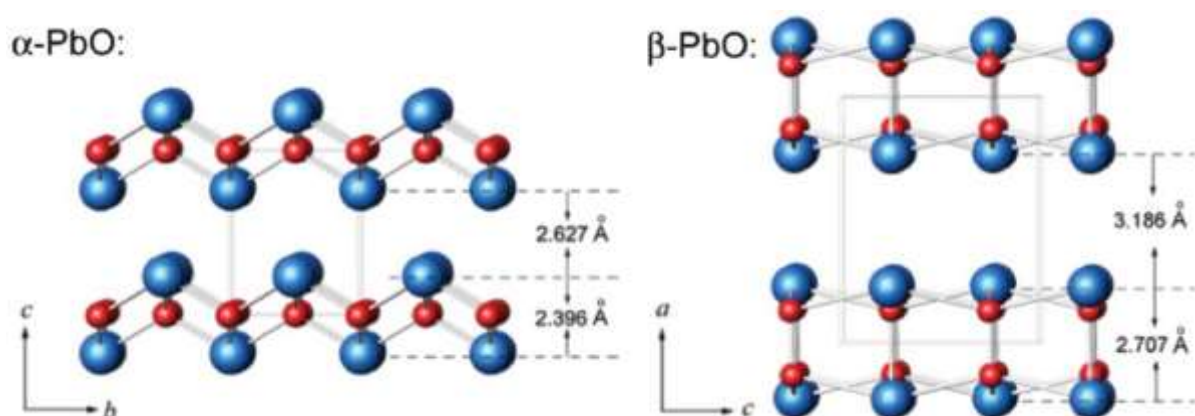


**Figure 5.1.1:** Tetragonal (left) and orthorhombic (right) crystal structure for the respective  $\alpha$  (litharge) and  $\beta$  (massicot) PbO phases. Blue and red spheres represent Pb and O atoms, respectively. (Republished with permission of the Royal Society of Chemistry, from ‘Selected-control hydrothermal growths of  $\alpha$ - and  $\beta$ -PbO crystals and orientated pressure-induced phase transition’, Wang et al., volume 23, issue 18, 2013; permission conveyed through Copyright Clearance Centre, Inc.)<sup>175</sup>

As an example of a commercially available PbO powder, presented here will be a full characterization of a product from J.T. Baker, marketed as Litharge, lead(II) Oxide.

### 5.1.1 Crystallography

Before testing in a LIB cell, some preliminary characterization was carried out for the commercially acquired PbO. Powder XRD analysis was performed on the material, which was crushed to a fine powder in preparation. For polymorphs like this one, crystal diffraction is often a useful way to determine phase purity of the material, especially when sourced externally. The XRD pattern in Figure 5.1.2 suggests that the litharge phase is not pure and that in fact there seems to be a substantial signal relating to both  $\alpha$  and  $\beta$  phases.<sup>172, 175</sup> The principle (100) and (001) peaks for massicot and litharge crystals respectively, are homologous and represent the ability to transform

directly from one to the other. Thermal treatment above 560 °C alone has been proven enough to force the  $\alpha \rightarrow \beta$  transition.<sup>176</sup> The polymorphic PbO sourced from J.T. Baker is a good starting point for the study, as much of the work presented in the literature involving novel synthesis and composite approaches report mixed phase oxides.<sup>177</sup> This will serve as a standard to compare the samples with higher phase purity later.

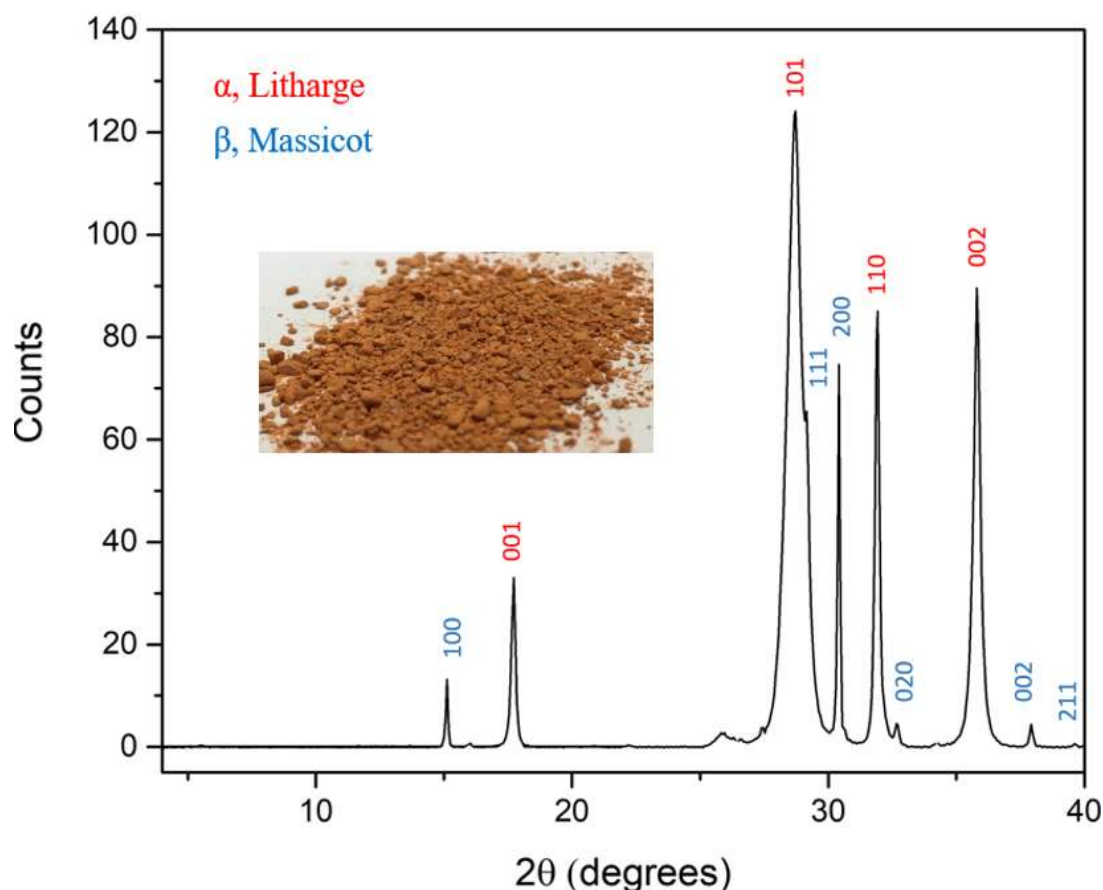


**Figure 5.1.2:** XRD pattern for commercially acquired PbO, using copper K $\alpha$  source.

Aside from its polymorphic nature, the sample displays good crystallinity and purity. The unmatched peak at  $2\theta$  value of 26 ° is not clear in its origin. It perhaps derives from some residual PbO<sub>2</sub> from the synthesis as it aligns somewhat with the (110) plane of tetragonal PbO<sub>2</sub>. As a contaminant this is not uncommon, in fact lead oxide electrochemistry often reveals that multiple oxides are present in small amounts in materials like this one, as we shall see in this section.

### 5.1.2 ‘Bulk’ Electrochemistry

One of the most effective ways to characterize PbO in terms of crystal quality, phase purity etc. is electrochemically. A number of systematic experimental and calculation based studies have been carried out to identify lithium alloying potentials for various distinguishable host materials.<sup>178, 179</sup> Here we present characteristic initial CV and galvanostatic cycling with potential limitation (GCPL) discharge curves vs Li/Li<sup>+</sup> (Figure 5.1.4) for the commercial PbO anodes formed in a slurry with 10 wt% carbon black and 10 wt% polyvinyl difluoride (PVDF) binder on copper foil. The full procedure is outlined pictorially in Figure 5.1.3 and explained in full detail in section 5.5.

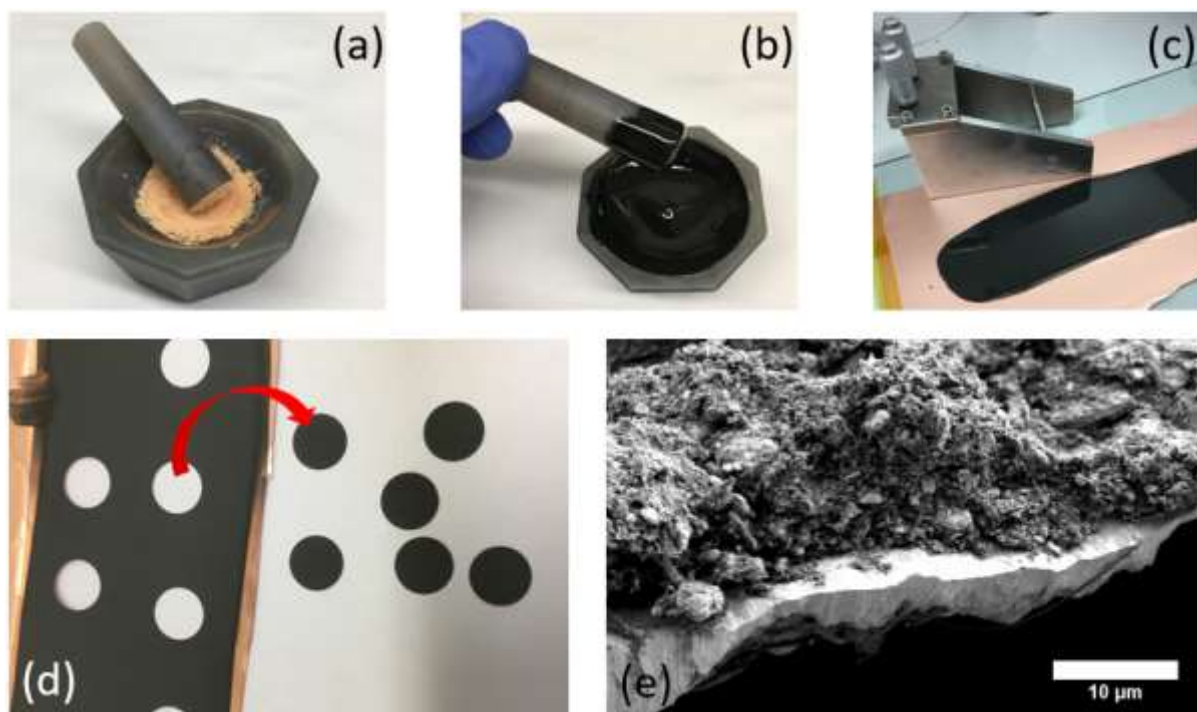


**Figure 5.1.3:** (a) – (d) Digital photographs representing the steps involved in preparing PbO slurries with carbon black and PVDF binder on copper foil, and (e) SEM micrograph of the edge profile of the dried slurry and substrate.

In the case of these preliminary tests, carbon black is used as a high surface area conductive additive while PVDF is used for its elastic mechanical properties, allowing for high enough levels of viscosity to be reached to allow for slurry formation. Electrodes prepared using slurries in this way are limited in their gravimetric output but serve well for first principle characterization studies. The CVs and GCPLs were acquired at relatively low sweep and discharge rates of  $0.1 \text{ mV} \cdot \text{s}^{-1}$  and  $0.1 \text{ C}$  respectively to ensure that the interesting features are captured. Voltammetry was used principally

in this work as a first step approach to characterizing assembled LIB half-cells. The well documented anodic and cathodic peaks serve as a solid reference on which one can characterize the cell. Figure 5.1.4 (a) represents a standard example of the peak placement for charging and discharging a mixed-phase PbO LIB cell. Particularly, the GCPL discharge profile holds a lot of character for the transitions of an alloying material during lithiation, which is reflected in the curves, where CV peaks should correspond to plateaus in the GCPL discharge profile.

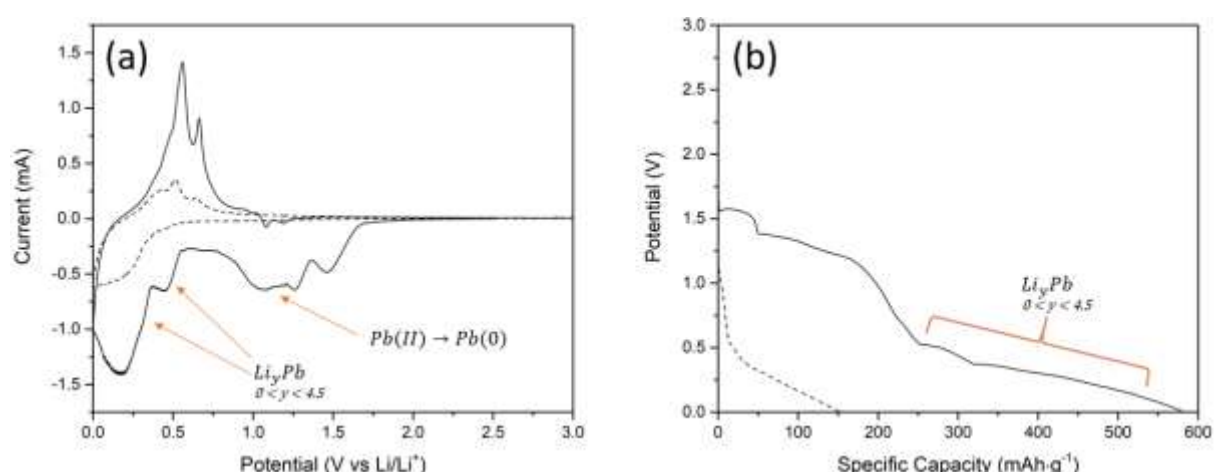
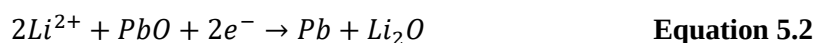


Figure 5.1.4: 1<sup>st</sup> and 2<sup>nd</sup> (a) CV cycles at 0.1 mV·s<sup>-1</sup> and (b) GCPL discharges at 0.1 C with areas of interest labelled.

Given that PbO is an example of a ‘conversion’ material in terms of Li<sup>+</sup> storage, the first expected occurrence during discharge is the reduction of lead(II) to a metallic state according to Equation 5.2. The reaction is reflected in the cathodic peak around 1.15 V vs Li/Li<sup>+</sup>.<sup>171</sup> Due to the irreversibility of the reaction, the peak does not show up in subsequent cycles, as can be seen in the second cycle CV (dotted line, Figure 5.1.4 a). One may notice an additional peak at a slightly higher potential to this, around 1.3 V, the origin of which is not well established. It has been reported however that multiple peaks in the region of 0.9 to 1.3 V for the initial discharge case can be attributed to the Pb(II) → Pb(0) conversion, whose nature is thought to be more complex than previously imagined. This point is perhaps more relevant in a polymorphic system like the one we are studying. Moving to higher potentials again, the feature just above 1.5 V is not known to belong to PbO activity. It is thought to possibly derive from the activity of some PbO<sub>2</sub> impurities in the sample.<sup>173</sup>



Moving to low potentials now, below 0.6 V the lithium alloying begins with lithium uptake from LiPb up to Li<sub>4</sub>Pb (litharge) or Li<sub>4.5</sub>Pb (massicot).<sup>173</sup> More than one train of thought appears in the literature for explaining precisely how the Pb forms alloys in this narrow potential range. For example, Huggins *et al.*<sup>178</sup> propose a number of potential plateau regions at which significant Li-Pb compositional changes take place. Namely, 0.601, 0.449, 0.374 and 0.293 V vs Li/Li<sup>+</sup> which occur in the potential region labelled on the initial galvanostatic discharge curve in Figure 5.1.4 (b). On the other hand, some studies report a more well-defined series of exact alloying intermediates in the same potential range. Pearson *et al.*<sup>179</sup> define them as LiPb, Li<sub>2.5</sub>Pb, Li<sub>3</sub>Pb, Li<sub>3.3</sub>Pb, Li<sub>3.5</sub>Pb and Li<sub>4</sub>Pb. Regardless, the precise alloys which form at this stage of the PbO discharge are difficult to designate from the CV peaks or GCPL plateaus in the figure so we label this potential region as the alloying cathodic range rather than specific voltage points vs Li/Li<sup>+</sup>. One final noteworthy observation from the 1<sup>st</sup> and 2<sup>nd</sup> charge/discharge data for the as-received commercial PbO is the extreme change in the behaviour after cycle number one.

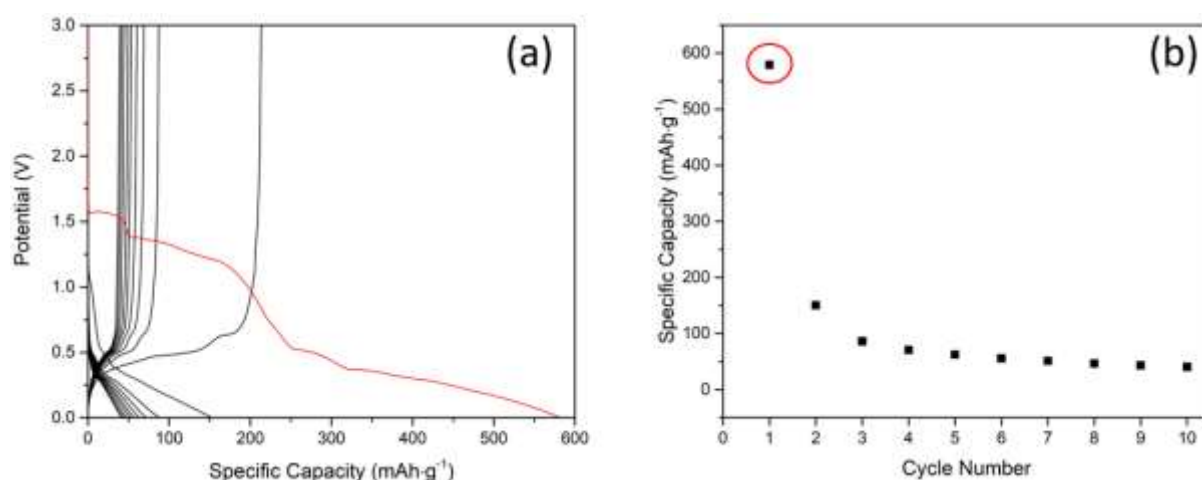


**Figure 5.1.5: (a) GCPL charge-discharge profile for the commercial PbO with 10 wt% carbon black and 10 wt% PVDF at 0.1 C and (b) graph of specific discharge capacity as a function of cycle number.**

A lot of processes take place during this initial cycle to influence the apparent specific capacity. A significant portion of these are irreversible and hence, may not be considered as processes which can contribute to the long-term capacity performance in a secondary battery. The conversion Pb(II) → Pb(0) is just one example of such irreversible reactions. Additionally, the formation of the solid-electrolyte interface (SEI) which generally occurs at a potential around 0.7 V, accompanied by

some decomposition of the electrolyte.<sup>171, 177</sup> The formation of a SEI during early battery lifetime is arguably the most essential step for establishing long term activity. By their very nature, LIB electrodes are strongly oxidising/reducing in the potential windows set for them. So, at voltages close to the potential limits there is always going to be a reaction between electrode and solvent from the electrolyte. Without the formation of a surface passivation layer these reactions would periodically break down the anode or cathode resulting in failure of the cell.<sup>180</sup> Summing up all of the reversible and irreversible processes, the discharge capacity value which is ultimately reached in the initial case is often greater even than the achievable capacity in theory. Figure 5.1.5 demonstrates the extent to which this can occur for the PbO under review in this section, with an apparent capacity drop of 74% from cycle number one to two. Because of this, the initial discharge reading is commonly disregarded in anode research for materials of this type so as not to introduce any ambiguity into the analysis. Herein, the “1<sup>st</sup> discharge” will refer to first accepted discharge capacity (second overall) to distinguish from the initial discharge (first overall).

### **5.1.3 Ball-Milling**

As can be seen in the digital photograph (inset in Figure 5.1.2), the PbO material comes in bulk, with some small granules and some larger pellets of a centimetre or more. Up to this point for preliminary analysis the material has been crushed by hand using a mortar and pestle to achieve a finer particulate morphology for slurry preparation (Figure 5.1.3 a). In order to achieve a finer initial powder, we implement here a ball-milling step. Ball-milling is a technique commonly used in the processing of nanomaterials for applications in electrochemical devices where a fine particulate sample is most desirable.

Ball-milling involves rapid rotation of the material in a cylindrical steel chamber along with steel balls of various sizes.<sup>181</sup> This grinds the material in the chamber to a great extent, producing an extremely fine powder and if performed correctly can allow for mechanical activation of the material in its electrochemical application. Ball-milling was performed here on the as-received PbO using a Planetary Ball Mill Machine (Lennox Lab Supplies) at 900 rpm for 3 hours. The procedure resulted

in a clearly more particulate sample based on SEM analysis. Figure 5.1.6 displays the key features observable by low resolution microscopy. Over wide range analysis, one can see a considerable reduction in the particle sizes, even though there remains the effect of clustering in the ball-milled case. Looking on the surface of some of the larger clusters using a secondary electron signal, it is possible to see that there is a significant increase in the sub 100 nm features from the fragmented PbO crystals.

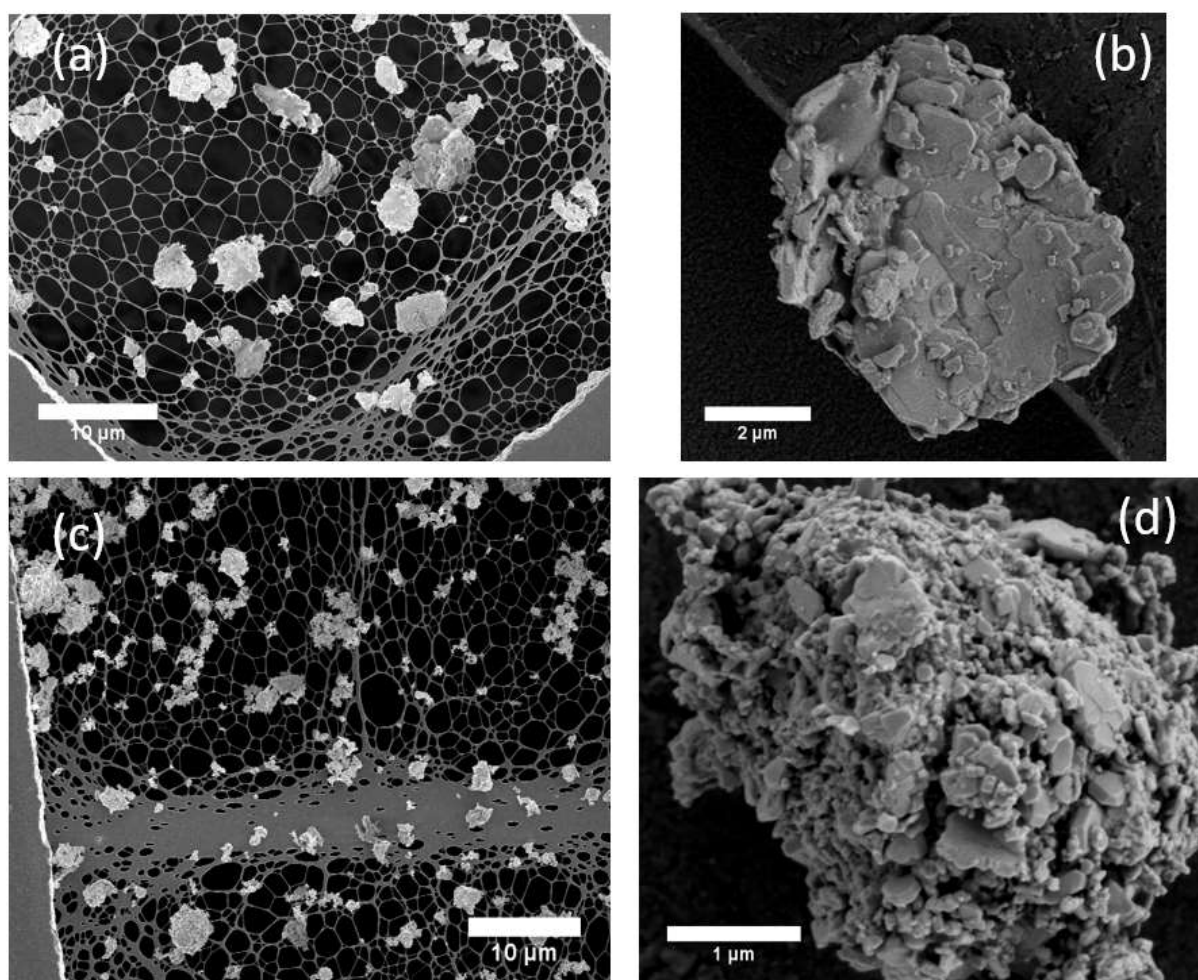


**Figure 5.1.6:** Lower and higher magnification SEM micrographs for commercial PbO after crushing by hand (a, b) and after ball-milling (c, d).

Early signs based on GCPL cycling for PbO-PVDF-carbon black using ball milled powder suggest that the performance can be enhanced to a reasonable extent using this method alone (Figure 5.1.7). Identical charge-discharge experiments at 0.1 C with anodes of 10 wt% carbon black and 10 wt% PVDF for the ‘bulk’ vs ball-milled PbO show a + 63 mAh·g<sup>-1</sup> increase in specific capacity through ten cycles. This fact alone taps into one of the previously mentioned processing techniques

at the forefront of research in electrochemically applied nanomaterial. Dimension reduction is flagged in almost every LIB anode materials review available in the literature.<sup>47, 167</sup> Intuitively, the theory makes sense that the effect of average particle size reduction would suppress the long range stress experienced by an alloy during  $\text{Li}^+$  insertion/deinsertion. This is reflected in the experiment as we can see a 40% specific capacity retention through 10 cycles, an improvement on the 26% for the material before ball-milling. Another intuitive thought is that size reduction will improve aspects like specific surface area and mean diffusion paths into the active component of the anode. These factors should have the effect of improved rate performance and energy density, the latter of which is clear in the figure below.

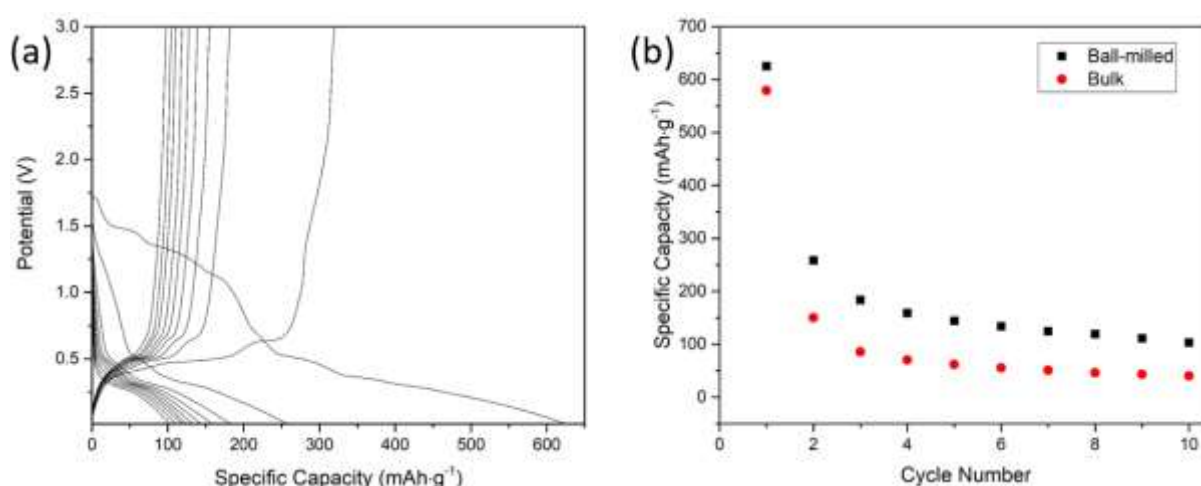


**Figure 5.1.7:** (a) GCPL charge-discharge profile for the ball-milled commercial PbO at 0.1 C and (b) specific discharge capacity cycling graph compared with the 'bulk' slurry.

### 5.1.4 Carbon Nanotube Composite

Up to this point carbon black composites with a PVDF binder has served as a useful system to lay the groundwork for the commercial PbO in terms of electrochemical characterization. However, in order to produce an anode whose gravimetric performance can be considered fully optimized, we must consider a single component which can marry the conductive and mechanical properties of carbon black and PVDF, respectively. As in Chapter 3, once again carbon nanotubes are introduced as performance enhancement additives which can potentially do just that. On top of their impressive tensile strength, conductivity and stability, there is the additional motivation that CNTs can perform lithiation with an impressive theoretical capacity ( $1116 \text{ mAh}\cdot\text{g}^{-1}$ ) in crossover

potential ranges with the PbO component.<sup>182-184</sup> CNTs store lithium by intercalation similar to their graphite allotropes, but with a higher theoretical capacity. The degree of lithiation is heavily dependent on defects and suffers from a large degree of irreversibility, similar to the PbO. The poor reversibility in the case of CNTs however, arises from difficulty in removing  $\text{Li}^+$  after initial discharge, rather than from issues with mechanical fracture as is often the case with alloying materials. So, despite the potential for high intrinsic LIB anode performance, CNTs are implemented here first and foremost to provide a highly conductive, mechanically strong matrix to help facilitate reversible Pb-Li alloying. The lack of any significant changes in early cycle life coulombic efficiencies for SWCNT composites in this study, compared with carbon black-PVDF, seems to suggest minimal energy storage contribution for the nanotubes (Figure A12). There exist a great number of examples of anodes based on CNT components combined with some other high theoretical performance metal or metal oxide to create a synergistic anode composite with improved performance in terms of factors like capacity retention with cycling and rate capabilities.<sup>168, 185, 186</sup> In this vein, lead(II) oxide's compatibility with SWCNTs will be tested by preparing slurries with the two principal components, similar to before.

To begin preparing SWCNT electrodes with the ball-milled commercial PbO, a solution of 0.4% SWCNT in  $\text{H}_2\text{O}$  with a polyvinyl difluoride (PVDF) surfactant (2%) from Tuball™ BATT will be used to prepare mixtures with PbO with high enough viscosity to behave as a slurry which is compatible with the Dr. Blade approach to film preparation. In this way, the electrode production process can present the same simple qualities as carbon black slurries with controllable thickness and component ratios. Once again, a comparative GCPL experiment through ten cycles is used at this point to determine the relative performance of the SWCNT and carbon-black based slurries. What is immediately obvious from Figure 5.1.8 is that there is indeed a noticeable improvement in both initial and cycled specific capacity values. With 10 wt% SWCNTs and discharged at a rate of 0.1 C, the new composite demonstrates an initial value of  $370 \text{ mAh}\cdot\text{g}^{-1}$  with a 62% capacity retention after the 10<sup>th</sup> cycle. This combination of ball-milling and composite treatment for the commercially acquired polymorphic PbO produces a satisfactory improvement in the preliminary lithium storage behaviour

to suggest that techniques like this can potentially work to improve the materials outlook. To achieve the goal of full optimization of this composite system, a systematic weight ratio study will be carried out on the PbO and SWCNT components before a final thermal activation step is applied in an attempt to remove any significant residual mass of PVDF which may be affecting the gravimetric performance.

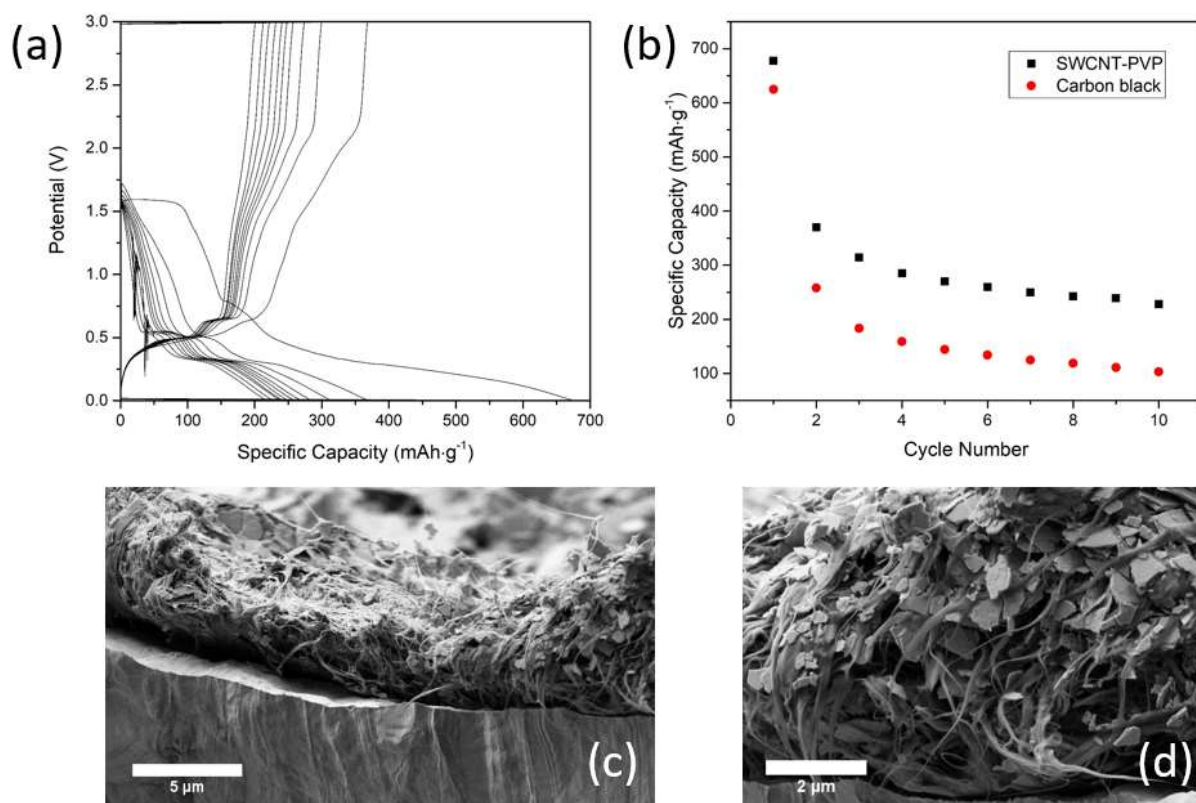


**Figure 5.1.8:** (a) GCPL charge-discharge profile for ball-milled commercial PbO with 10 wt% SWCNTs (Tuball) at 0.1 C and (b) specific discharge capacity graph compared with the analogous carbon-black based slurry. (c, d) SEM micrographs of the dried SWCNT slurry on copper substrate.

Electrodes were prepared for initial testing with 5, 10, 15 and 20 wt% SWCNT and deposited on a copper foil contact at 25 μm thickness using a doctor blade. The first forty cycles of the four cases at the thus far used 0.1 C discharge rate give a clear early look at the percentage range where the optimal SWCNT mass fraction will be (Figure 5.1.9). Predictably, the 5 and 20 SWCNT wt% anodes represent the highest and lowest initial energy density respectively, while the latter displays the greatest degree of capacity retention through 40 cycles (33%). In fact, the 1<sup>st</sup> discharge capacities show an inverse proportionality with respect to SWCNT wt%, while the capacity retention values demonstrate a direct proportionality. The apparent capacity loss with increasing nanotube wt% is

clearly a consequence of considering the entire electrode mass, rather than that of the active material alone, because the active mass fraction decreases. If one considers only the active mass, the composites improve in apparent specific capacity to a maximum value at 15 wt% ( $682 \text{ mAh}\cdot\text{g}^{-1}$ ) before decreasing again. There is a clear reliance of these active specific capacities on their composite environment, which suggest that charge transfer limitations are considerable for this material, which further justifies the necessity for an optimized SWCNT mass fraction. Based on Figure 5.1.9 alone, it would seem a value close to 15% would be considered optimum for cells operating at 0.1C discharge rate. What if we consider different rates of cycling now?

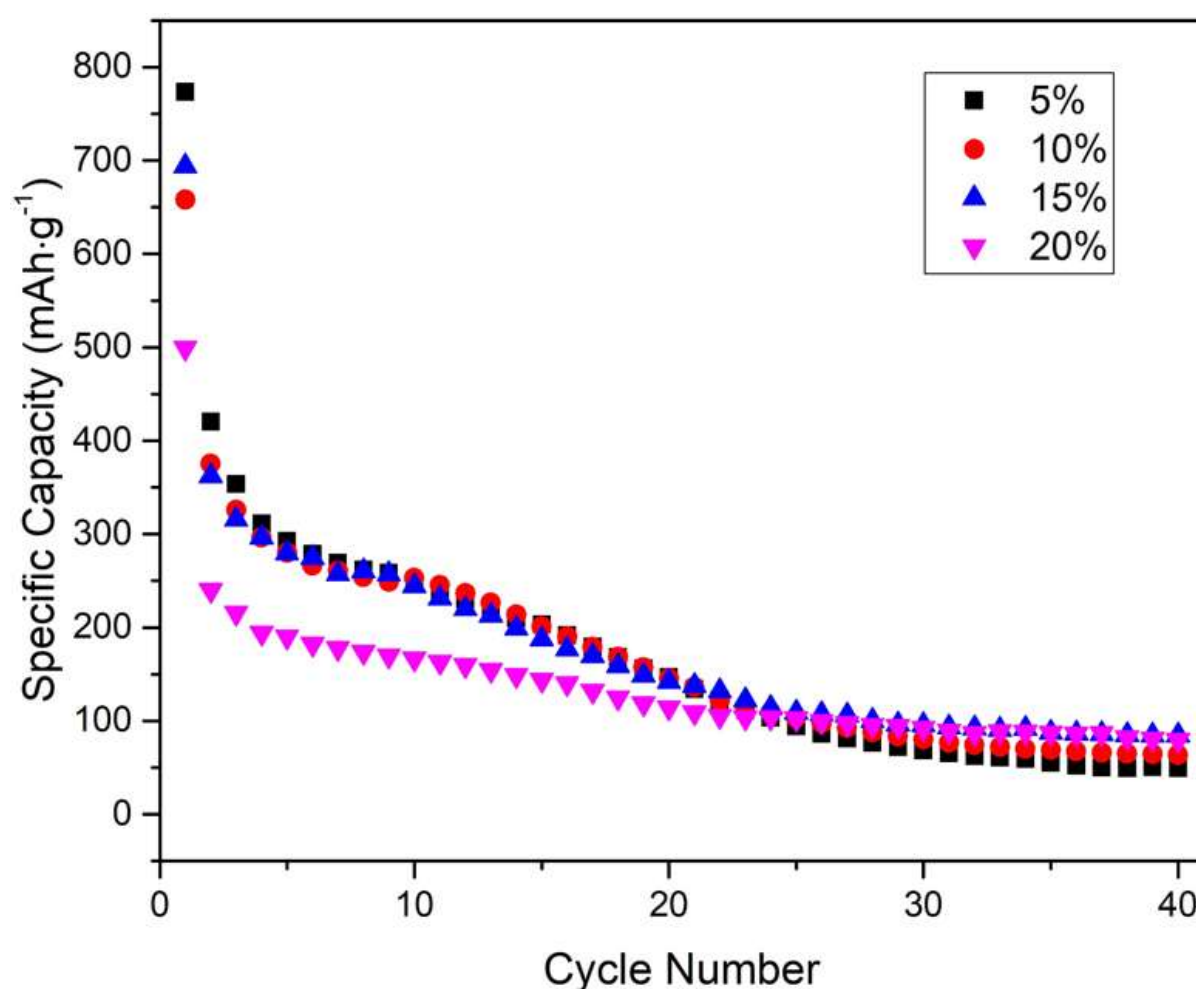


**Figure 5.1.9:** Specific discharge capacity cycling graphs for ball milled commercial PbO with various SWCNT (Tuball) mass fractions at 0.1 C through 40 cycles.

Figure 5.1.10 displays the result of all of the ten-cycle experiments which were carried out to this end, with the data summarized above in Table 2 in terms of 1<sup>st</sup> discharge and capacity retention. It is difficult to see an obvious trend in the data here. What can be seen, however, is

consistent under-performance of anodes with 20 wt% SWCNTs across all discharge rates. It is clear from the results that somewhere between 15 and 20% lies a critical mass fraction at which the performance drops off significantly. The 20 wt% anode shows the best capacity retention consistently but at the cost of having a detrimental effect on the energy density. While the 5 wt% electrode initially performs the best for moderate discharge rates, after cycling it is less clear. Regardless, what can be taken from the data is that the optimum values of SWCNT mass fraction for moderate discharge rate (i.e.  $\leq 1$  C) appears to lie between 5 and 10 wt%, in terms of gravimetric performance at least. From the four slurries examined here, 10 wt% is considered closest to ‘optimum’ with all things considered and so this mass ratio will continue to be used in the final thermal treatment step for this section.

**Table 2: 1<sup>st</sup> discharge ( $C_1$ ) and capacity retention data as a function of SWCNT wt% and discharge rate.**

|           | <u>0.05 C</u>                     |                        | <u>0.1 C</u>                      |                        | <u>1 C</u>                        |                        | <u>5 C</u>                        |                        |
|-----------|-----------------------------------|------------------------|-----------------------------------|------------------------|-----------------------------------|------------------------|-----------------------------------|------------------------|
| wt% SWCNT | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity Retention (%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity Retention (%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity Retention (%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity Retention (%) |
| 5         | 439                               | 64                     | 421                               | 56                     | 384                               | 55                     | 96                                | 72                     |
| 10        | 409                               | 64                     | 370                               | 62                     | 370                               | 65                     | 179                               | 76                     |
| 15        | 401                               | 61                     | 369                               | 66                     | 297                               | 65                     | 194                               | 67                     |
| 20        | 242                               | 72                     | 232                               | 69                     | 202                               | 65                     | 98                                | 76                     |

There remains a degree of improvement yet to be made to achieve reversible full-electrode specific capacities on the order of the 580 mAh·g<sup>-1</sup> theoretical value. The concept of strategic thermal polymer decomposition has been implemented already in this thesis. In chapter 3, the removal of PVP from NiFe LDH–SWCNT water-processed composites was deemed successful with heat treatment at 200 °C. It is hoped that the result can be mirrored in the case of PbO–SWCNT–PVDF (Tuball) to improve the gravimetric performance, as PVDF serves no purpose in the solid-state anode (it serves as a surfactant to assist viscous aqueous suspension of the nanotubes). The annealing data in Figure 5.1.11 below suggests encouraging improvements in the gravimetric performance after heat treatment at modest temperatures, carried out in vacuum of the order 10<sup>-2</sup> mbar. The comparative specific capacity values through 40 cycles appear to show some controllable behaviour in terms of polymer decomposition. There is an observable step up from the as-prepared electrode to the one where 3h of annealing at 230 °C was applied and then another when both temperature and time were

increased further. Based on this set of experiments there is an achievable  $38 \text{ mAh}\cdot\text{g}^{-1}$  improvement at  $300^\circ\text{C}$ , and upon viewing of the apparent high degree of PVDF which remains, further improvement of the capacity is expected for longer treatment times. There is a perceived limit to the treatment of this type for PbO as it is known that phase transition effects can begin to take place beyond  $350^\circ\text{C}$ .<sup>174</sup>

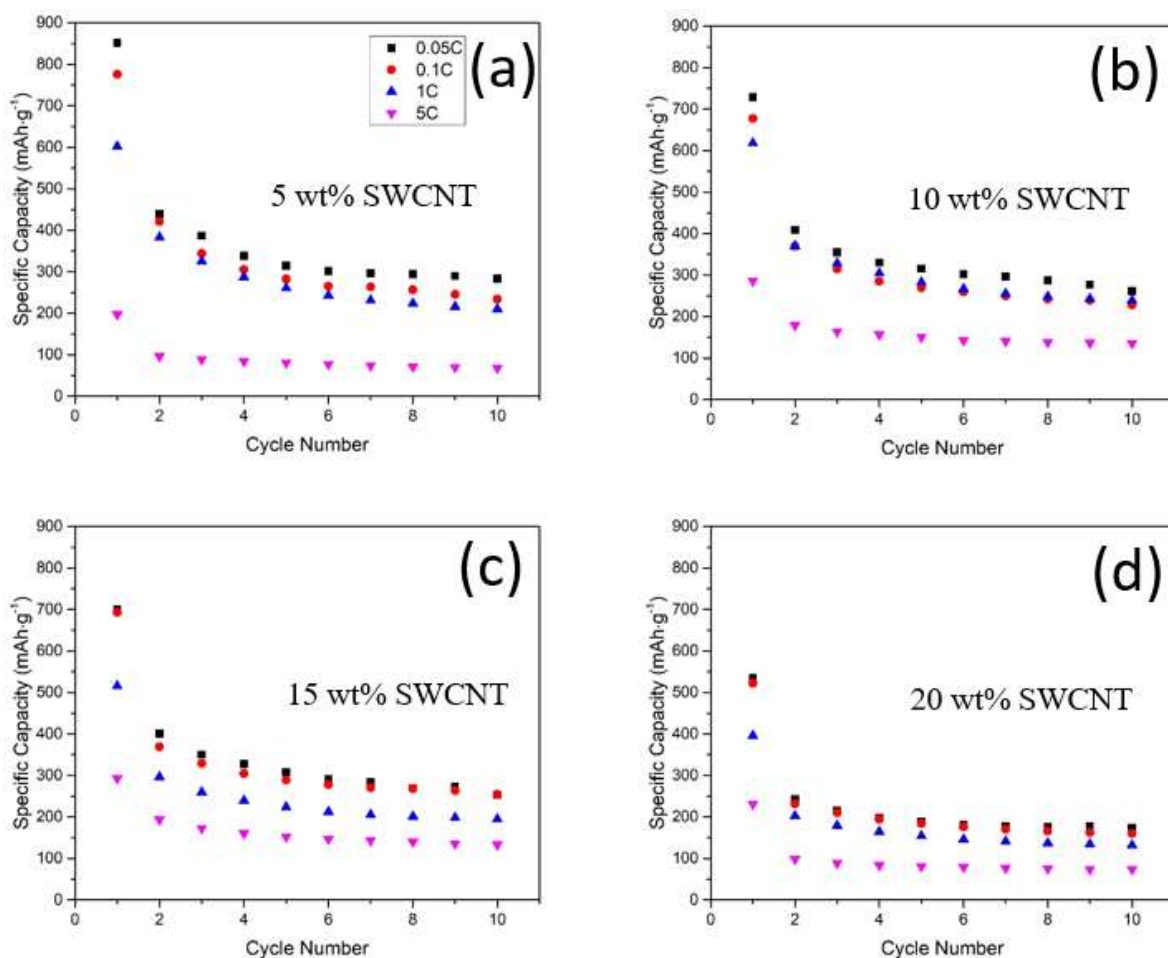


**Figure 5.1.10:** Specific discharge capacity cycling graphs for 5 – 20 SWCNT wt% (a – d) at various discharge rates.

Without demonstrating exceptional cycling behaviour to this point, the material processing steps thus far have produced encouraging improvements as well as a better understanding of where the performance enhancement will ultimately be found. The important limitation so far is that any significant presence of a non-active component like PVDF is going to significantly hinder gravimetric performances and while partial removal can be performed, the complete removal would prove to be a difficult high-energy process which is discouraging in terms of industrial compatibility.

In this chapter we will strive for a simpler, all active two-component system which should greatly improve upon the achievable gravimetric capabilities.

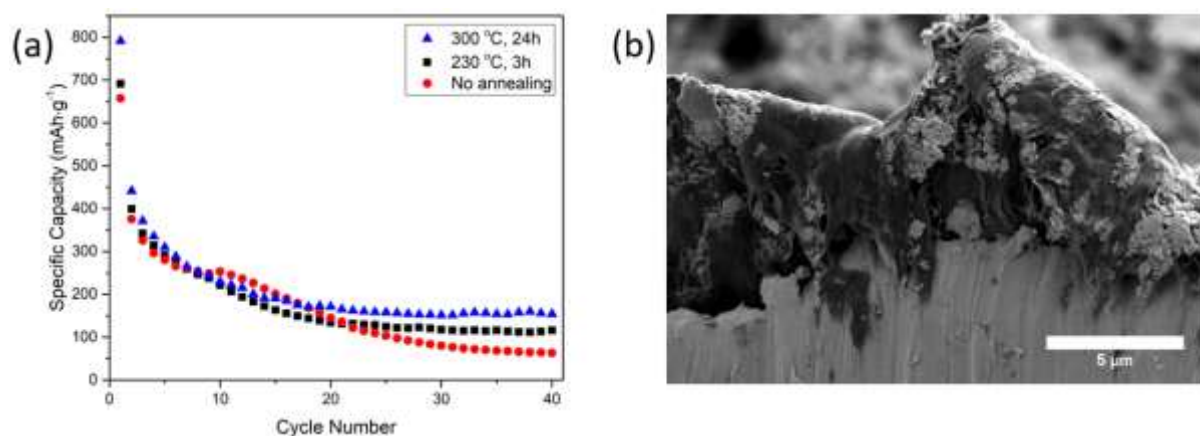


**Figure 5.1.11:** (a) Specific discharge capacity cycling graph for ball milled commercial PbO with 10 wt% SWCNTs (Tuball) at 0.1 C after various heat treatment steps, and (b) SEM micrograph of the thermal treated electrode.

## 5.2 Phase-Specific PbO

At this point in the study, the aim will move from using the commercially acquired, mixed-phase lead(II) oxide as the active anode material and instead introduce the oxide in phase pure forms. So far, the polymorphic material has performed well, with 441 mAh·g<sup>-1</sup> 1<sup>st</sup> discharge for the optimized SWCNT (Tuball) annealed composite sample (blue curve, Figure 5.1.11 a) with additional improvements in the cycling performance. The simple processing techniques have allowed the specific capacity to noticeably improve. However, from a theoretical perspective, there is still room for improvement in gravimetric performance. If one of the structural phases outperforms the other, then isolating that phase in its pure form will allow for improved specific capacity. In theory, the orthorhombic crystal structure of the  $\beta$ -phase PbO material is predicted to have a higher capacity to store lithium ions compared to the tetragonal  $\alpha$ -phase. Martos *et al.*<sup>173</sup> predict relative Li<sup>+</sup> alloying ratios of 4 and 4.5 per Pb atom for the respective phases, based on initial discharge GCPL curves at lower voltages and assuming no side reactions such as electrolyte decomposition etc. With that, the goal in this section is simply to synthetically isolate litharge and massicot crystals with a high degree of purity and categorize their respective capacity for Li<sup>+</sup> ion storage.

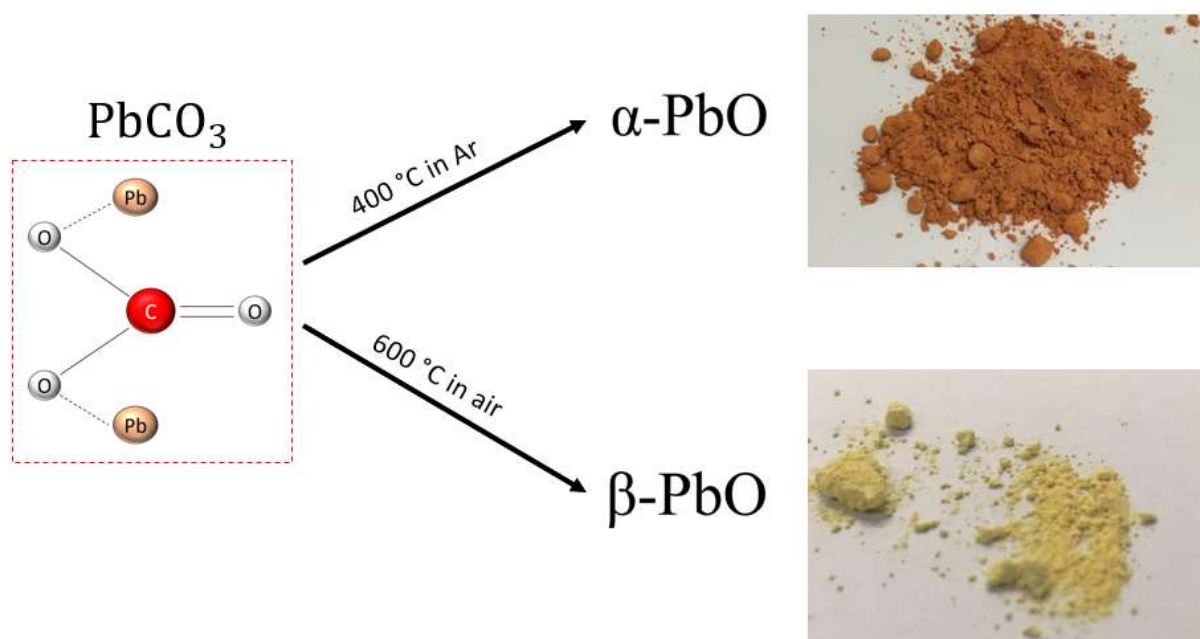


**Figure 5.2.1:** Schematic representation of the synthetic routes for phase pure  $\text{PbO}$  by thermal decomposition of  $\text{PbCO}_3$

There exist a number of unique synthesis routes for producing polymorphic and phase specific lead(II) oxide. At this point, we are interested in the latter, of which there are many examples. Wang *et al.*<sup>175</sup> use a hydrothermal approach in which a  $\text{Pb}(\text{NO}_3)_2$  starting material is treated at  $230\text{ }^\circ\text{C}$  in an autoclave with some additional transition metal nitrate reactant. The nature of the transition metal allows for phase selectivity. Namely, nickel nitrate for the  $\alpha$ -phase and chromium nitrate for the  $\beta$ -phase. Ng *et al.*<sup>177</sup> present a more unique and application-focused approach, spray pyrolysis. Using a lead nitrate precursor, the lead is mixed with sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) and spray pyrolyzed at  $800\text{ }^\circ\text{C}$  producing a  $\text{PbO-C}$  composite. In this case the resultant phase is determined by the  $\text{Pb:C}$  ratio selected in the initial conditions. Another alternative direction of approach is dry, thermal carbonate decomposition.<sup>187</sup>  $\text{PbCO}_3$  is a readily available compound which is in fact a by-product of lead-acid battery cycling, making it a more attractive starting point in terms of availability and the broader outlook on sustainability.<sup>174</sup> Under controlled conditions the carbonate can be gradually decomposed into both litharge and massicot by heating. The selectivity is derived by thermal treatment temperatures and time. This synthesis approach is what will be used for this work, and the graphical representation of the decomposition is displayed in Figure 5.2.1. Details of the procedure are given in section 5.5 later in the chapter. The methodology is carried out in line with findings by Yong *et al.*<sup>174</sup> who demonstrate controlled carbonate decomposition to litharge at temperatures up to  $490\text{ }^\circ\text{C}$ ,

beyond which some massicot phase contamination is detected. Pure massicot is synthesized at temperatures of 580 °C and above. Additionally, as can be seen in the figure, there is another requirement to control the environment for the  $\alpha$ -phase route because of the sensitivity of the thermal treatment to the intermediates which form, which in turn are influenced by carbon from CO<sub>2</sub> in air.<sup>188</sup>

### 5.2.1 Litharge

The same principle characterizations will be used for the first-principles analysis of phase pure PbO as were used in the previous section. In terms of determining phase purity, XRD is once again considered as the main tool for crystal classification. XRD data was acquired in this section using a molybdenum K $\alpha$  x-ray source. The diffraction pattern in Figure 5.2.2 (a) suggests a crystal is formed by heating lead carbonate in air to 400 °C, with a substantially higher degree of phase purity compared with the commercially sourced PbO pattern (Figure 5.1.2). The peaks, which are labelled in red in the figure, match almost exclusively with the tetragonal crystal symmetry associated with the  $\alpha$ -phase material. The tetragonal crystal has lattice parameters of  $a = 3.974 \text{ \AA}$  and  $c = 5.022 \text{ \AA}$  (COD ID: 9012700). The broad feature in the diffraction pattern at low  $2\theta$  values as well as the noisy signal around 11.75 ° are common in all of the powder XRD data for PbO analysis in this section which probably means they are a background signal from the instrument/sample holder or perhaps some additional oxide contaminant as touched on previously when looking at the commercial PbO diffraction pattern. There are additional unmatched peaks at 19.5, 23.5 and 23.7 ° which show up in the data with very low intensities. The origin of the peaks is not clear but crucially, they do not match any signal relating to an additional PbO phase. With that, it can be said that the synthesis route produces phase pure tetragonal PbO crystals with seemingly high levels of crystallinity.

Studying SEM micrographs of wide sample areas, it is clear to see that the synthesized litharge forms particles between 2 – 5  $\mu\text{m}$  in lateral dimensions and with relatively homogeneous morphology. There appears no obvious features of layered structure, seemingly consistent with the low intensity principle (001) basal plane diffraction peak, although this peak is repeatedly reported

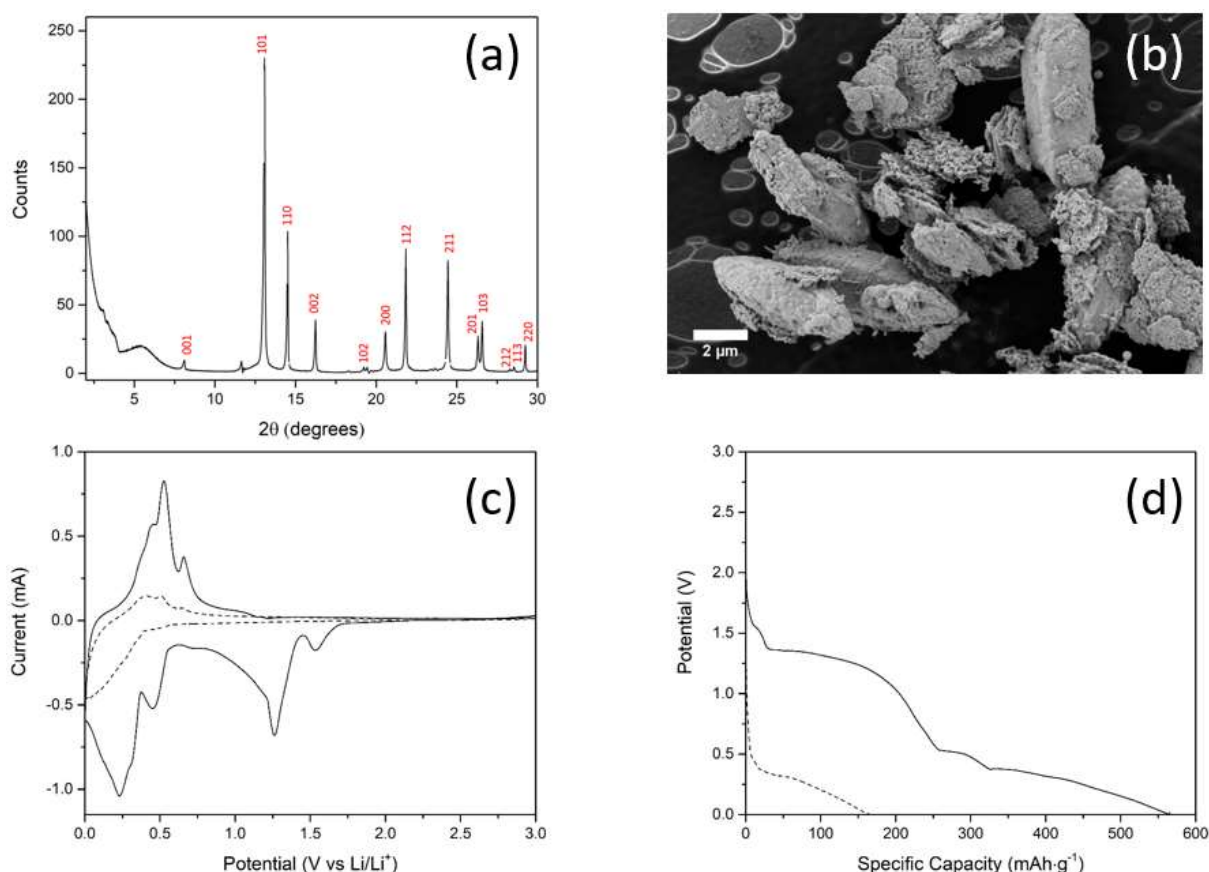


**Figure 5.2.2:** (a) XRD pattern with molybdenum Ka source, (b) SEM micrograph, (c) 1<sup>st</sup> & 2<sup>nd</sup> cycle CV at  $0.1 \text{ mV}\cdot\text{s}^{-1}$  and (d) GCPL discharges at  $0.1 \text{ C}$  for synthesized  $\alpha$ -PbO by  $\text{PbCO}_3$  thermal decomposition (slurries prepared with 10 wt% carbon black and 10 wt% PVDF, as before).

to have a low intensity relative to the second order (002) peak.<sup>175</sup> In terms of electrochemical characterization, the initial CV cycle and GCPL discharge are also examined here for pure litharge. Looking first at the cathodic CV peaks in Figure 5.2.2 (c), there appears to be an almost identical set of principle peaks at the potentials which were observed for the polymorphic case (Figure 5.1.4 a). Namely, multiple peaks in the region of 0.3 – 0.6 V which correspond to the Pb-Li alloying steps and higher potential peaks from 0.9 – 1.3 for the reduction of  $\text{Pb(II)}$  to  $\text{Pb(0)}$ . Additionally, the same irreversible activity around 1.5 V is seen here once again, thought to be the result of some contaminant activity, perhaps an additional oxide. The relative intensity of this current peak with respect to the others is seemingly less for the  $\alpha$  material here, compared to the more significant intensity in the commercial  $\text{PbO}$ 's CV. This point is reflected in the initial discharge GCPL curve (Figure 5.2.2 d) whereby a noticeably smaller plateau feature can be seen around 1.5 V (compared with the equivalent plateau in Figure 5.1.4 b). This may suggest the litharge material here is slightly

freer of the oxide contaminant. Aside from this, the discharge curve is identical to the polymorphic case.

### 5.2.2 Massicot

As per the reaction scheme above,  $\beta$ -phase PbO synthesis was attempted at 600 °C in air. The result this time was a yellow powder with significant differences in morphology and crystallinity, as would be expected. The diffraction pattern in Figure 5.2.3 (a) shows good agreement with the peaks of orthorhombic crystal symmetry with lattice parameters  $a = 5.893 \text{ \AA}$ ,  $b = 5.490 \text{ \AA}$  and  $c = 4.753 \text{ \AA}$  (COD ID: 9007710). The pattern contains mostly well-matched diffraction lines with a small number of noticeable exceptions. Similar to before, the low angle area up to about  $6^\circ$  of  $2\theta$  contains some unknown features along with the peak near  $11.75^\circ$  which is theorized to belong to some intermediate lead oxide compound existing as a residue in the synthesized material. There are also three weak peaks in the pattern at  $14.5$ ,  $16.2$  and  $21.8^\circ$  which correspond to the (110), (002) and (112) planes of the tetragonal crystal structure of a small amount of secondary litharge phase in the sample. From the signal, it is clear that the inclusion of a secondary phase is negligibly small and the XRD data, along with microscopic viewing, are enough to conclusively say that there is a near complete phase change from  $\alpha \rightarrow \beta$  with this synthesis route.

The SEM micrograph in Figure 5.2.3 as well as others which were captured over wide sample area analysis suggest that morphology of the material has completely changed compared to the  $\alpha$ -phase. It is now possible to see a more obvious layered structure in the particles as well as a shift in size, with the limits in this case being roughly  $1 - 3 \text{ }\mu\text{m}$  in lateral dimensions. Perhaps the more notable layering is a consequence of the swollen interlay galleries compared to the previous phase. According to XRD data the phase transition brings with it  $0.9 \text{ \AA}$  swell between layers.

The electrochemistry is interesting for this material because it shows somewhat of a removal from the characteristic discharge of the polymorphic material, compared with the  $\alpha$ -phase which was relatively similar. Looking at the cathodic features in Figure 5.2.3 (c), for the first time the previously

unmatched 1.5 V peak is not observed. If the theory is to be believed that the peak represents an irreversible decomposition of some additional lead oxide like  $\text{PbO}_2$ , then the synthesized massicot here is free of it, meaning perhaps the contaminant cannot withstand the hotter decomposition conditions. Additionally, the potential regions for lead reduction ( $0.9 - 1.3$  V) are unique for the  $\beta$ -phase while alloying ( $0.3 - 0.6$  V) appears much the same. The lead reduction in oxides like these is known to be a conversion with some ambiguity surrounding it, and perhaps quite complex. In this case, we see a broad feature in the expected voltage range, rather than specific peaks relating to the individual formation of intermediates.<sup>189</sup>

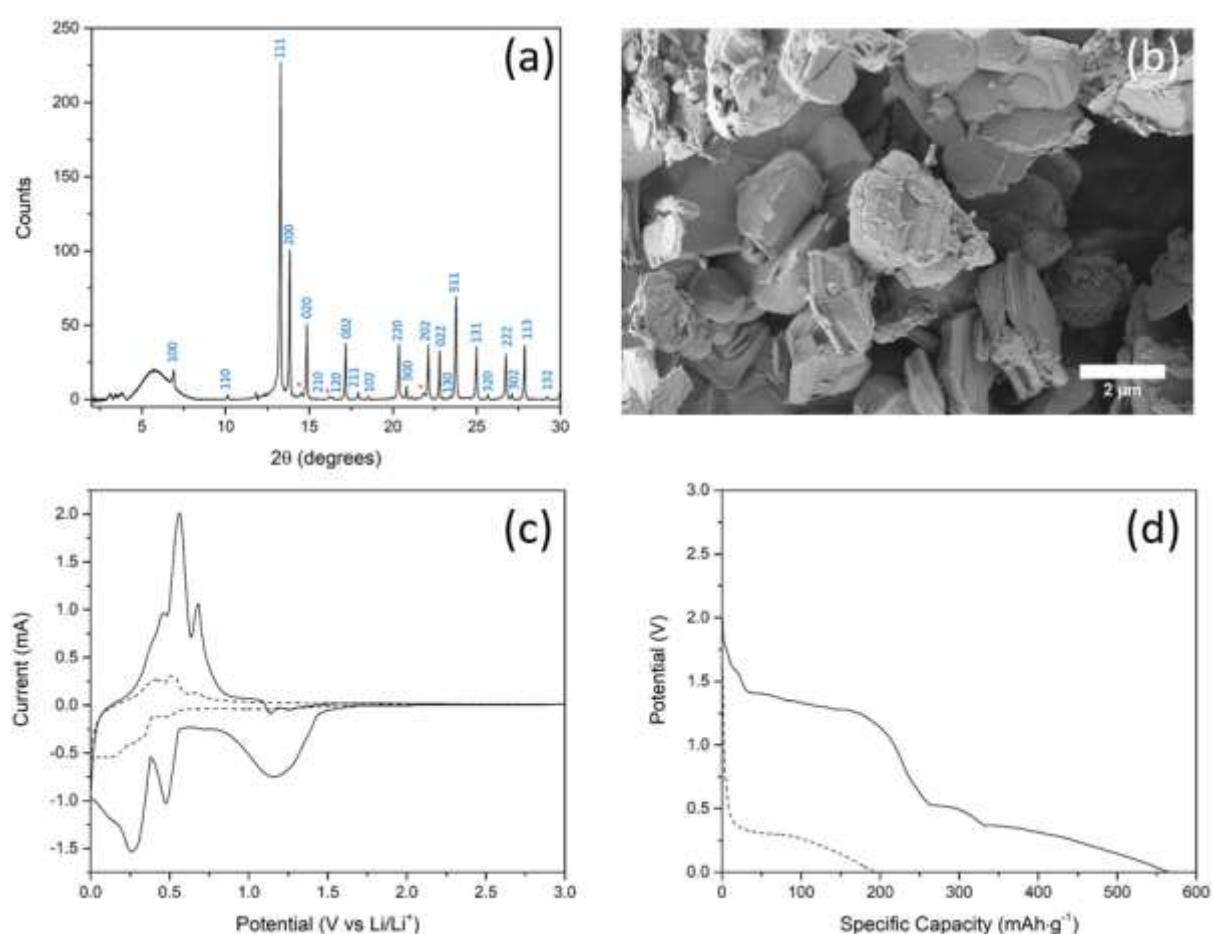


**Figure 5.2.3:** (a) XRD pattern with molybdenum  $K\alpha$  source, (b) SEM micrograph, (c) 1<sup>st</sup> & 2<sup>nd</sup> cycle CV at  $0.1 \text{ mV}\cdot\text{s}^{-1}$  and (d) GCDL discharges at  $0.1 \text{ C}$  for synthesized  $\beta$ -PbO by  $\text{PbCO}_3$  thermal decomposition (slurries prepared with 10 wt% carbon black and 10 wt% PVDF, as before).

All-in-all, the major take-away from this section so far is the high selectivity which can be achieved in terms of crystal phase by way of simple thermal treatment of the readily available  $\text{PbCO}_3$  precursor. With access to phase pure materials, the next step will be to determine if one or the other

can perform with any noticeable superiority as a LIB anode. If this is the case, the higher activity phase pure anode will likely outperform the polymorphic commercial material if similar steps are applied to optimize the cell performance.

### 5.2.3 Performance Comparison

For this section, short term cycling of the respective phases was compared in electrodes prepared with carbon black and PVDF slurries on copper foil, as before. The electrodes were cycled five times after initial discharge to get an idea of the relative intrinsic lithium storage capacities and cycling capabilities. Figure 5.2.4 summarizes the data with the cells being cycled at 0.1 C charge/discharge rates. The performance in both cases is predictably poor, with no post-synthesis processing or composite additives. Ignoring the initial discharges, the 1st discharge capacities reached were 164 and 193  $\text{mAh}\cdot\text{g}^{-1}$  for the respective  $\alpha$  and  $\beta$  phases. The superior gravimetric capacity of the latter is likely reflective of the greater theoretical capacity based on alloying models. However, after just six cycles the  $\beta$ -phase struggles to retain the initial value. The capacity falls to 31  $\text{mAh}\cdot\text{g}^{-1}$  on the 6<sup>th</sup> cycle which represents an 84% loss, compared to  $\alpha$ -PbO which drops to 32  $\text{mAh}\cdot\text{g}^{-1}$ , an 80% loss. These margins may seem slim but the effect of poor cycling in early stages will likely result in a drastic capacity loss in practical applications involving prolonged activity. The trade-off between theory and practicality is an important one and quite evident here. Although theoretically superior, the  $\beta$ -phase may not represent the more attractive material from the two phases in the long run.

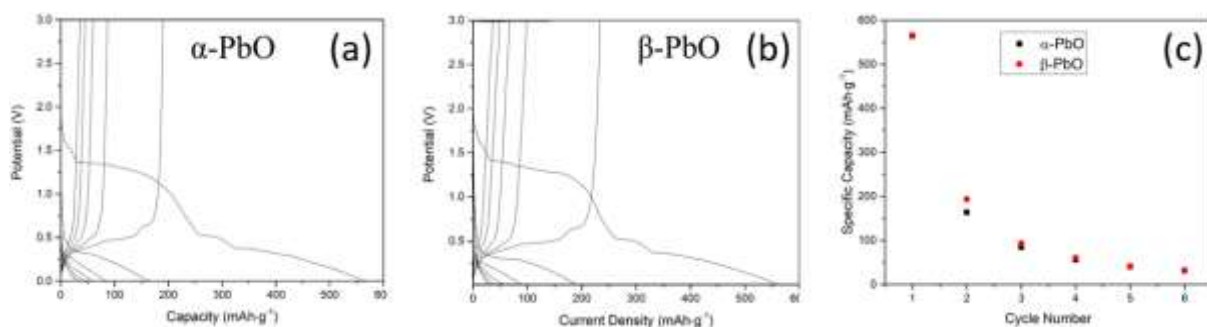


**Figure 5.2.4:** (a, b) GCPL charge-discharge profiles at 0.1 C and (c) specific discharge capacity cycling graph through six cycles for the  $\alpha$  and  $\beta$  phase material.

With the aim of looking at intrinsic capabilities, the data in Figure 5.2.4 representing cycling at 0.1 C is slightly inconclusive as the cells demonstrate near identical specific capacity values in the end. So, the experiments are repeated at a lower charge/discharge rate. Figure 5.2.5 displays the data for a similar set of experiments as before but at 0.05 C, half the previous rate. The hope is that lowering the applied rate will further nullify any kinetic limitations in the respective cells and allow us to directly observe intrinsic specific capacity limits. This time the first cycle capacities reach 162  $\text{mAh}\cdot\text{g}^{-1}$  ( $\alpha$ ) and 159  $\text{mAh}\cdot\text{g}^{-1}$  ( $\beta$ ). These first indications suggest near identical behaviour but once again it is the cycling capabilities of the phases which appear to set them apart. Through six cycles, the  $\alpha$ -phase discharges with 51  $\text{mAh}\cdot\text{g}^{-1}$  while the  $\beta$ -phase does so with just 34  $\text{mAh}\cdot\text{g}^{-1}$ , representing respective capacity losses of 69% and 79% with respect to the 1<sup>st</sup> cycle. So, it would appear based on this first glance classification of the two PbO phases that it is the tetragonal crystal which will support repeated lithiation more so than the secondary orthorhombic structure. This point is reflected in the literature. Martos *et al.*<sup>173</sup> report a similar outcome when comparing LIB cell performance of the two phases. The initial capacities appear similar but with cycling they too observe a gradual discrepancy in performance. This is suggested as a result of an improved  $\text{Li}^+$  diffusion coefficient calculated for the litharge material compared to massicot, which they say is perhaps down to the lower crystallinity of the phase, allowing it to facilitate ionic transport more so than the more highly ordered one.

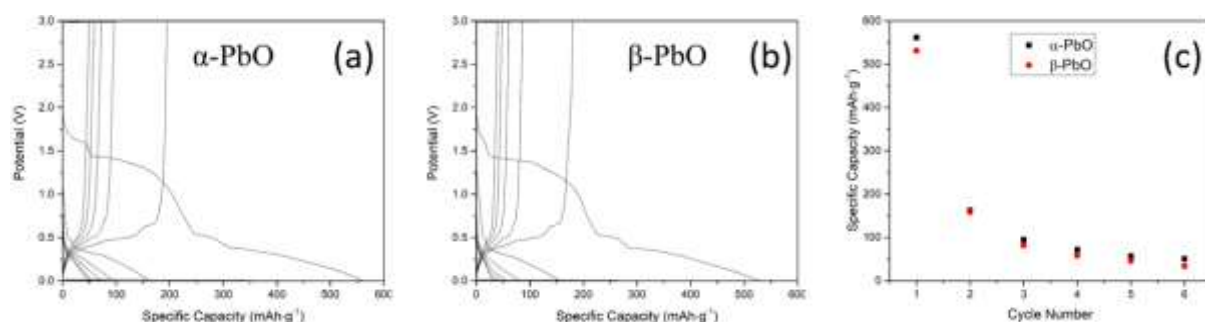


**Figure 5.2.5: (a, b) GCPL charge-discharge profiles at 0.05 C and (c) specific discharge capacity cycling graphs through six cycles for the  $\alpha$  and  $\beta$  phase materials.**

So, despite the perceived superior lithium alloying capabilities of  $\beta$ -PbO it is the  $\alpha$  phase which cycles the better. As a final step in attempting to understand the behaviour, conductivity tests are carried out on the carbon black – PVDF composite electrodes containing the respective phases.

To do this, relatively thick slurries were prepared at 100  $\mu\text{m}$  using the Dr. Blade on a glass substrate so as not to affect to conductivity measurements. A four-point probe setup was used to carry out the current-voltage measurements over a range of areas on the dried slurries. From this, taking the dried sample thickness into account, in-plane conductivities were calculated at  $0.207 \pm 0.071 \text{ S/m}$  for  $\alpha$ -PbO and  $1.087 \pm 0.321 \text{ S/m}$  for  $\beta$ -PbO. Both values are extremely low, most likely because of the considerable PVDF content in the slurries which has not at this point been removed by heating. The uncertainty in the calculations derive mostly from the inhomogeneous thicknesses across the sample when the slurries dry out. Even when the error values are considered though, the results are still conclusive in that the massicot-based slurry proves to be the more conductive composite. This is once again a counter intuitive result which would suggest, along with the theoretical lithium storage capabilities, that the  $\beta$  phase should outperform the  $\alpha$ -PbO as a LIB anode, but it does not. It is clear that litharge relies quite heavily on its superior lithium ion diffusion capabilities for its higher intrinsic anode performance, as well as perhaps the slightly lower crystallinity of the polymorph which is thought to also allow better long term capacity retention with cycling compared to the more crystalline massicot.<sup>173</sup>

With that, litharge-based anodes were prepared with identical processing step to the treatment of the commercial material in section 5.1 i.e. composite preparation with SWCNTs (Tuball) and heat treatment at 300 °C under vacuum. Figure 5.2.6 displays the results, with similar cycling capacity improvements seen here as in the commercial PbO case. Crucially, the specific capacity through 40 cycles ( $148 \text{ mAh}\cdot\text{g}^{-1}$ ) shows no improvement over the performance for the polymorphic case (Figure 5.1.11 a). The phase pure litharge here does, however, perform with a slightly greater capacity retention after 40 cycles. Still, this is an underwhelming result as the phase pure material fails to give a convincing improvement in gravimetric performance. One possibility for this is the larger grain sizes for the  $\alpha$ -PbO based anodes. The as-produces  $\alpha$ -phase material synthesizes as a relatively fine powder compared with the commercial PbO and as such, ball-milling was not deemed a necessary precursor step during electrode preparation. This may have been an oversight, meaning the commercial PbO (Figure 5.1.11 a) and  $\alpha$ -PbO (Figure 5.2.6) samples in this

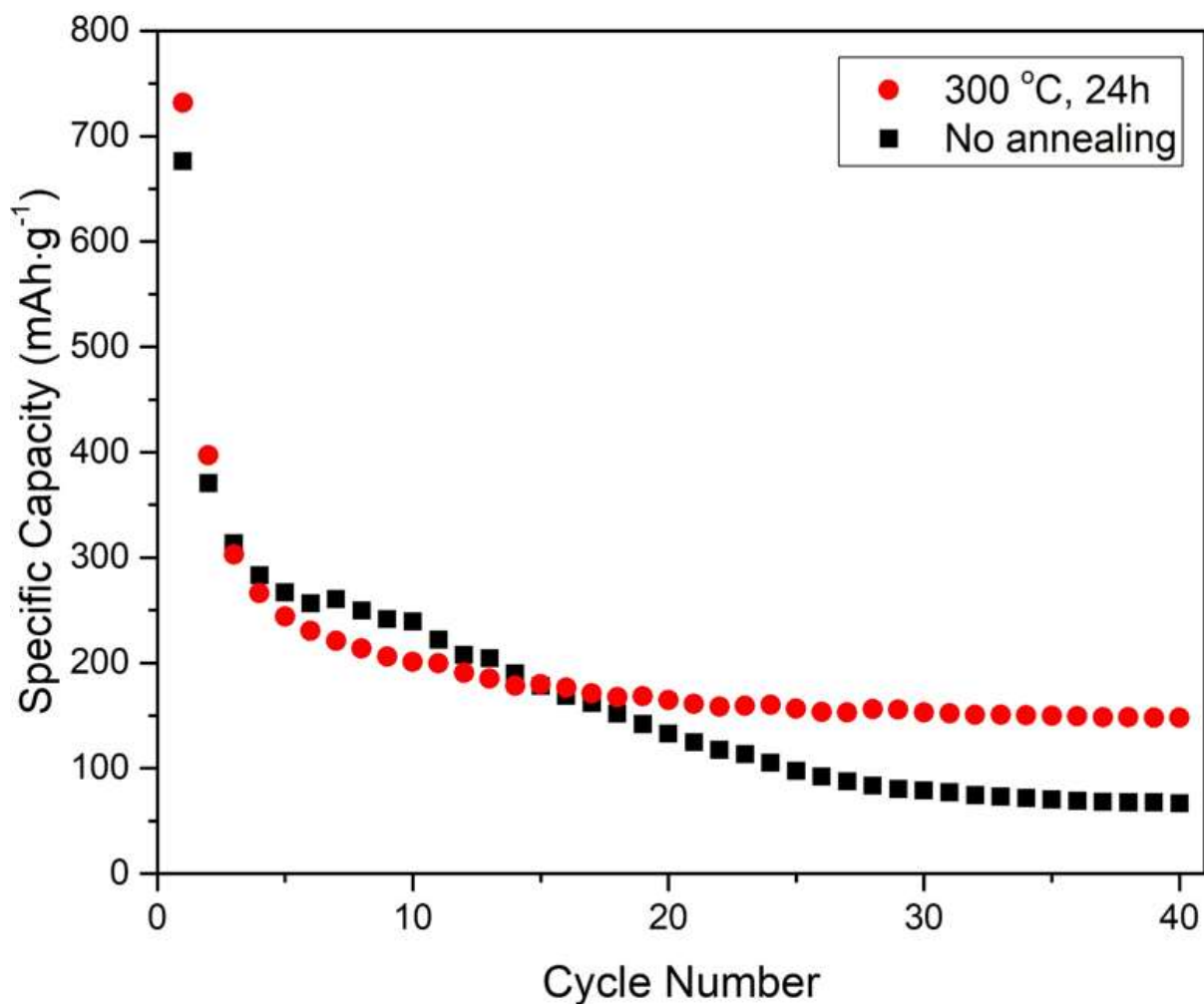


**Figure 5.2.6:** Specific discharge capacity cycling graph for  $\alpha$ -PbO with 10 wt% SWCNTs (Tuball) at 0.1 C before and after heat treatment.

case cannot be reliably compared. In the subsequent study, ‘exfoliation’ steps will remove any uncertainty regarding preliminary grain sizes. Litharge will be used for the remainder of this study as the phase pure standard against which the polymorphic commercial material will be measured. Next, attempts will be made to further alleviate the long-range fracturing for PbO composite anodes by way of exfoliation in an attempt to realize a higher degree of capacity retention with cycling, the most detrimental drawback of the material in terms of practical and commercial applications.

## 5.3 Nanocomposite LIB Performance

### 5.3.1 Exfoliation

Across numerous fields of metal oxide research, exfoliation of the bulk material to monolayer or few-layer 2D sheets has always been an attractive prospect with the potential for changes in the material's intrinsic properties and hence, a widening of prospects in terms of applications. There exists a broad range of predictive computational<sup>190</sup> and demonstrative experimental<sup>191</sup> studies outlining the extent to which the properties of layered materials like metal oxides can be altered and tailored by controlling the materials layered structure, including PbO which can exhibit changes in its electronic and vibrational band structure upon exfoliation as well as a shift in optical properties according to computation models.<sup>192</sup> With that said, however, the utilization of liquid-phase exfoliation of lead(II) oxide particles in this work is much less intricate than others found in the literature which rely on highly selective layering for tailoring properties in areas like electronics and optoelectronics. Here the goal is mainly to achieve particle size reduction along with exfoliation in a high-power sonication procedure in an attempt to improve the outlook of PbO in terms of long-term lithium ion cycling.

There are a number of reasons in principle why the control of particle size and dimensionality can have an effect on the performance of a LIB anode material like PbO. The first and most obvious is perhaps the significant increase in surface area. Although battery materials aren't limited to surface activity, the surface area is still a limiting factor as it is the first point of contact at which lithiation can begin so improving specific surface area in an electrode should improve the rate capabilities to some extent. The second consideration with reduced particle size is the reduction in the mean diffusion path lengths which must be covered by active ions and electrons in order to fully lithiate the host material in each charge/discharge cycle. Again, this can have the effect of improving rate capabilities. The most significant point here though pertains specifically to alloying type materials like silicon and many metal oxides and concerns long-range stress within the active crystal structure. In materials which can store lithium at high ratios of lithium to host metal, repeated cycling can cause

the host structure to fracture and crack due to the stress applied by the foreign ions. This point is introduced in section 1.3 and displayed graphically in Figure 1.3.3 (b) as an example of silicon fracture by alloying. Significant reduction in the mean particle size of the host can have the effect of mitigating these long-range stresses and improve the materials battery lifetime in terms of capacity retention. The improvement is well documented to become most effective at sizes below 100 nm and when supported by some conductive matrix.<sup>50</sup>

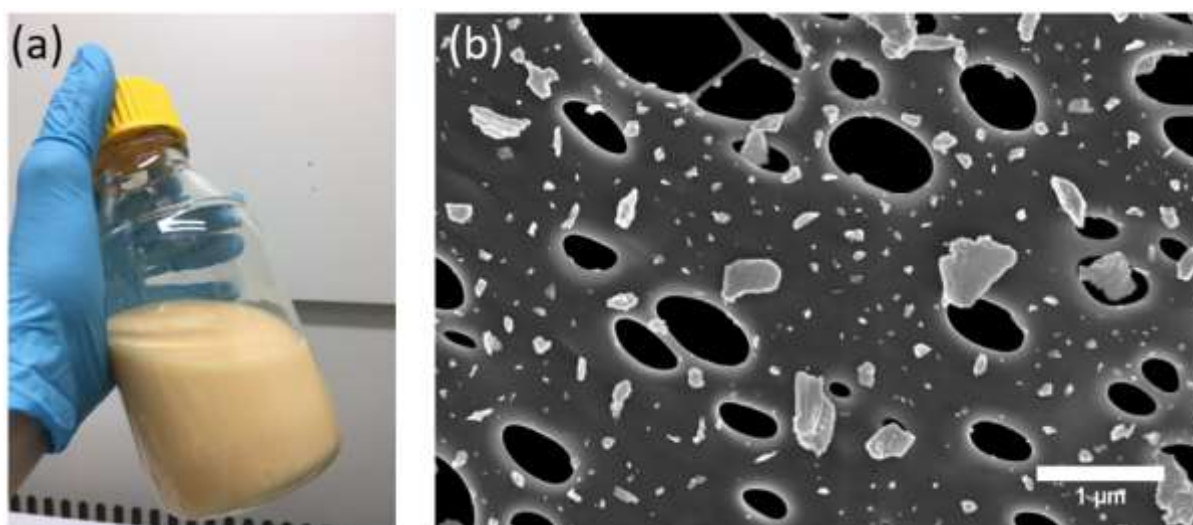


**Figure 5.3.1:** (a) Digital photograph and (b) SEM micrograph for commercial PbO after liquid-phase exfoliation was performed in IPA.

For this work exfoliation was performed on the PbO powders in liquid suspensions. Sequential bath sonication and centrifugation in IPA led to considerable particle size reduction. The exact method is outlined in section 5.5 of this chapter. Figure 5.3.1 shows the degree of exfoliation on the material in terms on mean particle sizes. Throughout this section, the extent to which these steps can improve the LIB anode performance will be monitored along with SWCNT mass fraction optimization.

### 5.3.2 SWCNT Composites

To test the exfoliated material, composites were made using a combination of the IPA dispersed material and SWCNT suspensions. The SWCNT composites were prepared with controllable carbon mass fractions by determining precisely the respective concentrations and adding

appropriate volumes of each before shaking and vacuum filtering onto a separator (full details in section 5.5). Once again, the foremost point of characterization to be considered will be electrochemical. Figure 5.3.2 displays the first and second discharge CV and GCPL curves for the exfoliated commercial PbO with 10 wt% SWCNT. Starting with the voltammogram, the most striking feature is the retention of the peak intensities from first to second cycles compared to the same experiment for the as-received material in a carbon black – PVDF matrix (Figure 5.1.4). The first cycle (black line) shows an initial characteristic discharge with identical peak potentials to the previous case, with the reversible lithiation features in the low potential from around 0.6 V and the irreversible features around 1.15 V pertaining to the  $\text{Pb(II)} \rightarrow \text{Pb(0)}$  reduction. Once again there is a sharp feature at 1.5 V whose origin is unclear but not thought to be a feature of the  $\text{PbO}_2$  or some other secondary lead oxide phase. The massive reproducibility of the CV peaks between first and second cycle compared to previous experiments is a direct result of the size treatment applied to the active oxide particles. As discussed, the exfoliation has been shown to produce a system much better suited to dealing with the local stresses associated with lead-lithium alloying. This is a satisfying first look at the immediate improvement of the anode performance with exfoliation but does not give much information as to the extent of rate improvements from size reduction. This point will be clarified by carrying out a full rate performance study at 0.05C, 0.1 C, 1C and 5C with various SWCNT mass fractions as was done with the slurry composites previously in section 5.1.

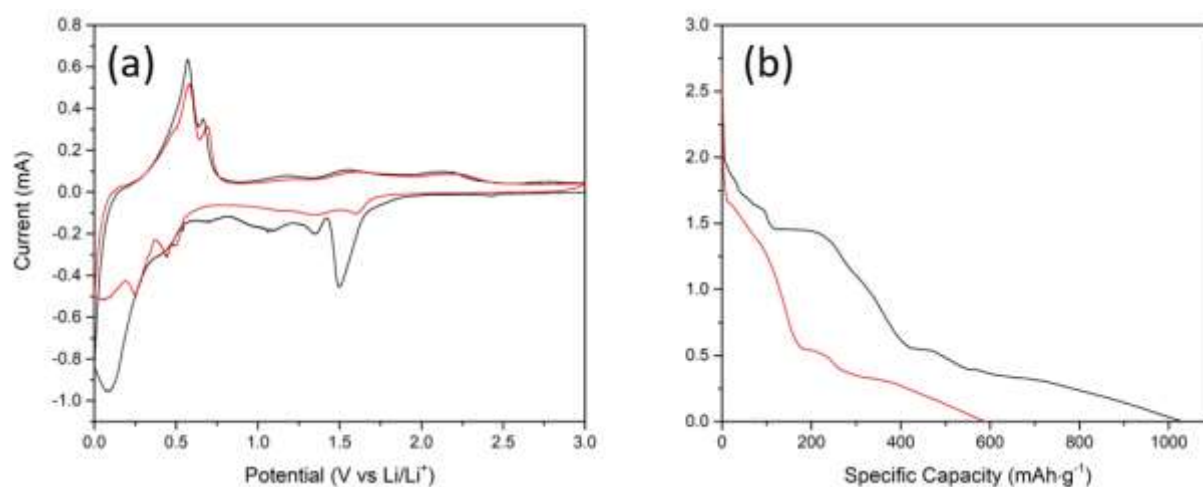


**Figure 5.3.2:** 1<sup>st</sup> and 2<sup>nd</sup> (a) CV cycles at 0.1 mV·s<sup>-1</sup> and (b) GCPL discharges at 0.1 C for exfoliated PbO with 10 wt% SWCNT.

The same cycling improvements are reflected in the GCPL first and second overall specific capacity discharge curves. Similarly, the irreversible high voltage activity can be observed as significant plateaus in the initial discharge and then disappear. The ability of the composite to store lithium with a high capacity is clear from the GCPL data here, as the second cycle fully discharges at  $590 \text{ mAh}\cdot\text{g}^{-1}$ , exceeding even the theoretical value for PbO. This value is a reminder of the  $\text{Li}^+$  storage capabilities of the SWCNT component which is clearly contributing to the performance to an extent.

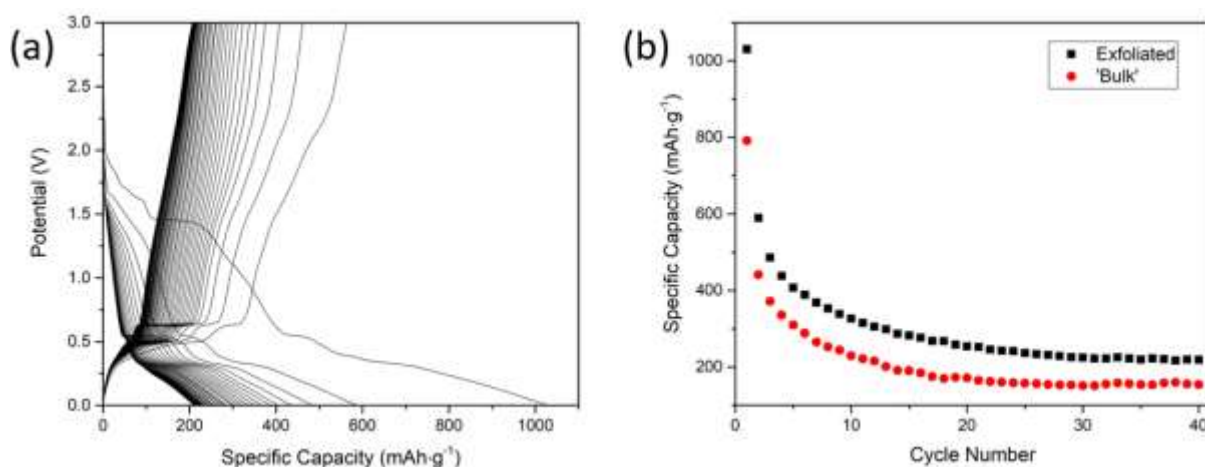


**Figure 5.3.3:** (a) GCPL charge-discharge profile for exfoliated commercial PbO with 10 wt% SWCNT at 0.1 C and (b) the specific discharge capacity cycling graph compared with the optimized 'bulk' performance (10 wt% SWCNT-Tuball, 300 °C annealed).

To build on these early observations, GCPL cycling data should allow for more of an insight into how the reduced long-range stress within the lithiated, exfoliated material can affect the long-term capacity retention from consecutive voltage sweeps. The longer-term cycling data presented in Figure 5.3.3 displays the extent of that improvement in comparison with previous highest performing standard for the anodes studied in this work using the commercial PbO. The data suggests that the main improvement is the gravimetric enhancement of the anode when no inactive components like PVDF are present, while the capacity retention through 40 cycles appears to be much the same for two anodes.

**Table 3: 1<sup>st</sup> discharge ( $C_1$ ) and capacity retention data as a function of SWCNT wt% and discharge rate.**

|           | <u>0.05 C</u>                     |                              | <u>0.1 C</u>                      |                              | <u>1 C</u>                        |                              | <u>5 C</u>                        |                              |
|-----------|-----------------------------------|------------------------------|-----------------------------------|------------------------------|-----------------------------------|------------------------------|-----------------------------------|------------------------------|
| wt% SWCNT | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity<br>Retention<br>(%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity<br>Retention<br>(%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity<br>Retention<br>(%) | $C_1$<br>(mAh · g <sup>-1</sup> ) | Capacity<br>Retention<br>(%) |
| 5         | 406                               | 38                           | 410                               | 43                           | 351                               | 25                           | 54                                | 40                           |
| 10        | 546                               | 53                           | 590                               | 55                           | 445                               | 51                           | 340                               | 49                           |
| 15        | 615                               | 66                           | 553                               | 59                           | 490                               | 66                           | 409                               | 61                           |
| 20        | 657*                              | 84                           | 584                               | 71                           | 507                               | 74                           | 200                               | 58                           |
| 25        | 633                               | 77                           | 594                               | 68                           | 577                               | 71                           | 443                               | 65                           |
| 30        | 615                               | 79                           | 577                               | 81                           | 541                               | 63                           | 362                               | 64                           |

However, it is important to note at this point that unlike the Tuball-based composite in Figure 5.3.3 (b), the exfoliated PbO composite has not yet been optimized in terms of SWCNT mass fraction and as such has not in theory reached its optimum performance in terms of range of cycling and rate capabilities. From Figure 5.1.10 and Table 2 in section 5.1 of this chapter, one can see with most clarity the ideal wt% of SWCNTs in the anode when a thorough investigation is performed comparing mass fractions at various C-rates. For the study, cycling data was acquired at 5, 10, 15, 20, 25 and 30 wt% SWCNT with respect to the exfoliated active component. Table 3 summarizes the data while Figure 5.3.4 shows the graphical representation. For clarity, the 5 SWCNT data is not presented in the figure because of low relative performance across all rates. Without any additional binder, 5% SWCNT in the electrode is simply too low to support reasonable capacity retention after a number of cycles, even at discharge rates as low as 0.05 C. The data for the 5% SWCNT cells are available in Appendix A (Figure A13 a). The results for this study are considerably clearer than previously. Without question, from the mass fraction considered, the anodes display a continuous improvement in performance with increasing SWCNT wt% based on the criteria of 1<sup>st</sup> discharge specific capacity and capacity retention through ten cycles. The anodes with 25% of nanotubes by mass performed the best. Only at 0.05 C discharge rate did the 20% electrode perform better. This suggests that the higher PbO content is allowing for a superior intrinsic capacity, but at more practical discharge rate (i.e. 0.1 C and above) the denser nanotube matrix becomes the most significant factor. It also suggests that at some point of SWCNT inclusion above 25%, the loss of active PbO material will begin to limit the gravimetric capacity. This is exactly what happens when the wt% is increased

to 30% (Figure A13 b). The energy density appears to saturate at this point as one can see the 1<sup>st</sup> cycle specific capacity drop across all discharge rates. Additionally, the capacity retention values at high C-rates appear to reach a limit, with no observable improvements at 30 wt%.

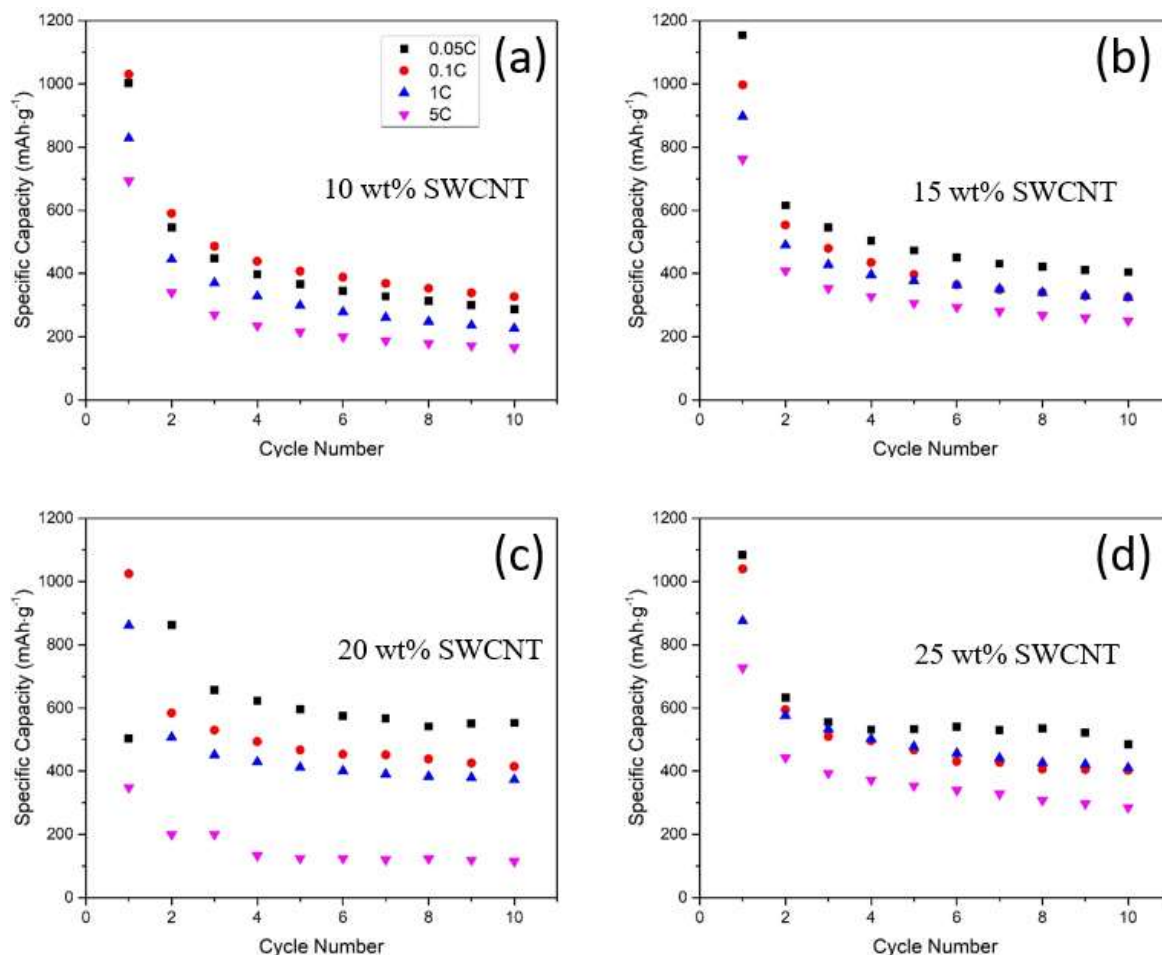


**Figure 5.3.4:** Specific discharge capacity cycling graphs for 10 – 25 SWCNT wt% (a – d) at various discharge rates.

An important point to be sure of is that for high mass fractions, the SWCNTs continue to play a supporting role in the anodic lithiation/delithiation mechanism, rather than contributing significantly to the energy storage themselves. To be sure, one can continue to check the initial discharge curve and match it to the characteristic curve for the PbO material. The initial discharge for the 25% SWCNT anode at 0.1 C is available in Appendix A (Figure A14) and continues to display the same potential plateaus compared with previous samples.

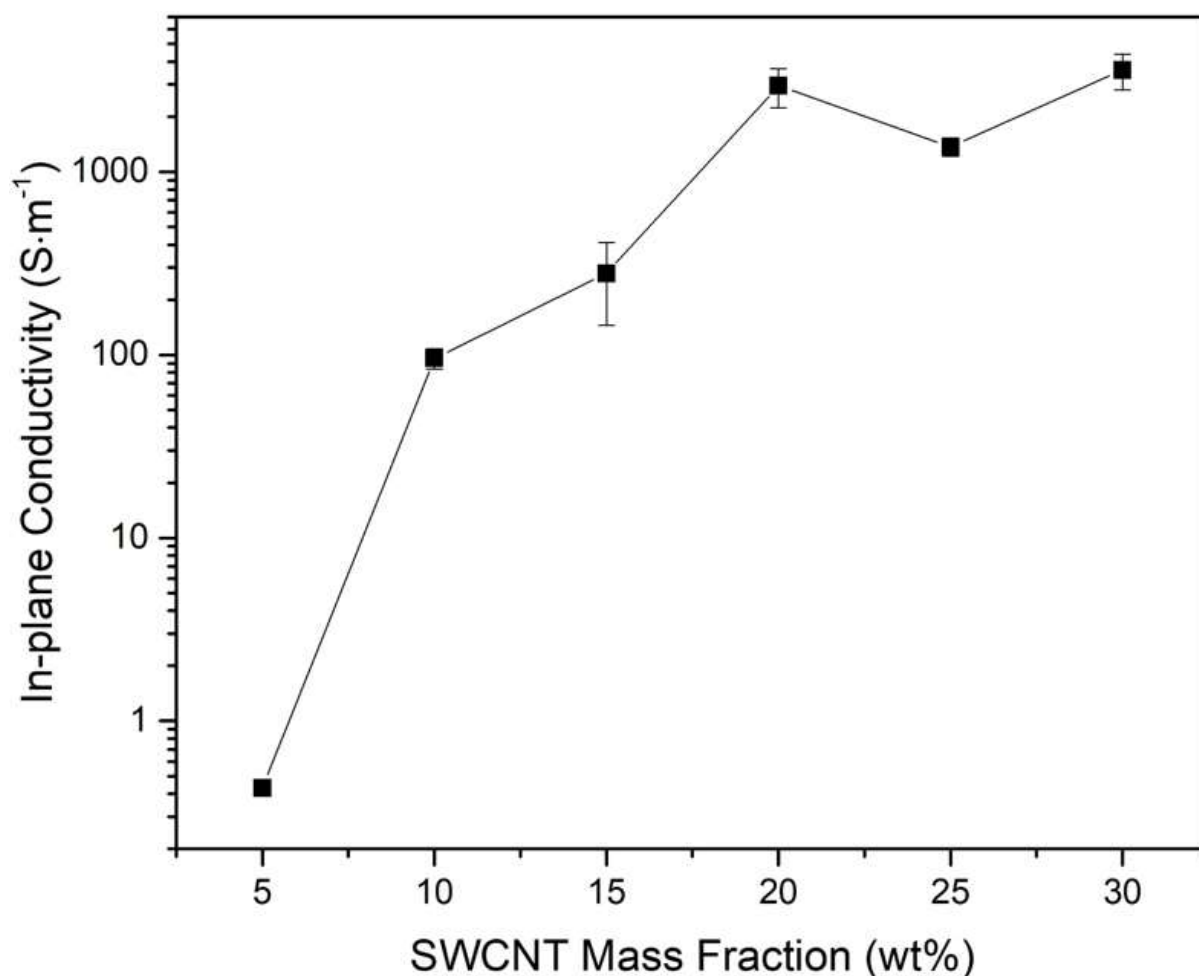


**Figure 5.3.5:** *In-plane conductivity as a function SWCNT mass fraction (wt%).*

So, what are the principle factors for the impressive performance at high nanotube fractions. Presumably conductivity plays a role. In-plane conductivity was measured for each mass fraction from 5 – 30% SWCNTs using a four-point probe setup. Measurements were carried out on dried electrode prepared by filtration on a polymer separator anchored by a rigid glass substrate with sample thickness being considered in each case. The in-plane conductivity measured in this way produced an apparent exponential increase for the SWCNT wt% range between 5 and 20, before levelling off for higher mass fractions. This is somewhat reflective of what we see for the GCPL data. At high discharge rates (i.e. 1 C and 5 C) where superior conductivity is most important to the capacities, the improvement in the  $C_1$  values improves notably from 5 to 20 wt% and not to the same extent at higher mass fraction.

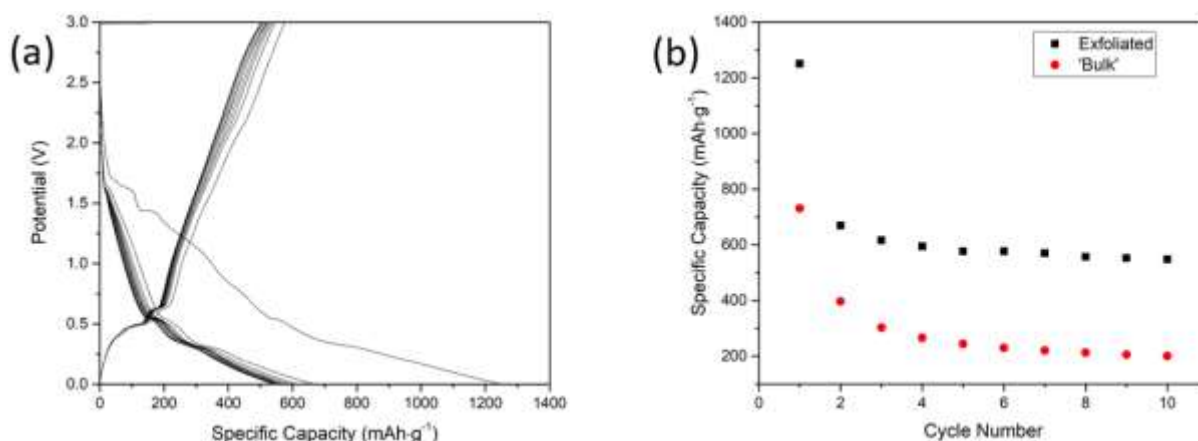


**Figure 5.3.6:** (a) GCPL charge-discharge profile for exfoliated  $\alpha$ -PbO with 25 wt% SWCNT at 0.1 C and (b) specific discharge capacity cycling graph compared with the optimized 'bulk' performance (10 wt% SWCNT-Tuball, 300 °C annealed).

In section 5.2 it was established that in the case of phase pure material, it is the  $\alpha$ -phase polymorph which demonstrated a greater intrinsic cycling performance in a basic carbon black – PVDF matrix. So, with that in mind, identical processing steps of exfoliation and composite preparation will be applied to the litharge material in the hope of improving further upon the optimization of the commercial, mixed-phase material. Figure 5.3.6 shows the results for the exfoliated  $\alpha$ -phase PbO with 25% SWCNT mass fraction, compared with the optimized case of the 'bulk' material. The result is the most impressive capacity retention for the material through ten cycles. With a 1<sup>st</sup> discharge capacity of 670 mAh·g<sup>-1</sup> and a final value of 548 mAh·g<sup>-1</sup>, the cycling data in Figure 5.3.6 (b) represents an 82% capacity retention for the anode, the highest value for cells discharged at 0.1 C in this study. Once again here the 1<sup>st</sup> discharge value exceeds even the expected theoretical limit for lead meaning there are likely Li<sup>+</sup> storage contributions from the SWCNT component in the early cycle life, among other affects.

Ultimately, the in-lab synthesis processing techniques of particle dimension reduction and controlled composite preparation for a material like PbO can help make substantial progress towards a goal of reversible full-electrode gravimetric capacities which are on the order of those theoretically predicted, by nullifying the harmful degradation effects caused by unregulated, repeated alloying with lithium ions. In a final demonstration of LIB cycling performance, Figure 5.3.7 compares the specific discharge capacities for the fully optimized, exfoliated  $\alpha$ -PbO and the commercially acquired

polymorphic PbO. Both demonstrate much improved 1<sup>st</sup> discharge and capacity retention values, but it is clear from the data that if one is to attempt to fully realize the specific performance of the PbO material, isolating the phase pure litharge is most certainly a worthwhile step. While the initial capacity is better to begin with, it is determinately the superior cycling and capacity retention which make the  $\alpha$ -PbO system a more attractive anode. The data mirrors that of the  $\alpha/\beta$  intrinsic performance comparison carried out in section 5.2 in which an improved relative cycling performance was rather unexpectedly observed for the litharge electrodes and theorized to be the result of superior ionic diffusion capabilities as well as the unique crystalline qualities of the tetragonal structure.

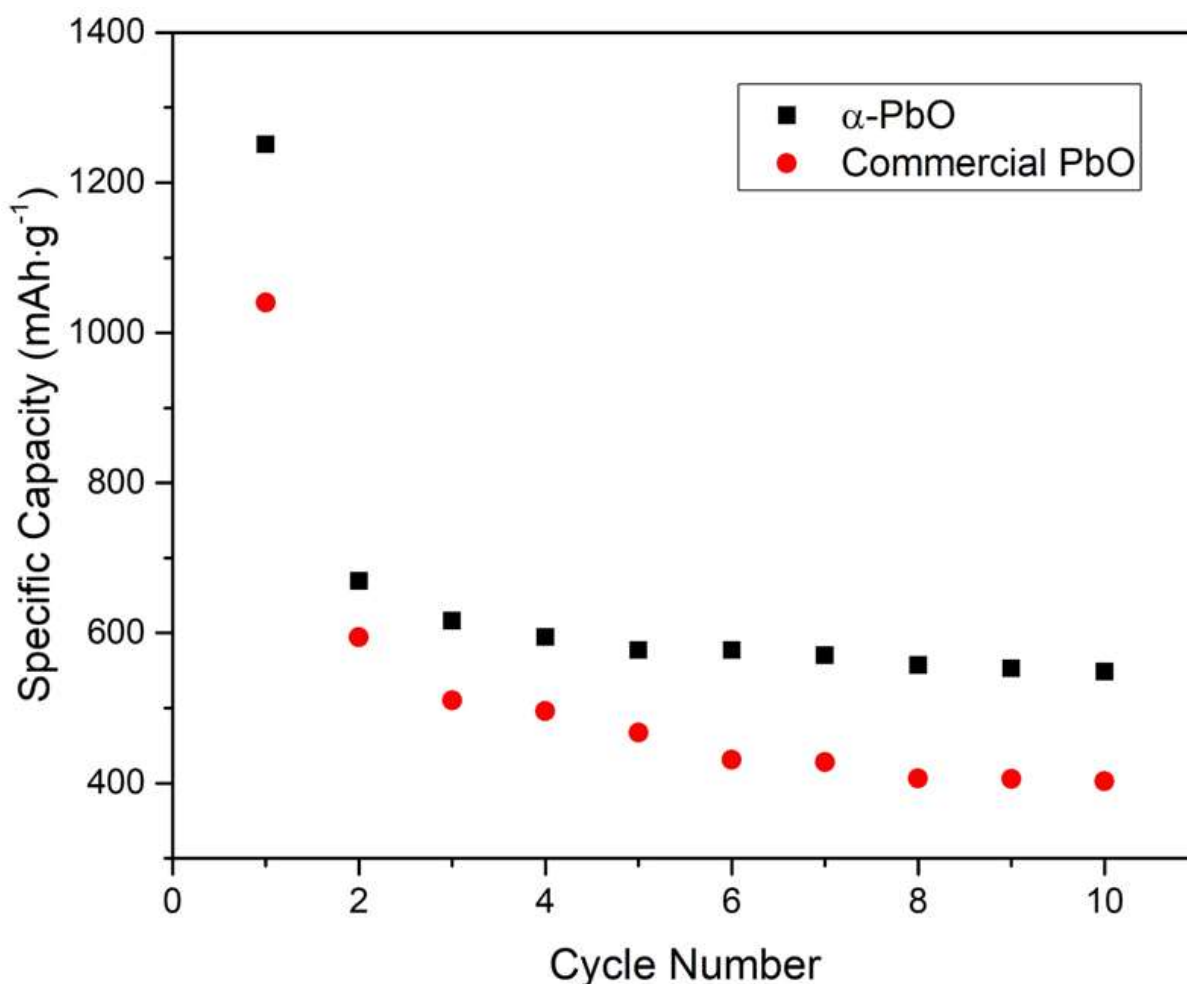


**Figure 5.3.7:** Comparative specific discharge capacity cycling graph for fully optimized exfoliated PbO – SWCNT composites, using commercially acquired polymorphic PbO and synthesized  $\alpha$ -PbO, respectively.

## 5.4 Conclusions

The outlook for alloying and conversion materials like PbO is constantly growing in research today. With such high performance in theory, alloying LIB anode components must be considered as major potential contributors to the field of next-generation battery performance despite their perceived drawbacks. Studies like this can have the effect of highlighting the extent to which the intrinsic performance can be harnessed and reproduced using simple, transferable lab-based processing techniques. The results compliment the achievements in Chapter 3 of this thesis in which similar size and composite control of the active NiFe LDH material was tailored to fit its electrochemical application in a reproducible manner.

So, where does that leave lead(II) oxide as a feasible LIB anode component in practical next-generation battery applications? The results from this chapter suggest that the material can repeatedly charge to near its theoretical capacity in the lithium half-cell setup within a 25 wt% SWCNT composite matrix when the phase-controlled synthesis route is applied. While this work provides impressive performance of the material in principle, PbO will still face a number of challenges before it is commercially recognized. One such issue is cost effectiveness. While the lead carbonate synthesis route can be considered cost effective and environmentally friendly because of the recycled reactant, the use of significant fractions of high-quality nanotubes cannot be considered as such. Because of the small scale production of highly pure nanotubes, samples can cost around 750 \$/g, as of 2002.<sup>193</sup> As the basis of nanotube applications continues to grow however, large-scale production is expected to drive down the cost of good quality material. Tuball™ is an example of a modern supplier of SWCNT suspensions, available at an increasingly affordable cost for scaling up applications. Other potential generic hurdles to overcome are environmental considerations and full-cell compatibility in terms of operational potential windows.

## 5.5 Experimental

**‘Slurry’ composite preparation:** An appropriate mass of the PbO powder (commercial material sourced from J.T. Baker, phase pure material synthesized in-lab) was weighed using a Sartorius Cubis® Analytical Balance and crushed using a mortar and pestle for 10 – 15 minutes until a fine, particulate powder was observed. At this point, for carbon black – PVDF slurries, the carbon black powder was similarly weighed and added to the mortar, crushing for a further 10 minutes or so until the resulting powder appeared to be homogeneously mixed. At that point, an appropriate volume of viscous 2.5 wt% PVDF (Sigma-Aldrich) in n-methyl-2-pyrrolidone (NMP) was added to the mortar and mixed well (the slurry will lighten in colour upon thorough mixing of components). The slurry was placed on an IPA-cleaned copper foil surface, supported by a flat glass plate and spread evenly to 20  $\mu\text{m}$  thickness using a Doctor Blade (KJ Group). The slurry was allowed to dry in air for 48 h before punching electrodes 12 mm in diameter using a EL-Cut (EL-Cell) tool. For SWCNT - PVDF slurries, appropriate volumes of Tuball™ BATT 0.4% SWCNT in NMP (2% PVDF HSV 900) were added to the mortar after PbO crushing. Annealing steps were carried out using a Buchi Glass Oven B-585 with vacuum system.

**Cell Assembly:** Cells were assembled for electrochemical testing according to the schematic in Figure 2.9. The separator used was Celgard polyolefin, 15  $\mu\text{m}$  thickness and the cell lid, spacer, spring and base were purchased from Pi-Kem Ltd. Cells were assembled in a controlled Ar environment in an MBraun LabMaster Pro glove box using punched pure lithium counter electrodes. The electrolyte used was 1 M lithium hexafluorophosphate ( $\text{LiFP}_6$ ) solution in ethylene carbonate (EC) and dimethyl carbonate (DMC) 50:50 mixture. Crimping of the cell components together was performed using an MSK-110 Hydraulic Crimping Machine (KJ Group). After removal from the glove box, the cells were rinsed in a small amount of IPA to remove dried electrolyte.

**Litharge/Massicot synthesis:** Samples were prepared by way of thermal decomposition of lead carbonate powder (Alfa Aesar) heated in a ceramic crucible. For  $\alpha$ -phase synthesis, the crucible was placed in a Carbolite tube furnace and heated to 400  $^{\circ}\text{C}$  for 4 h under vacuum on the order  $10^{-2}$

mbar and Ar flow and allowed to cool to RT under the same conditions. For  $\beta$ -phase synthesis, the crucible was placed in a WiseTherm muffle at 600 °C for 1 h in air before cooling.

**Exfoliation procedure:** 0.5 g of bulk PbO was weighed separately into eight centrifuge tubes along with 40 ml of IPA in each. The material was ultrasonicated as such using a Fisherbrand 112xx Series Advanced Ultrasonic Cleaner operating at 37 kHz and 100% power for 3 h. Then the material was centrifuged using a Heraeus Multifuge X1 Centrifuge at 1000 rpm for 1 h. From there, the supernatant was removed and discarded, and the precipitate was redispersed in 40 ml of IPA in each tube and sonicated for a further 4 h at 60% power. The supernatant was removed in which the product of exfoliation was suspended.

## 6 Conclusions and Outlook

At the beginning of this work, the goal was set out to take effective, transferable methods of layered nanomaterials processing to help realize their full potential to applications in the field of state-of-the-art energy solutions. In doing so, the secondary goal would be to understand more comprehensively where the materials fall short in terms of the performance required to achieve commercial success. Two device applications were considered in the work. Firstly, as an example of a modern energy-transfer solution, alkaline electrolyser cells, focusing on the OER half-cell reaction of alkaline water electrolysis, NiFe LDH being the catalyst of interest. Secondly, as an example of a next-generation energy storage device, LIBs were studied, looking specifically at the applicability of lead(II) oxide-based nanocomposites as a high performance anode.

The catalytic mechanism of NiFe LDH is an area under constant review and as of yet not fully agreed upon. What is more accepted (although not always) is that the vast majority of active sites for catalysis exist at platelet edge terminations. This point, however, is rarely demonstrated in certain terms. In this work, through the use of platelet size control by mechanical size reduction and controlled centrifugation the edge site density was significantly increased and particles with different lateral dimensions were compared in OER. The smaller platelets with higher edge exposure achieved overpotential values as low as  $245 \pm 7$  mV (vs RHE) for the pure active material, exceeding the overpotentials obtained for larger counterparts. Building on that, controllable SWCNT composite preparation allowed for much improved long-term activity of the catalyst in alkaline media, both in terms of cycling and constant current performance. The results not only demonstrate the relationship between platelet size and catalytic activity, but also the sensitivity of the catalyst performance to the processing conditions, including the choice of solvent, and touch on the possibility of further improvement to align the catalyst with the requirements which would be expected for application on the industrial scale.

Following that, the next point to be considered was to classify what was causing the fluctuating OER overpotentials within the LDH material during its active lifetime. Two principle

effects are thought to be at the forefront of the unusual behaviour. Namely, a subtle, but gradual phase transition within the active crystal during early cycle life, followed by a sequential loss of activity in response to the preferential leaching of iron from the system. *Ex-situ* experimentation proved more than adequate to address both of these points. In terms of phase analysis, the NiFe LDH catalyst after cycling showed highly similar behaviour to that of the interchangeable  $\alpha$  and  $\gamma$  phases of a  $\text{Ni}(\text{OH})_2$  catalyst. Predictably, the transition to the much more densely packed  $\beta$  phase is blocked for the iron containing LDH. The  $\alpha \rightarrow \gamma$  transition is not affected by ageing in alkaline media as it is brought about as a result of the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  at 1.4 V (vs RHE), meaning the initial catalytic improvements will always be seen to some extent in early cycle life for NiFe LDH catalysts. After the phase transition is established, iron leaching is believed to take over as the factor of highest influence in subsequent cycles. The outlook for this work, in terms of proving the theory, is promising. There is much that can still be done to provide more evidence of the leaching effect, including repeated AAS and ICP-MS/ICP-OES experiments directed at clearly observing the leaching effect, both in the active LDH structure as well as the electrolyte. The timescale of such experiments is unfortunately significantly lengthened at present due to restricted access to instruments and laboratories and could not align with the current report.

Not dissimilar to the processing steps taken for NiFe LDH catalyst optimization, PbO anodes responded well to the application of size control measures and implementation in carbon composites. Aside from that, another important point which was addressed here was the importance of phase control to the electrochemical performance of PbO. This is an intrinsic property of the  $\alpha$ -phase material whose tetragonal crystal structure can better facilitate the charging and discharging of  $\text{Li}^+$  in the long term. Composites performed at their best with 25 wt% SWCNTs with phase-pure  $\alpha$ -PbO, demonstrating a full-electrode gravimetric capacity of  $548 \text{ mAh}\cdot\text{g}^{-1}$  through 10 cycles at 0.1 C charge/discharge rate. The SWCNT component likely contributes some capacity here but the majority of the nanotube work load is to facilitate the alloying of PbO within a well-integrated, robust conductive matrix.

The relatively simple, reproducible, and transferable nature of the techniques presented in this work means that the steps can be further applied to a range of similar materials. For instance,  $\text{Co}(\text{OH})_2$  and  $\text{SnO}$  are examples of materials showing promising properties in alkaline water splitting and LIB anode performance respectively, with similar morphological properties to the NiFe LDH and  $\text{PbO}$  examples considered here. Both are under considerable review in the respective fields of application in the Nicolosi group and beyond.<sup>194, 195</sup> The major outlook of this thesis will be to apply the performance enhancing processing steps to additional layered nanomaterials.

# Appendices

## Appendix A: Additional Figures

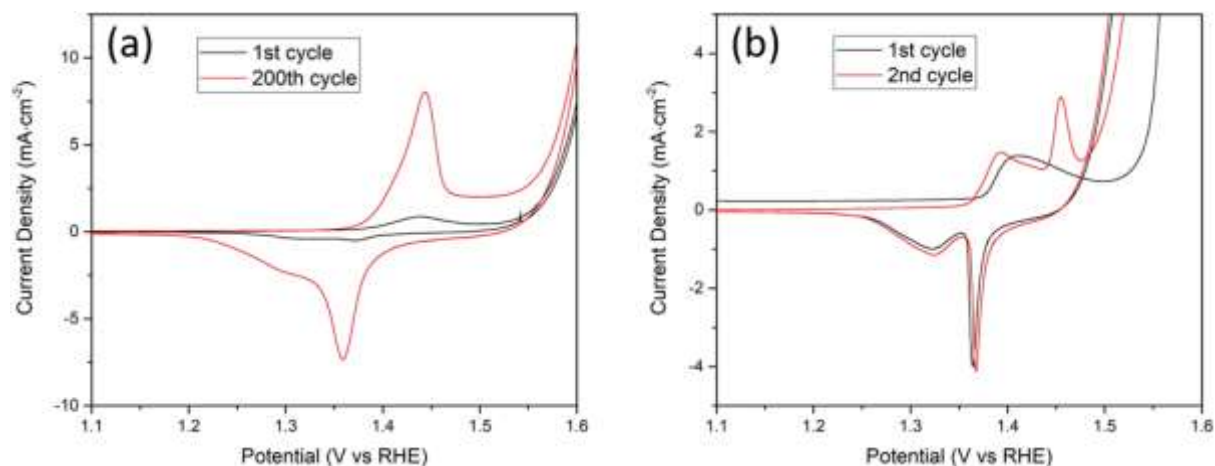


**Figure A1:** (a) 1<sup>st</sup> & 200<sup>th</sup> CV cycle for Ni foam, and (b) 1<sup>st</sup> & 2<sup>nd</sup> CV cycle for NiFe LDH on Ni foam, performed in 1 M KOH at 5 mV·s<sup>-1</sup>. One can observe in both examples, the Ni<sup>2+</sup> ↔ Ni<sup>3+</sup> redox couple for pure nickel (1.36 V) and for NiFe (1.42 V) in the second cycle. The pure nickel CV analysis displays peak splitting throughout its cycle life, suggesting the presence of both  $\alpha/\gamma$  and  $\beta/\beta'$  phase transitions. This is observable to an extent for the NiFe loaded catalyst (b), where the nickel foam component demonstrates multiple phase peaks in the second anodic sweep, the NiFe redox couple does not. Both CVs exhibit sequential peak growth due to hydrous oxide growth at the surface with cycling.<sup>141</sup>

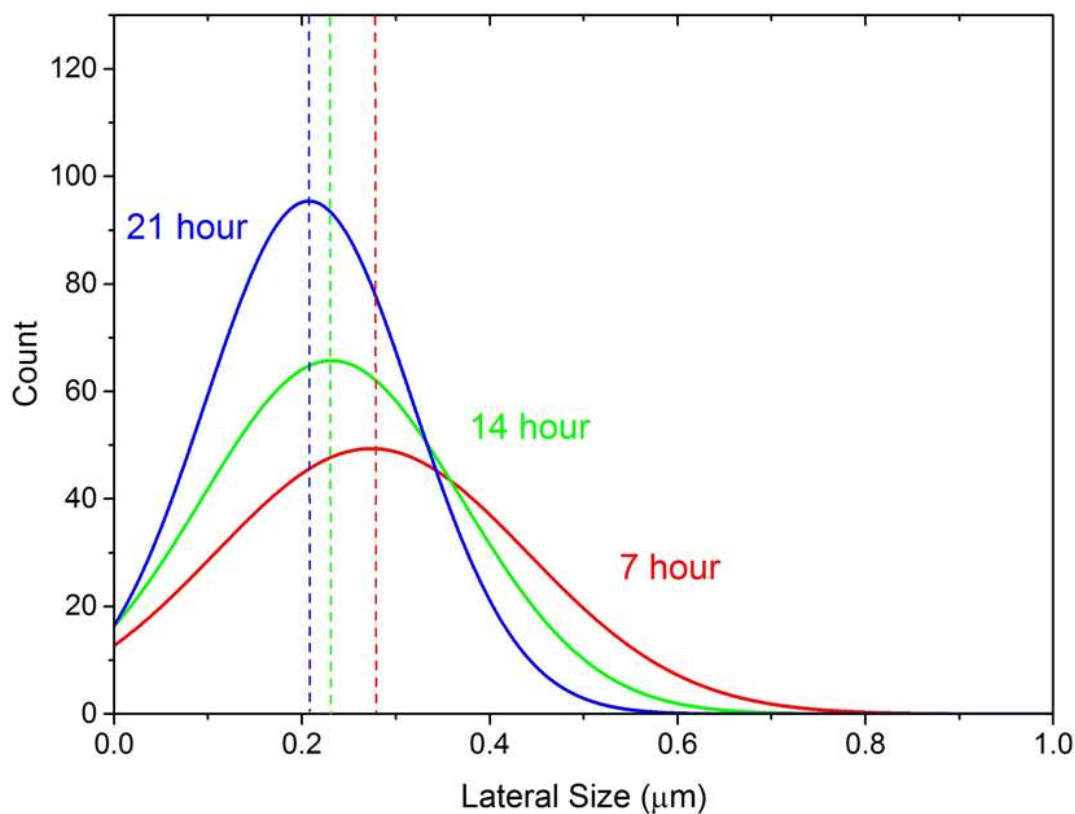


**Figure A2:** Platelet size distributions for sr-NiFe LDH subjected to various time periods of tip-sonication, demonstrating the effect that sonication time alone can have on the controllability of  $\langle L \rangle$  and  $\sigma$ .

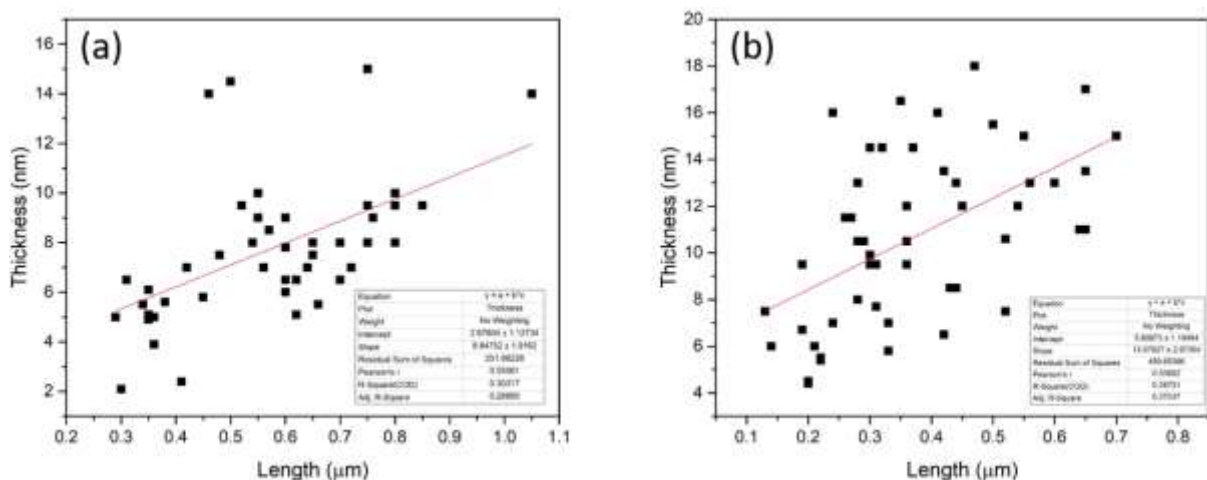


Figure A3: Length-thickness dependence for NiFe LDH platelets (a) before and (b) after size-reduction treatment. The data suggests a reduced correlation of the variables after treatment.

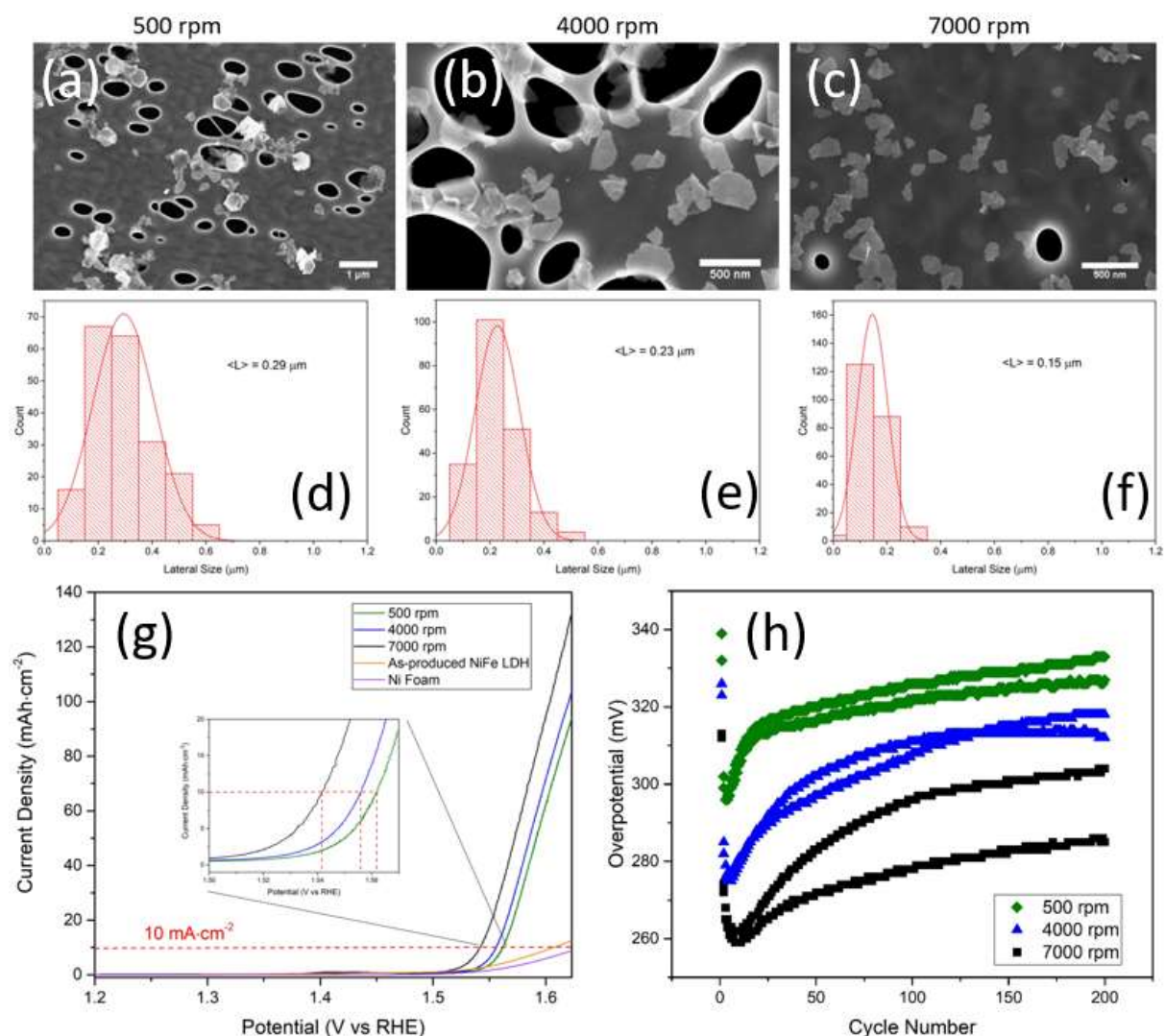


Figure A4: (a) - (c) SEM micrographs and (d) - (f) accompanying size-distribution histograms for sr-NiFe LDH with final centrifugation rate 500, 4000 and 7000 rpm respectively. (g) Polarization curves for electrodes prepared with each dispersion and (h) cyclic overpotentials as a function of cycle number (performed twice in each case). Despite having a narrow range of  $\langle L \rangle$  in the size-selected samples, the size distributions in each case appear to demonstrate more unique overpotentials compared to the data set presented in the Chapter 3. The size-activity relationship is perhaps more obvious here due to the minimal overlap of the respective distributions.

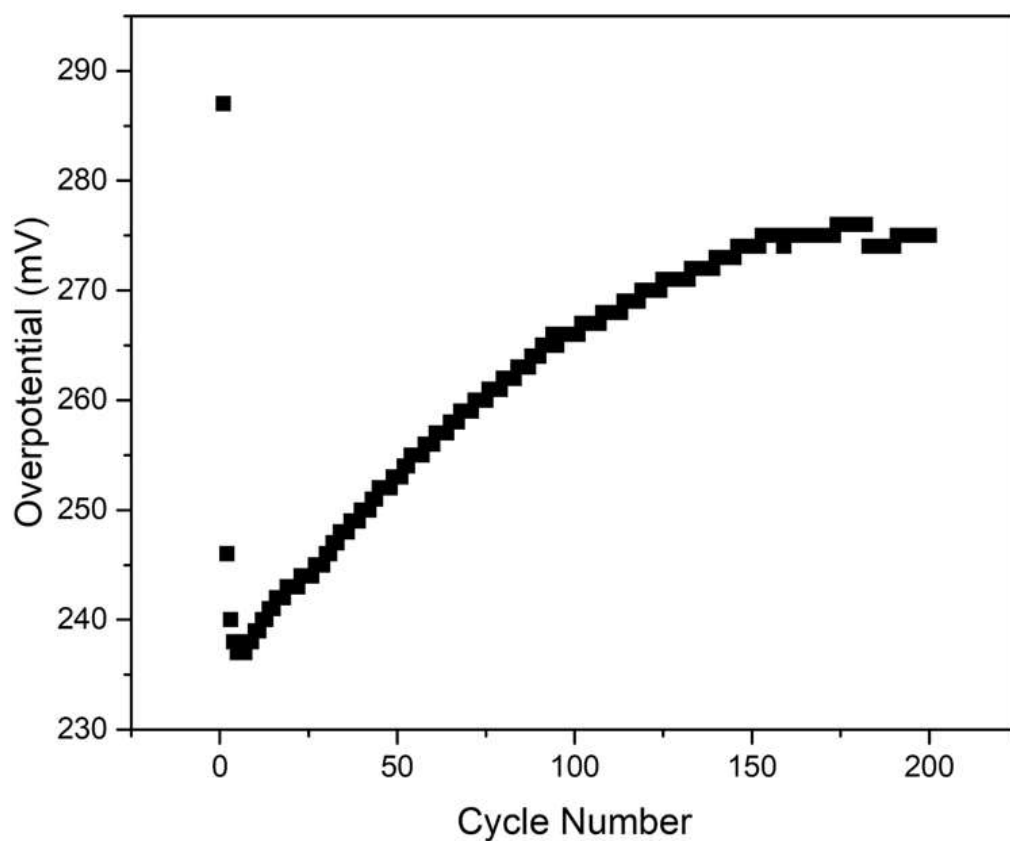


Figure A5: Overpotential values as a function of cycle number through 200 cycles for electrode prepared using size-selected sr-NiFe LDH with 20 wt% SWCNT on nickel foam.

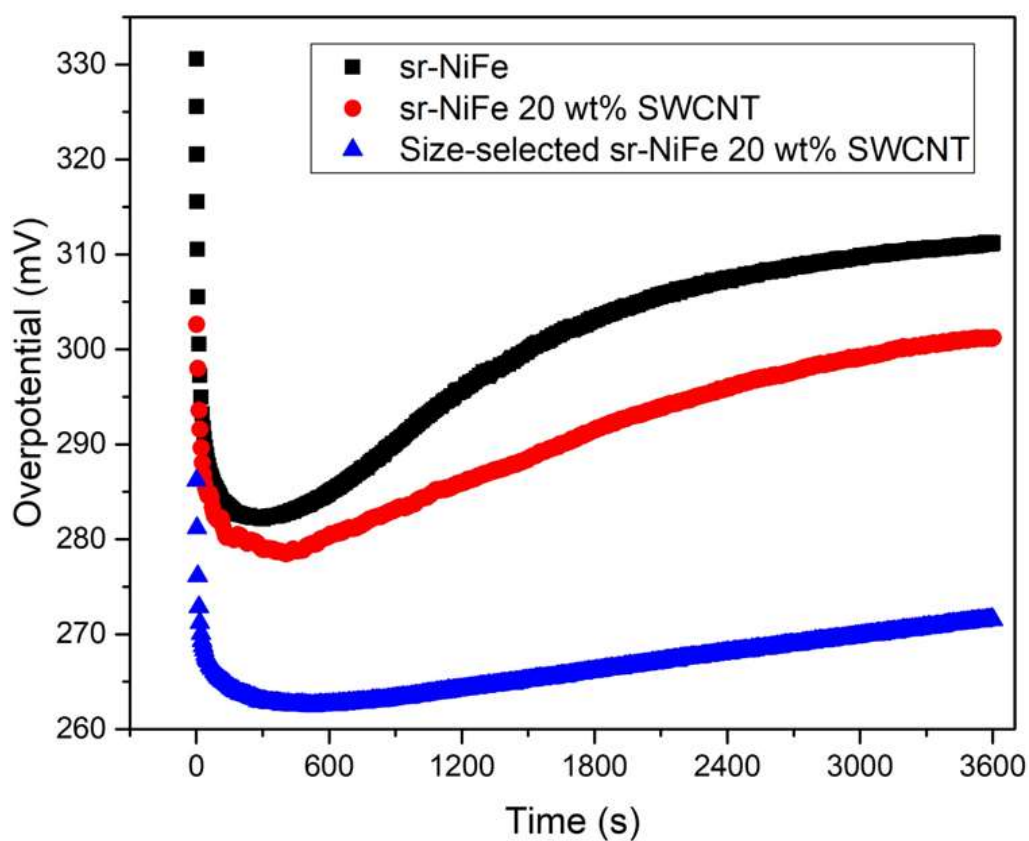


Figure A6: Comparative chronopotentiometry curves for sr-NiFe LDH catalysts over a period of 1 hour at  $10 \text{ mA}\cdot\text{cm}^{-2}$ .

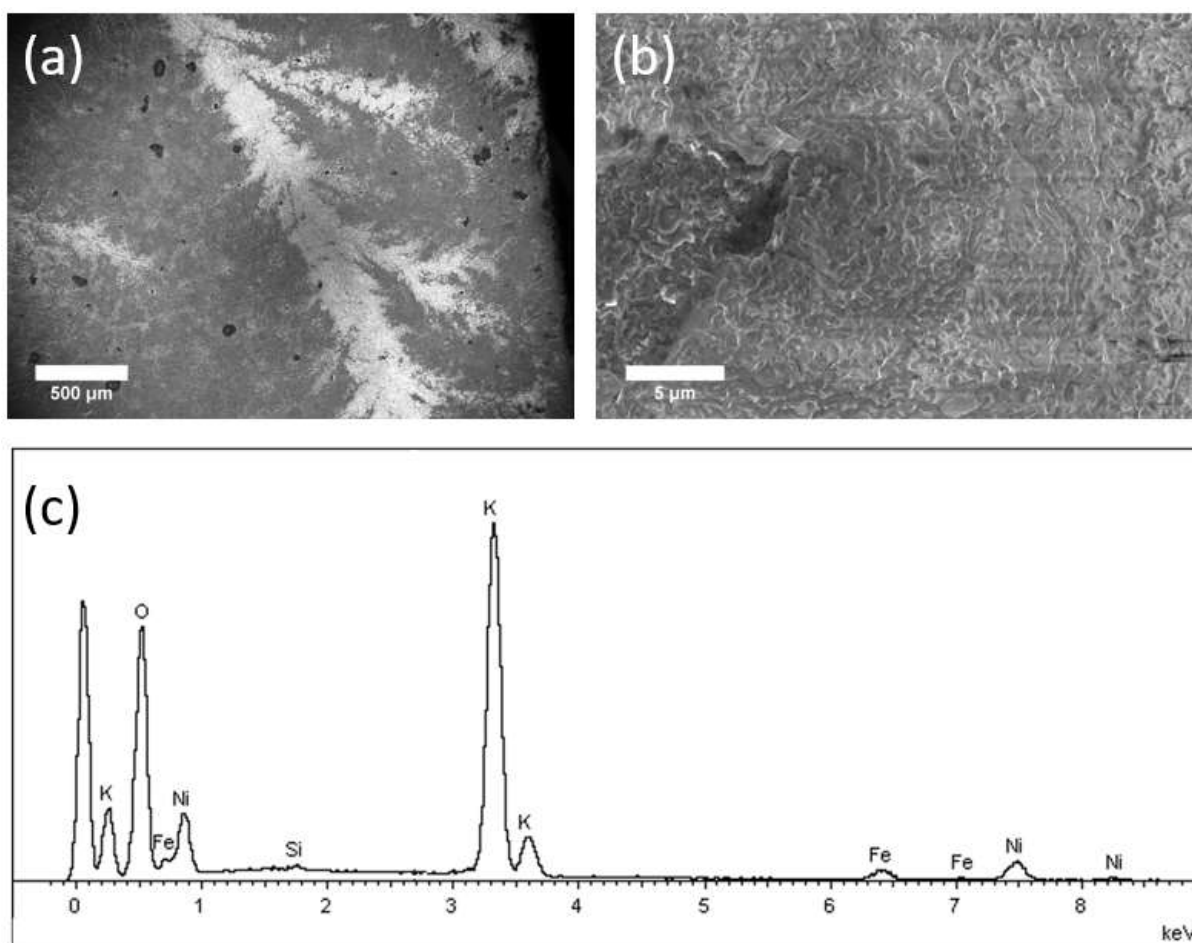
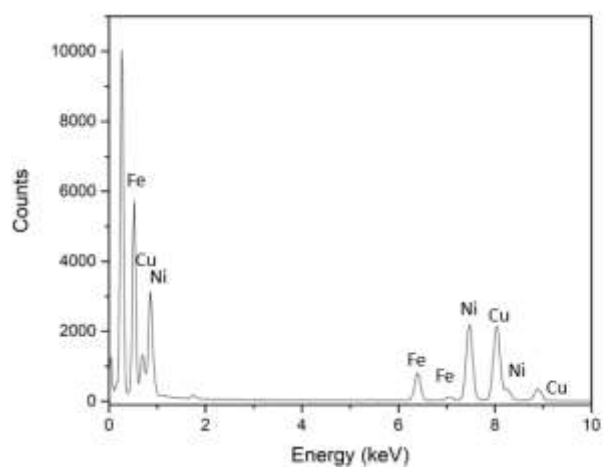
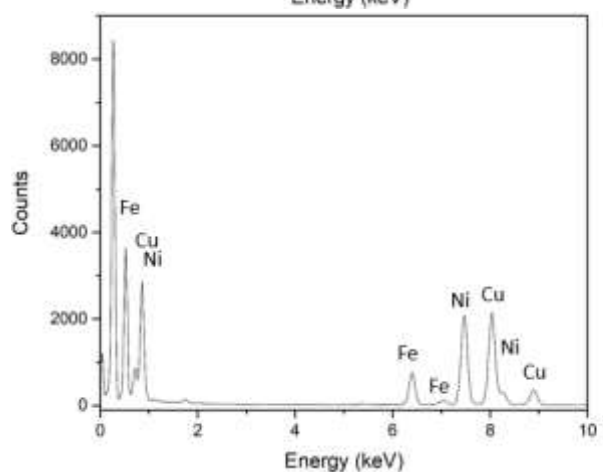
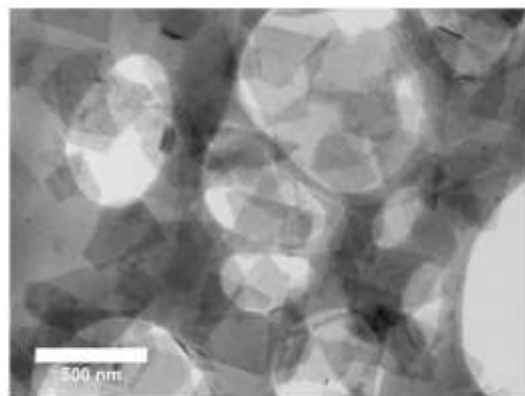


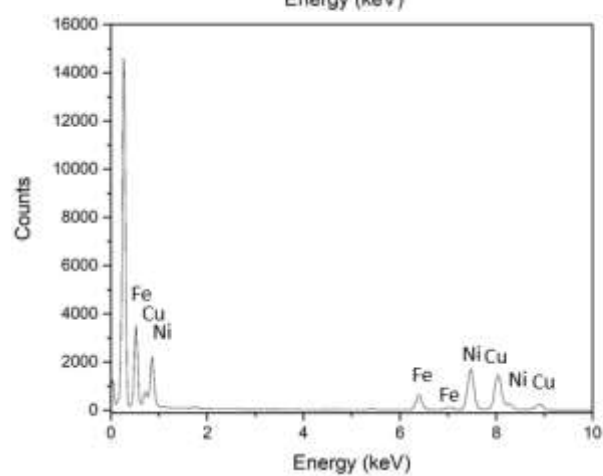
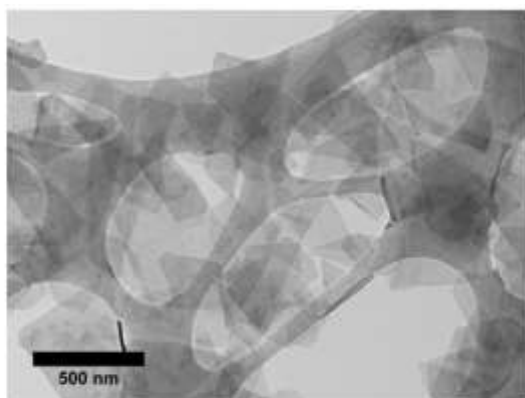
**Figure A7:** (a) Lower and (b) higher magnification SEM micrographs showing the surface of a cycled sr-NiFe LDH electrode covered in a layer of dried KOH, indicated by the EDX spectrum for the area (c).



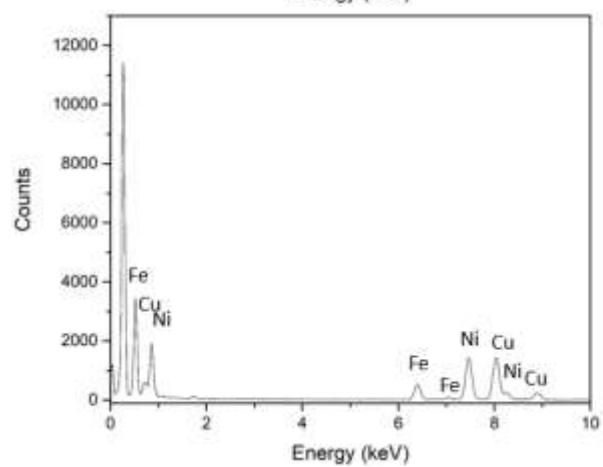
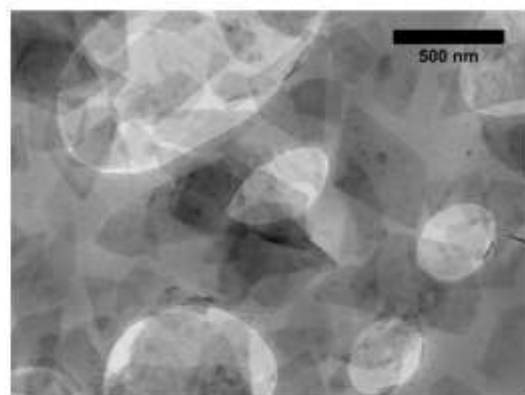
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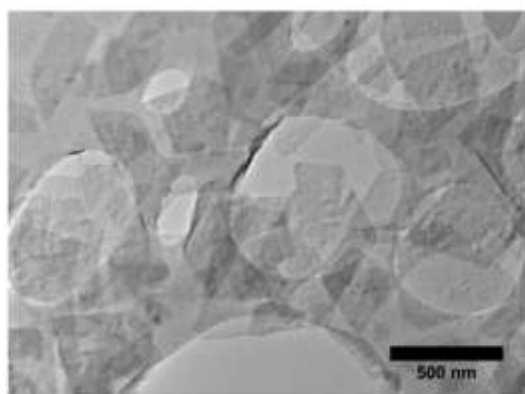
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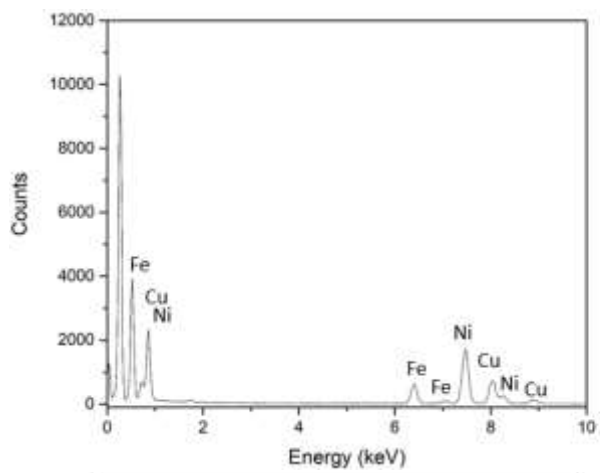


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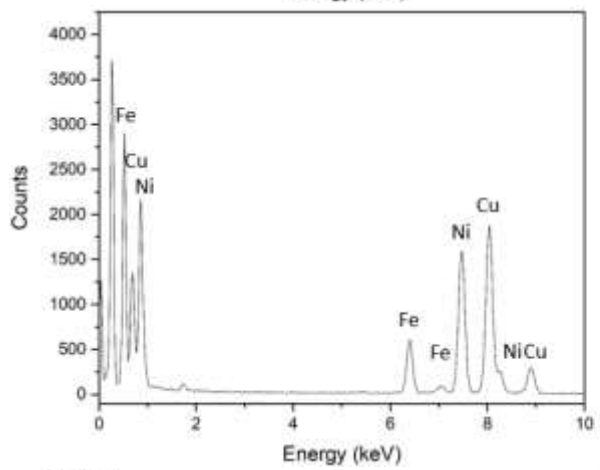
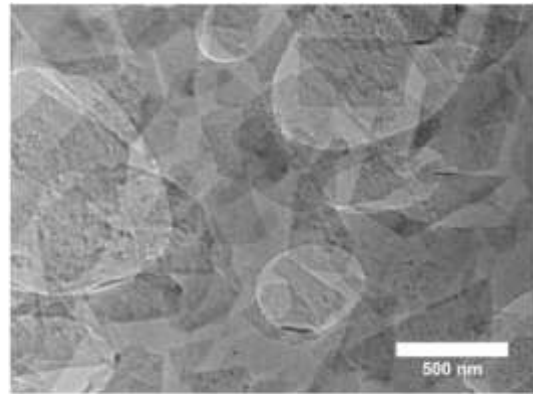


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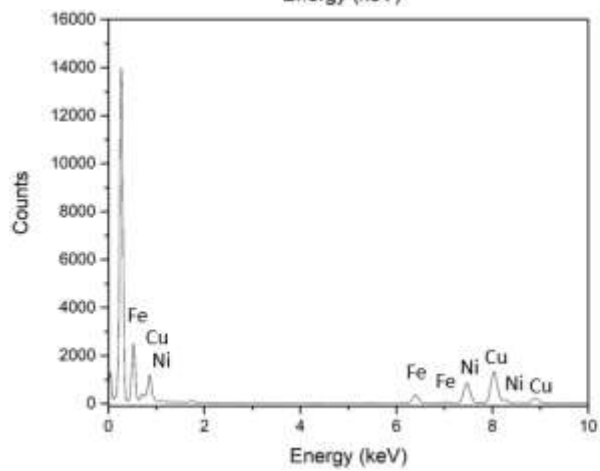
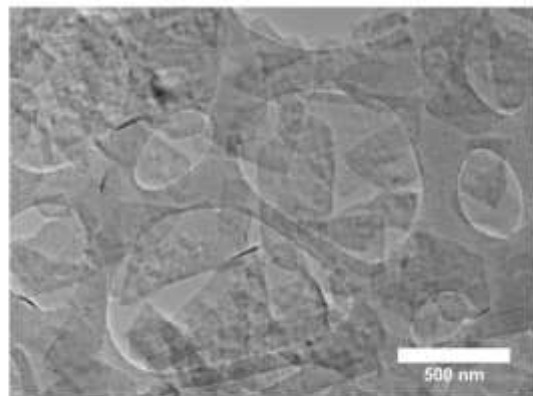




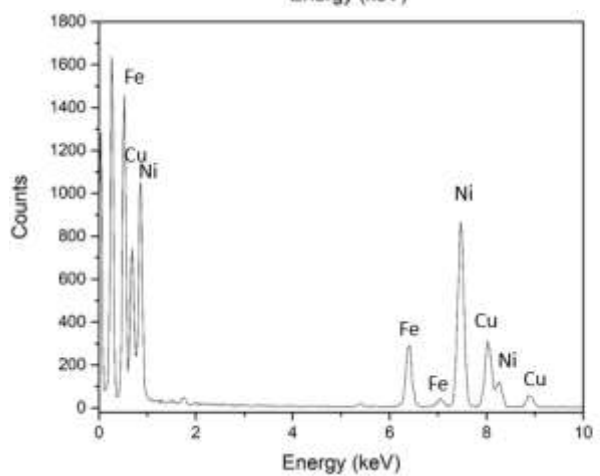
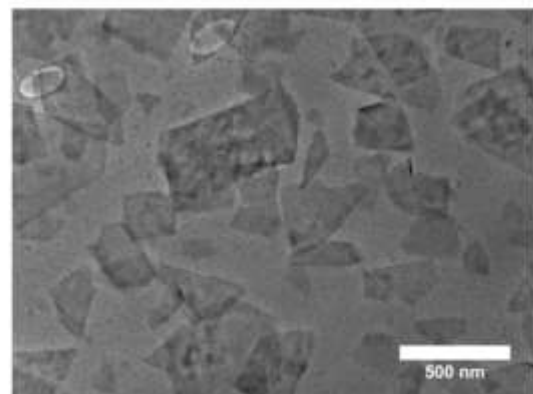
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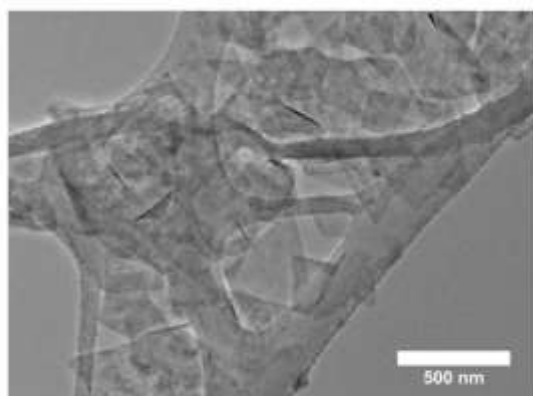
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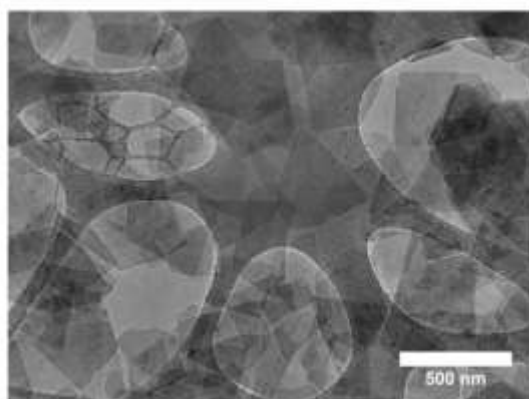
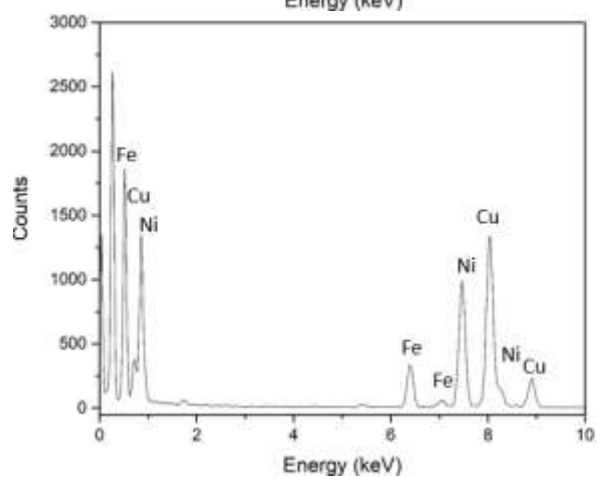
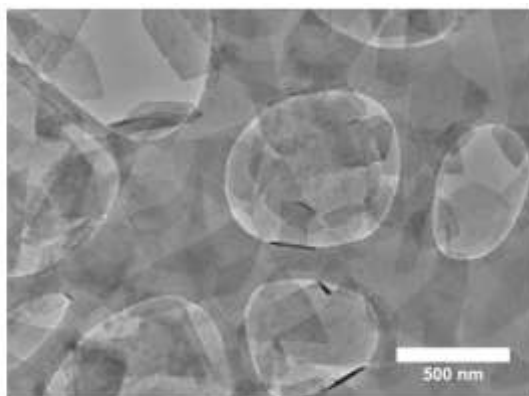
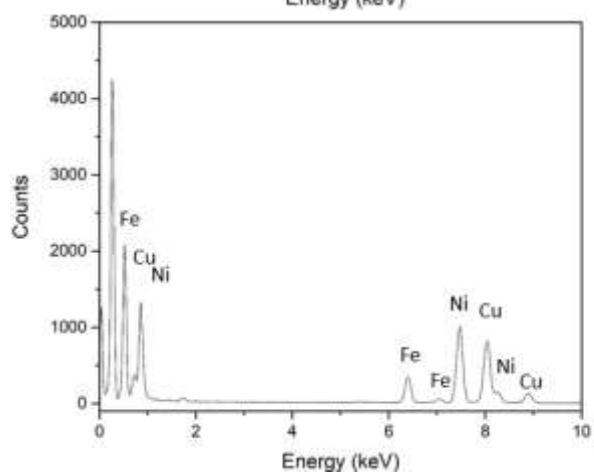
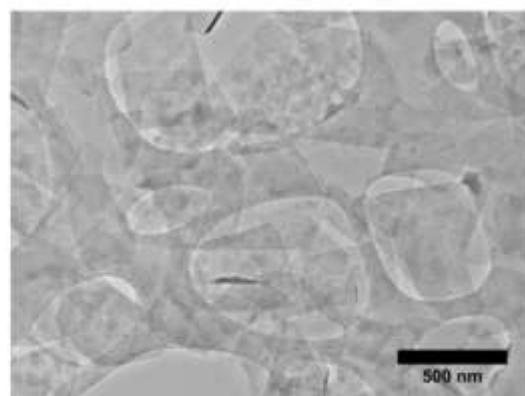
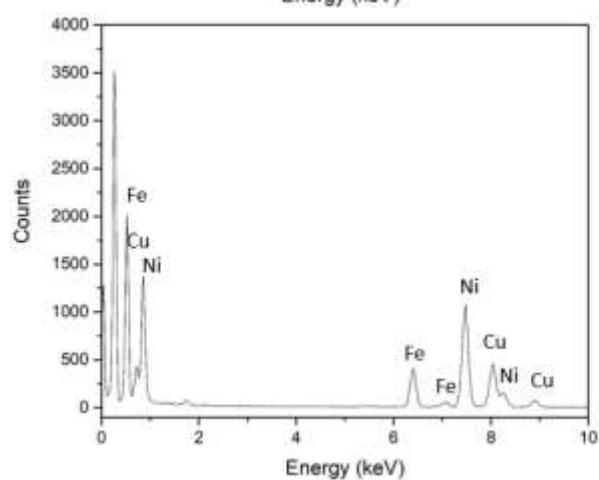
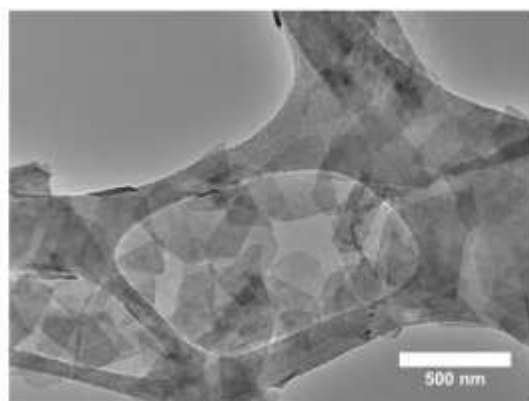
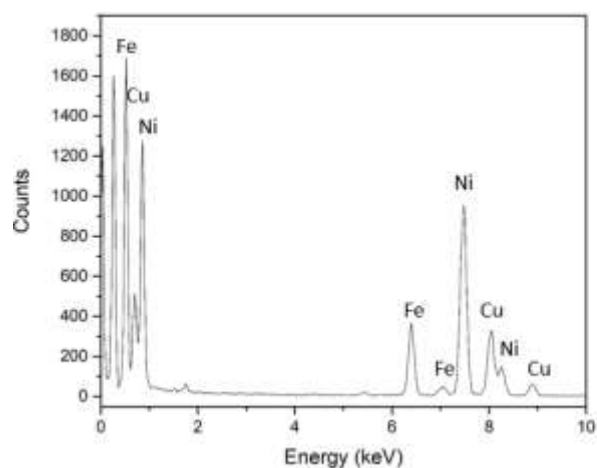


(g)



(h)





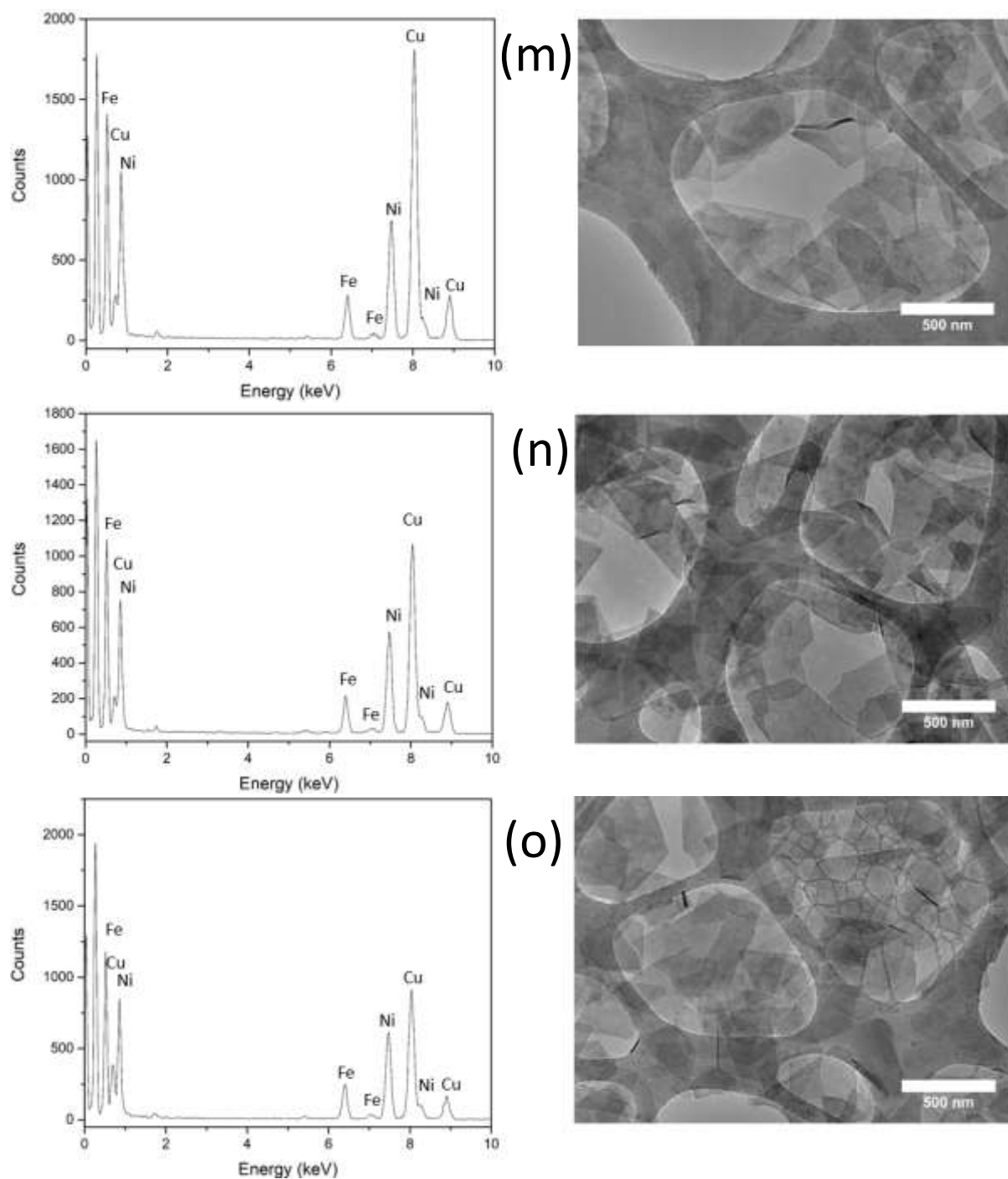
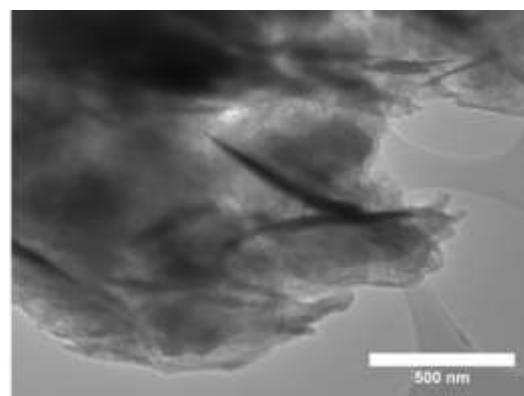
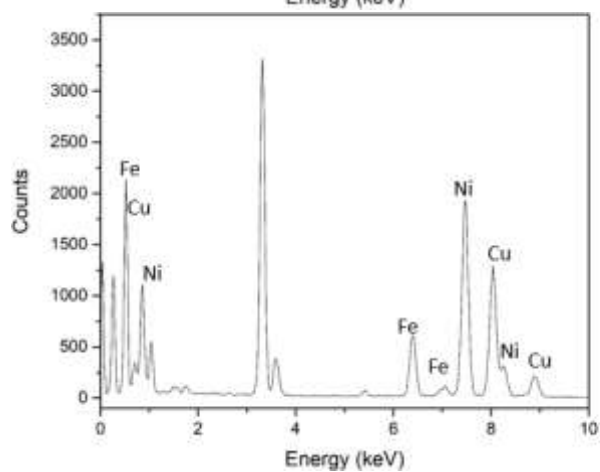
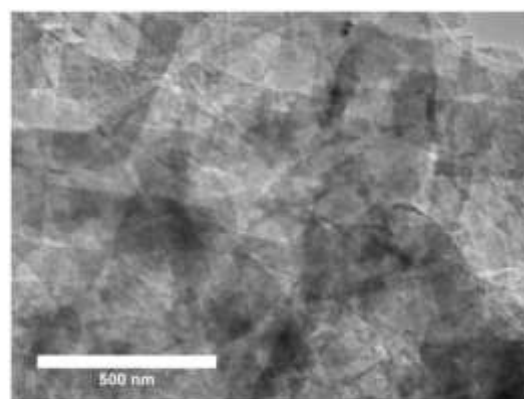
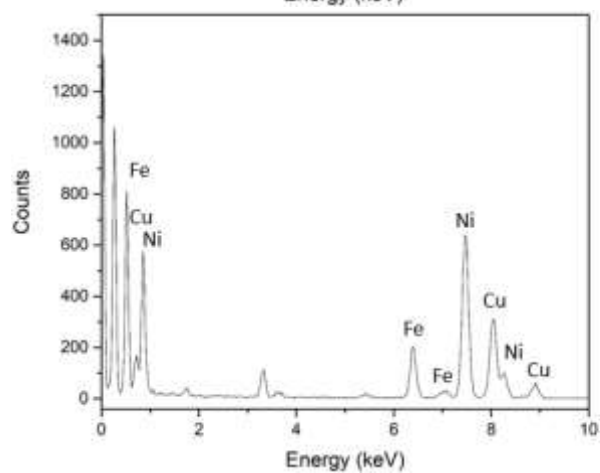
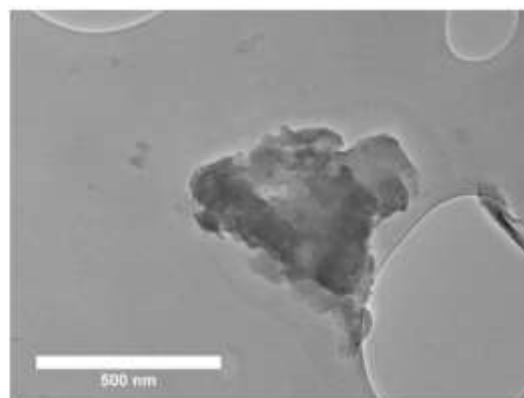
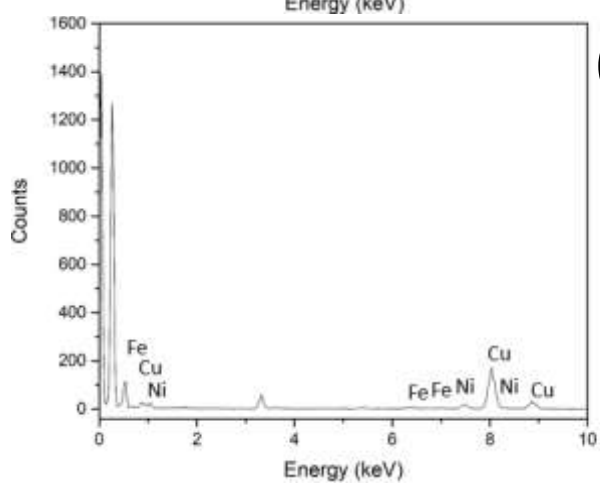
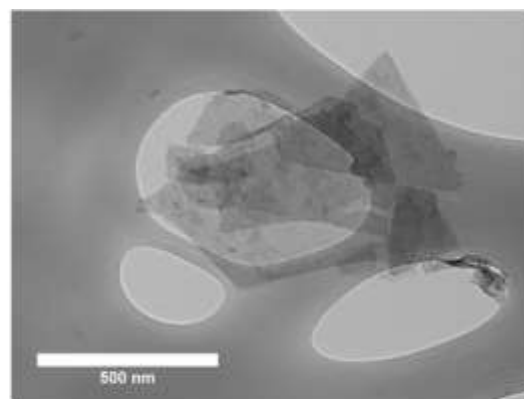
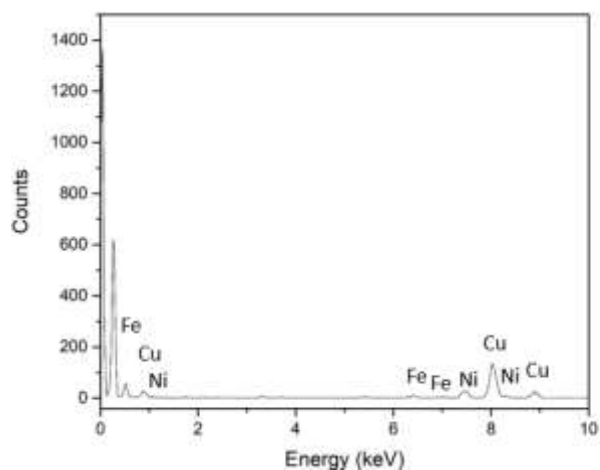
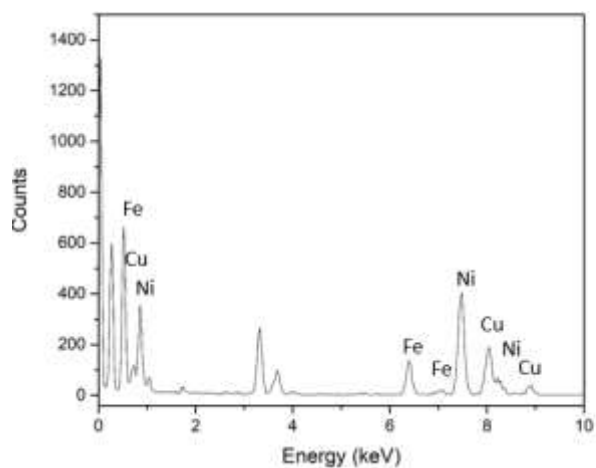
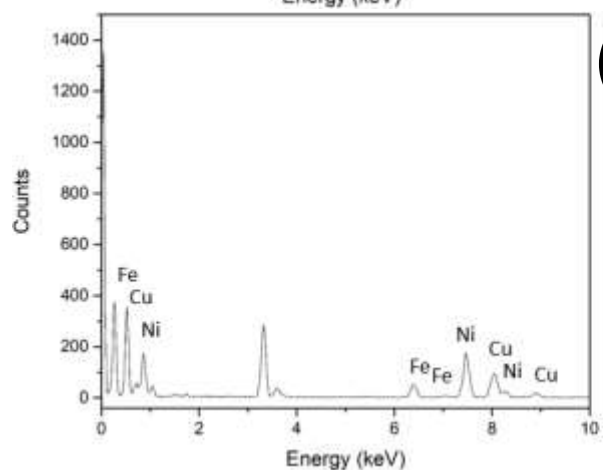
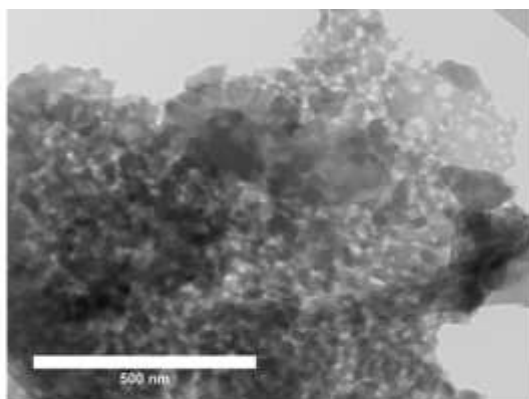


**Figure A8:** EDX spectra and accompanying TEM images for the pre-cycled sr-NiFe LDH, corresponding to the data presented in Figure 4.2.2 (a) – (o) in Chapter 4.

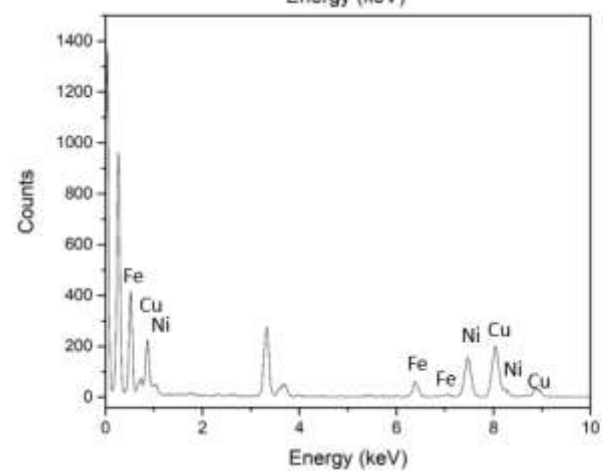
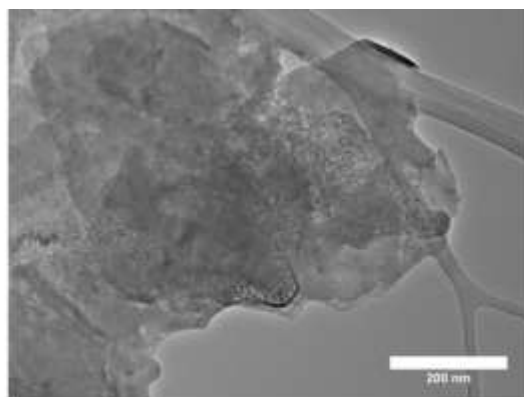




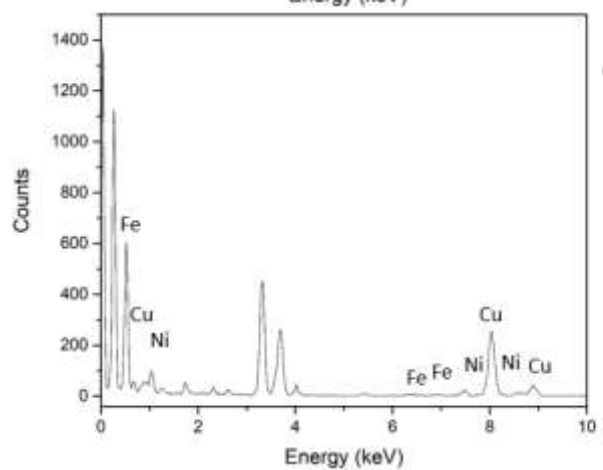
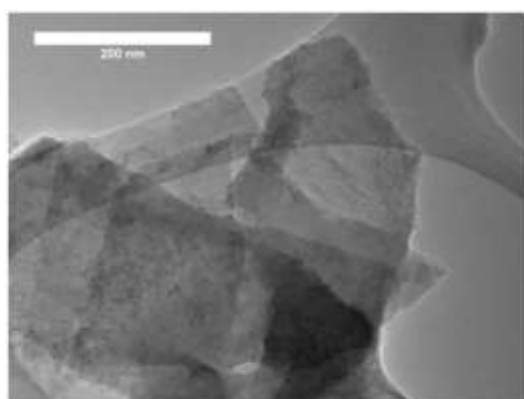
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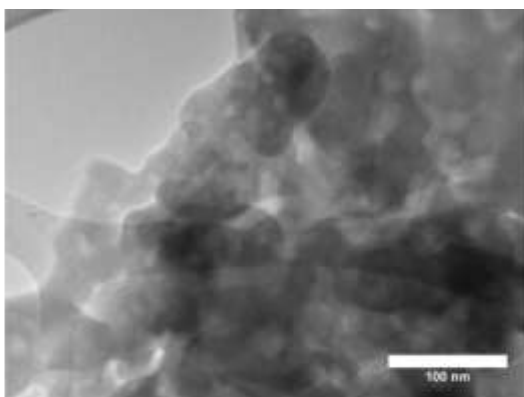
(f)

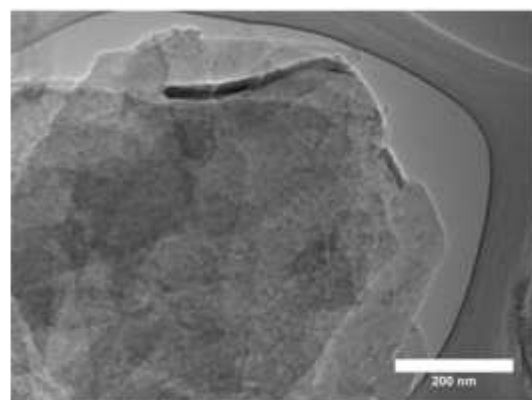
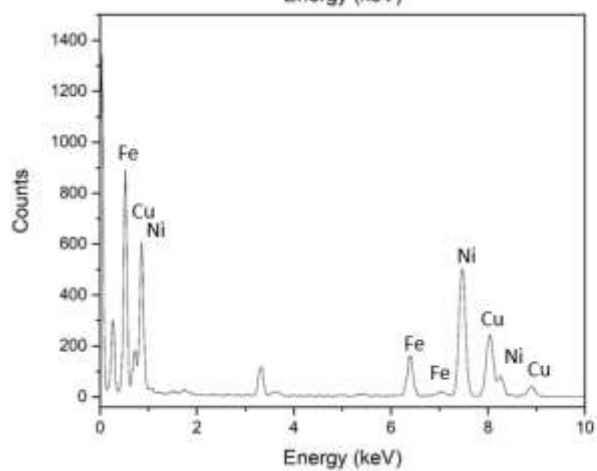
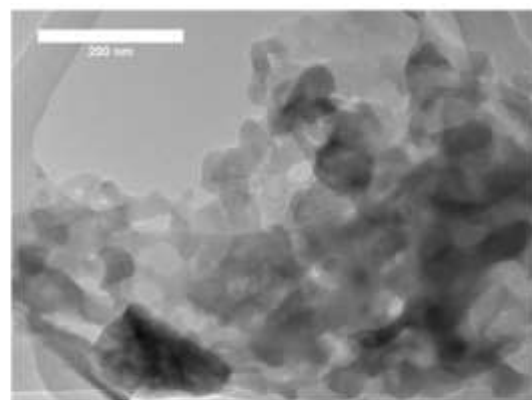
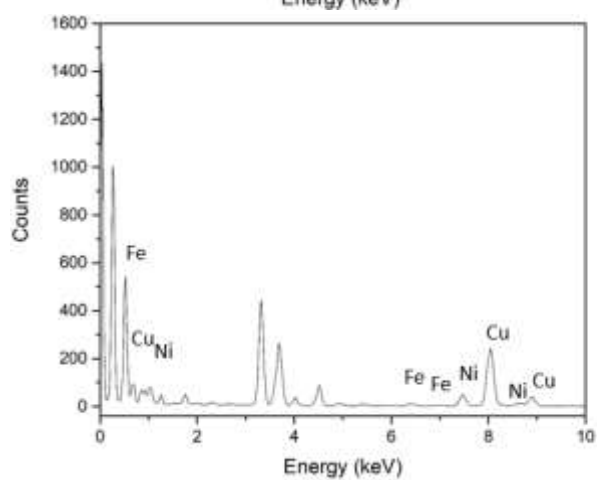
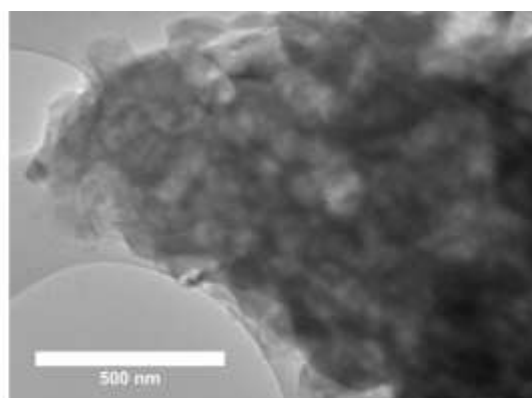
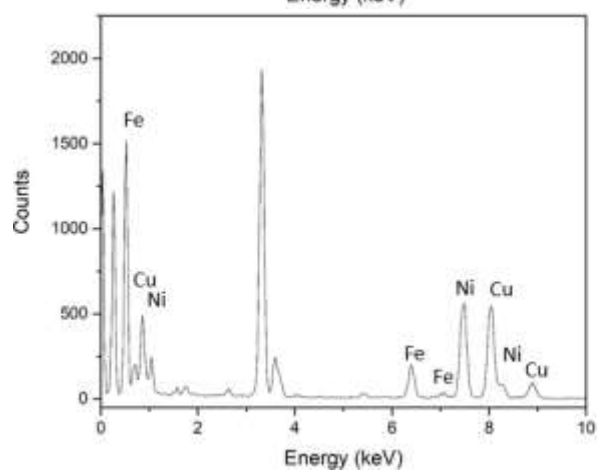
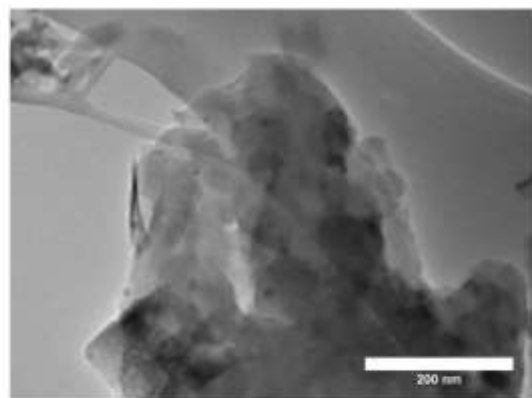
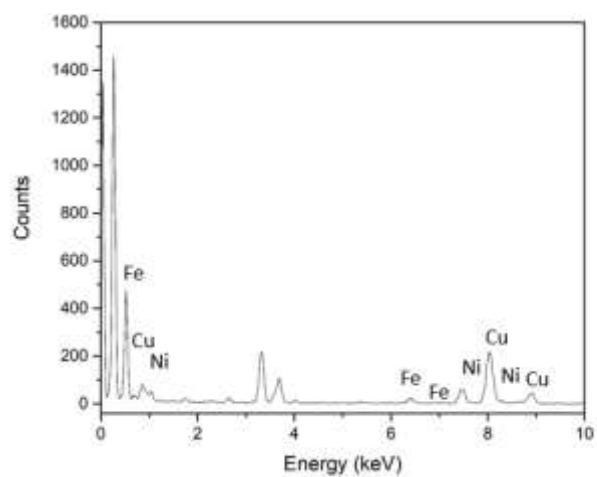


(h)



(h)





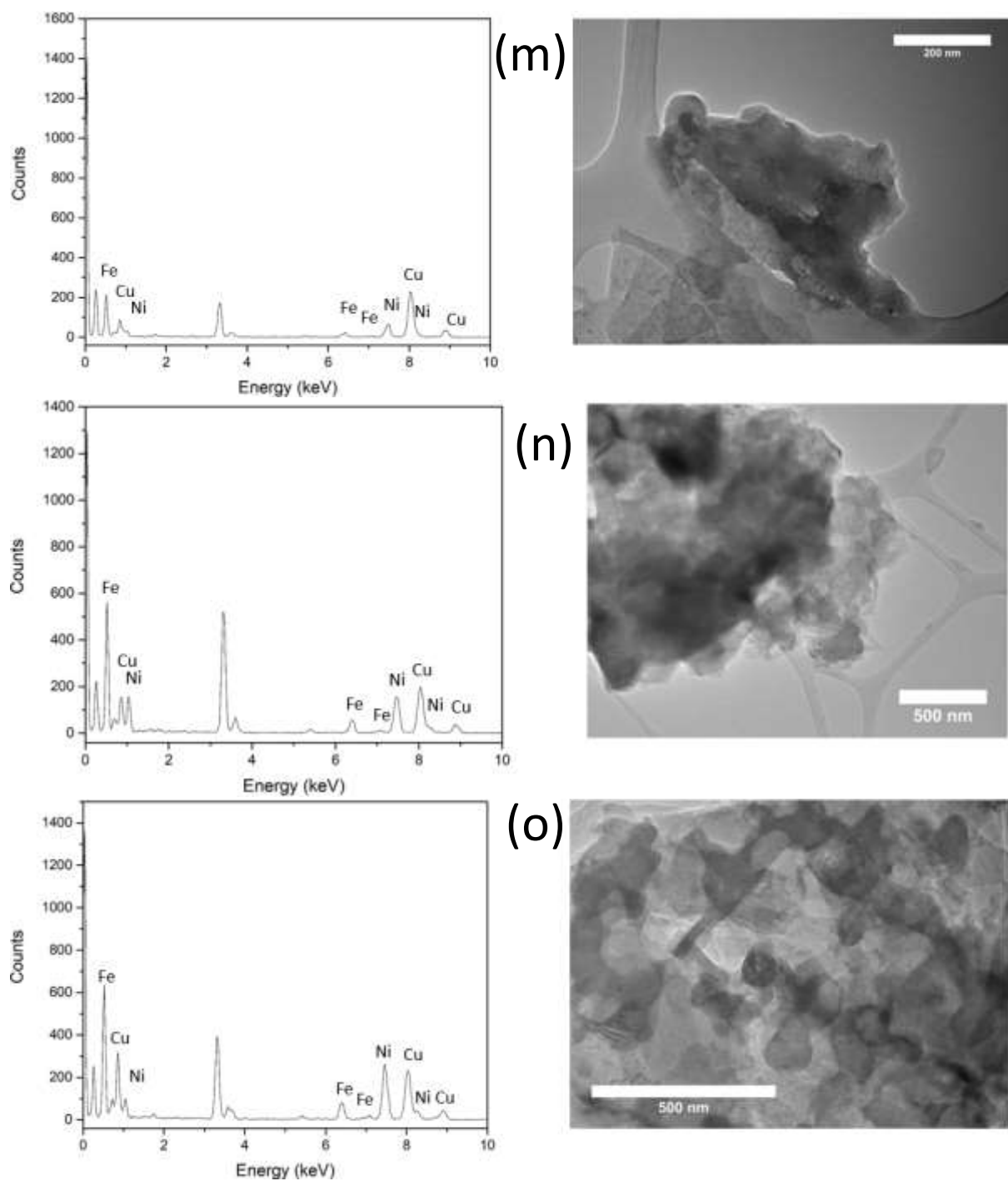


**Figure A9:** EDX spectra and accompanying TEM images for the post-cycled sr-NiFe LDH, corresponding to the data presented in Figure 4.2.3 (a) – (o) in Chapter 4.

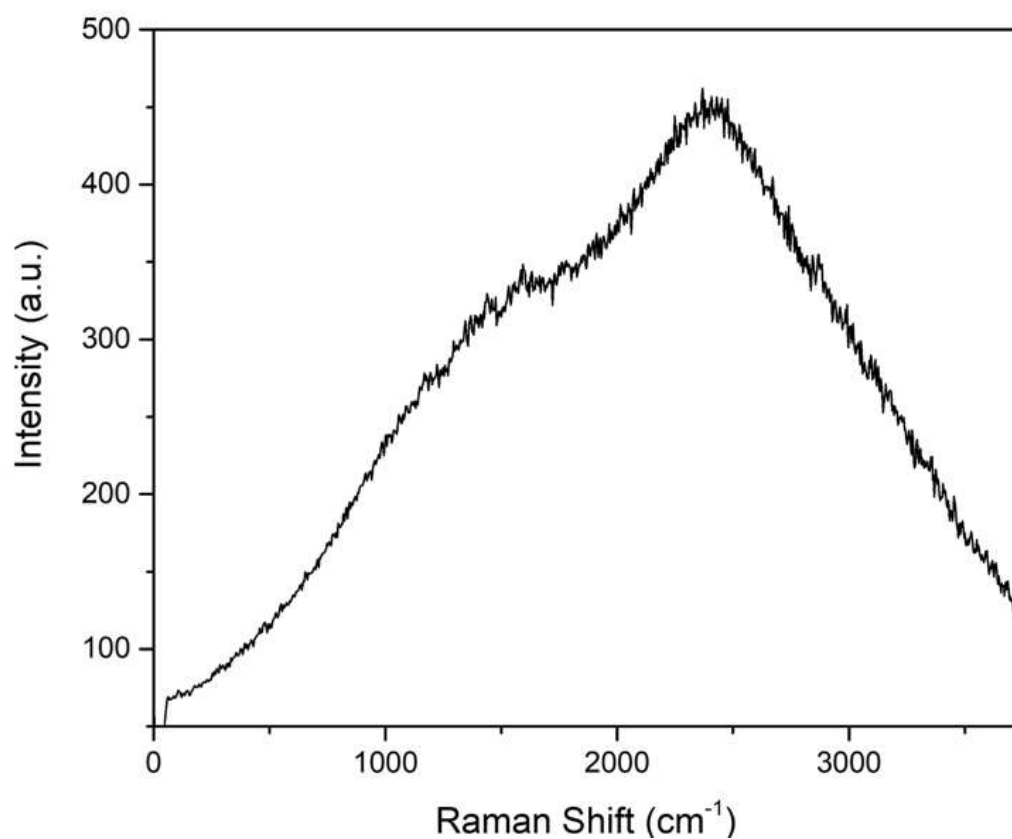


*Figure A10: Raman spectrum for pure nickel foam, carried out using a 532 nm excitation source at 1 mW with 600 lines/mm spectral gratings.*

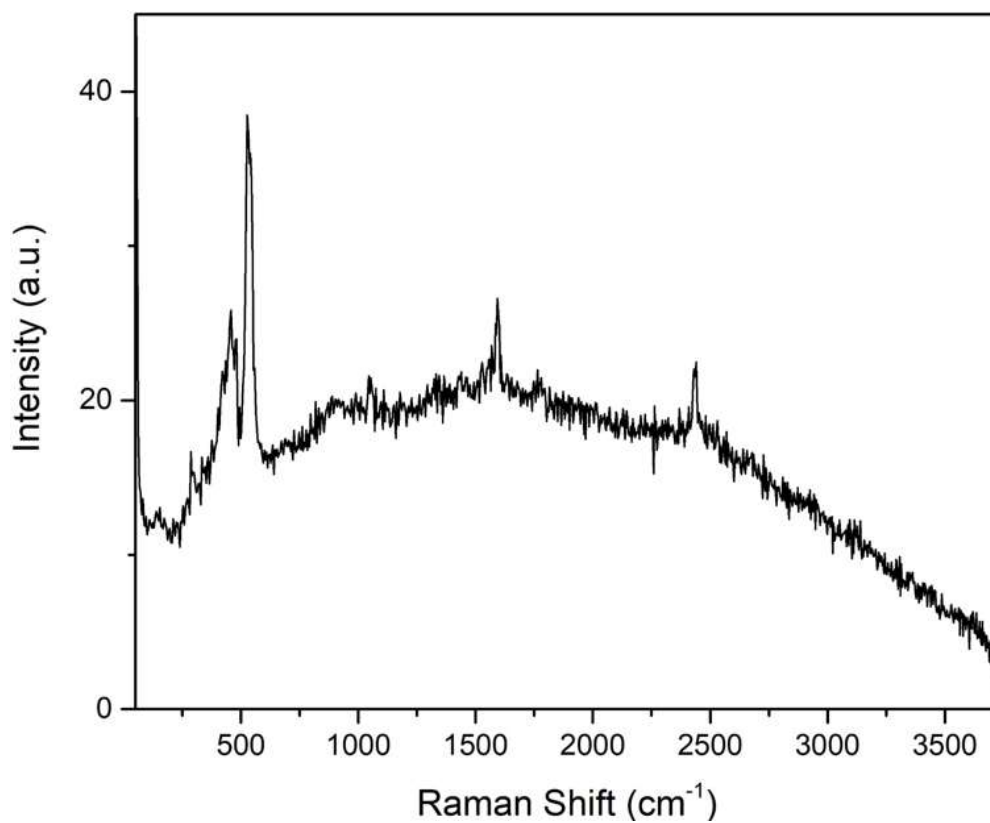


*Figure A11: Raman spectrum acquired for pre-cycled sr-NiFe LDH on Ni foam using a 532 nm excitation source at 1 mW with 600 lines/mm spectral gratings.*

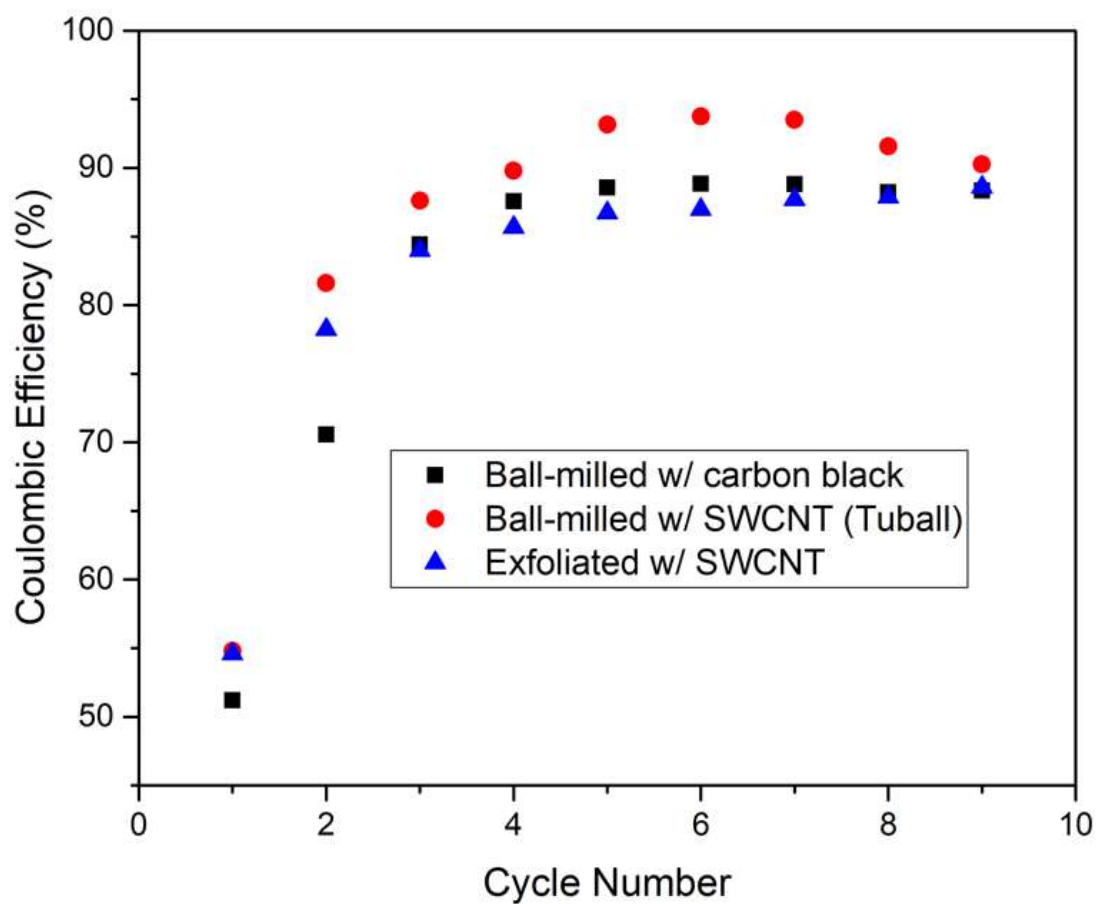


Figure A12: Coulombic efficiencies with cycling for commercial PbO composite anodes produced with different processing steps.

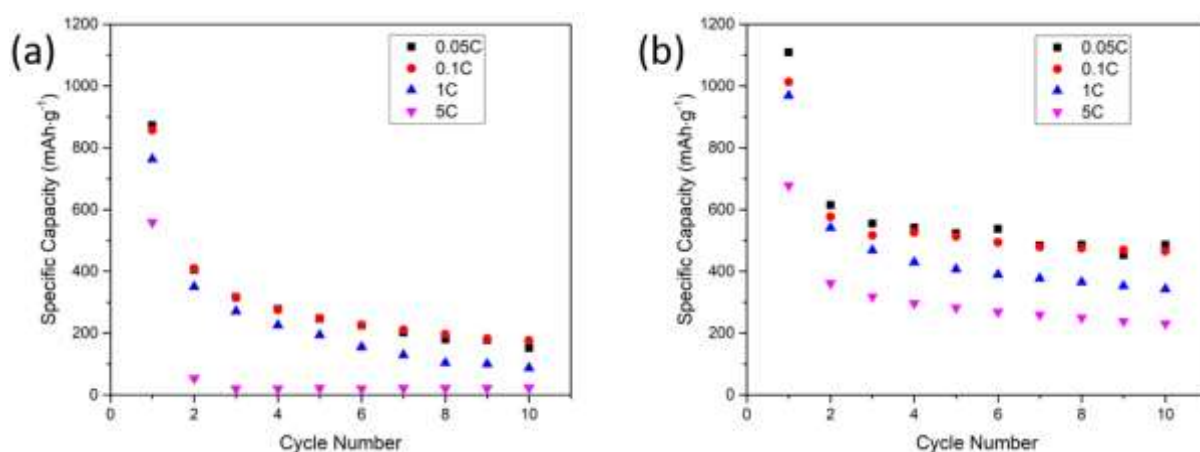


Figure A13: Specific discharge capacity cycling graphs for (a) 5 wt% and (b) 30 wt% SWCNT at various discharge rates.

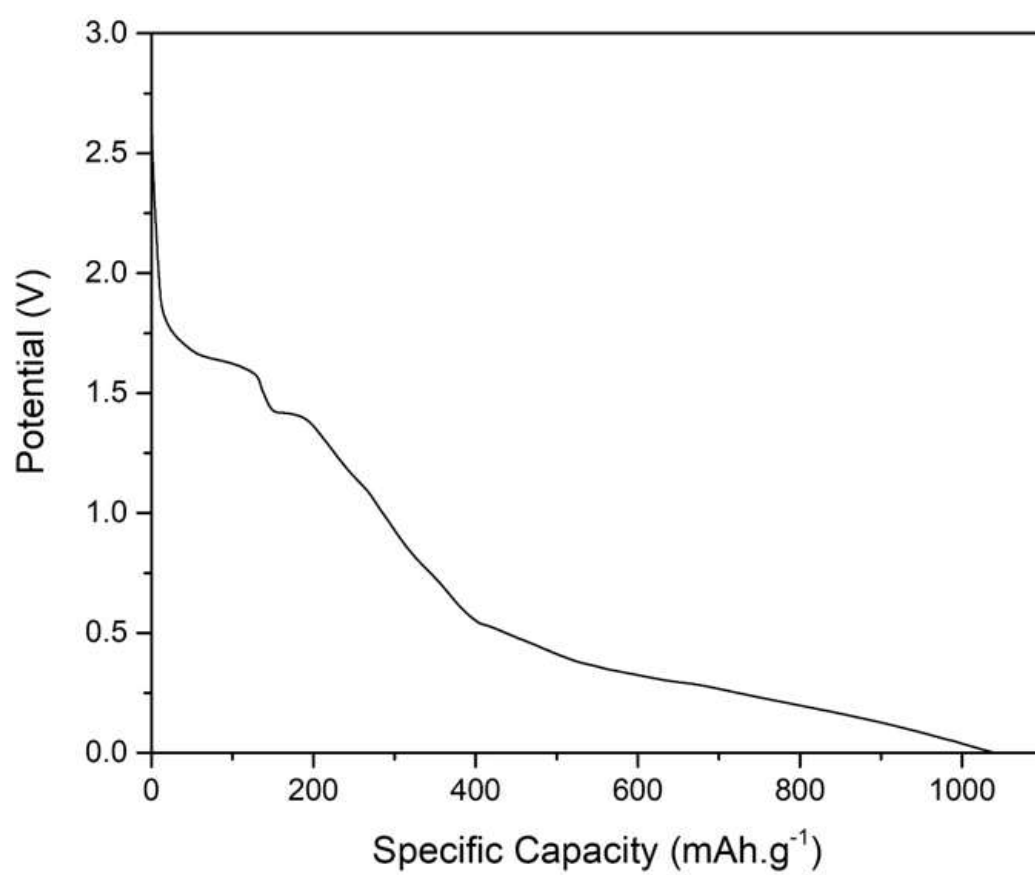


*Figure A14: GCPL initial discharge at 0.1 C for exfoliated commercial PbO with 25 wt% SWCNT.*

## Appendix B: Error and Uncertainty Analysis

Uncertainties were considered throughout the thesis where appropriate and included in the data analysis. For the most part, errors were calculated as an accumulation of systematic instrument values as well as those introduced by human error. One example of human error in the research arises from the measuring of mean platelet lateral dimensions  $\langle L \rangle$  from measuring individual platelets of SEM-acquired images. The accuracy with which individual flakes were measured was determined as follows. For each sample where  $\langle L \rangle$  is calculated, a sample set of 10 particles of all sizes is taken and measured repeatedly 5 times each. Then, the standard deviation of the 5 measurements are taken and finally, the standard deviations for each of the 10 particles are averaged and rounded to the decimal places of the accuracy of the measurements (0.001  $\mu\text{m}$  in most cases). The value for  $\langle L \rangle$  in consecutive sediments will be expected to decrease sequentially to the smallest value in the final sediment.

Once individually established, the propagation of errors in the data were calculated using the Gaussian distribution model with uncertainty values treated as standard deviations from the mean. For example, the propagation of errors from two variables added together ( $a + b$ ) to give a product ( $p$ ) is treated as in Equation 7.1 (a), where  $\varepsilon$  represents the respective error values, and more generally in (b) for  $n$  total individual variables  $i$ .

$$\varepsilon_p = \sqrt{\varepsilon_a^2 + \varepsilon_b^2} \quad \text{Equation 7.1 (a)}$$

$$\varepsilon_p = \sqrt{\sum_{i=1}^n \varepsilon_i^2} \quad \text{Equation 7.1 (b)}$$

Error propagation looks slightly different when variables are multiplied/divided by one another. Once again, the two-variable specific and general versions of the uncertainty equations are given in Equation 7.2 (a) and (b) respectively, where  $p$  is the value of the product.

$$\varepsilon_p = p \sqrt{\left(\frac{\varepsilon_a}{a}\right)^2 + \left(\frac{\varepsilon_b}{b}\right)^2} \quad \text{Equation 7.2 (a)}$$

$$\varepsilon_p = p \sqrt{\sum_{i=1}^n \left( \frac{\varepsilon_i}{i} \right)^2} \quad \text{Equation 7.2 (b)}$$

## Appendix C: Electrochemical Surface Area Analysis

ECSA analysis can be performed by analysing electrochemically induced currents in the non-faradaic, OER inactive potential regions of a material to determine its active surface area. The currents induced in such regions result in electrochemical charging of the material across a double layer at the surface. The associated double-layer capacitance ( $C_{DL}$ ) has a distinct reliance on the charging current ( $i_c$ ) as demonstrated in Equation 7.3, where  $v$  is the scan rate in  $\text{mV}\cdot\text{s}^{-1}$ .<sup>196, 197</sup>

$$i_c = vC_{DL} \quad \text{Equation 7.3}$$

By cycling the active material within an appropriate potential range at sequentially higher scan rates, one can determine the materials  $C_{DL}$  value from the slope of the curve. The final value is taken as the average of the capacitances calculated using cathodic and anodic currents. From there, one can use the relationship between ECSA and the ratio between double-layer and specific capacitances (Equation 7.4) to estimate the active surface area.<sup>198</sup>

$$ECSA = \frac{C_{DL}}{C_s} \quad \text{Equation 7.4}$$

The specific capacitance ( $C_s$ ) is an ‘ideal’ value of the capacitance on an atomically smooth surface of the active material. It is not always practical to directly determine this value for a catalyst in a particular system so one generally relies on indexed values which are well reported for various catalysts in alkaline and acidic environments.<sup>199</sup> A value of  $C_s = 0.04 \text{ mF}\cdot\text{cm}^{-2}$  was used for NiFe LDH catalysts in 1 M KOH for this work.<sup>39</sup>

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