



UNIVERSITY OF
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Investigating the Electrochemistry of
Critical Metals on Carbon Black by
Nano-Impact Techniques

by

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Abstract

Our transition towards net zero emissions has necessitated the increased demand for critical metals such as manganese, nickel and ruthenium for use in batteries and other renewable technologies. The finite nature of these metals, coupled with the negative environmental and social impact of primary extraction methods, has led to the growing need for sustainable recovery techniques from secondary sources. Inefficiencies in primary extraction and metal recovery from secondary sources leads to the generation low-concentration metal waste streams. However, current recovery methods such as chemical precipitation, absorption and ion exchange are not suited to such low concentrations, often requiring costly pre-concentration steps. On the other hand, electrochemical methods, appear more well-suited due to their higher selectivity and energy efficiency. In particular, nano-impact electrochemistry has recently emerged as a promising recovery method for low-concentration solutions with the added advantage of higher rate of mass transport to the nanoparticles.

This thesis explores the use of nano-impact electrochemistry as a potential method for recovering manganese, ruthenium and nickel from low-concentration solutions (0.5 – 1 mM) using inexpensive carbon black nanoparticle cores. Firstly, the electroreduction and electrooxidation of Mn(II) from 0.5 mM manganese sulfate and 20 mM potassium sulfate was investigated. Reductive impacts were observed in the presence of 5 pM carbon black and the deposition product was confirmed to be Mn(0) via scanning electron microscopy/ energy dispersive x-ray spectroscopy (SEM/EDX). Oxidative impacts were also observed in the presence in 5 pM carbon black and the deposition product was confirmed to be MnO₂ and various other intermediate products via SEM/EDX and X-ray photoelectron spectroscopy (XPS).

Next, the electroreduction and electrooxidation of ruthenium from 1 mM ruthenium(III) chloride and 10 mM hydrochloric acid and 10 mM potassium chloride was studied. Impact electrochemistry was conducted and in the presence of 25 pM carbon black, reductive and oxidative impacts were recorded for the two respective processes. A long-term upscaled impact experiment for the reductive process yielded Ru-modified carbon black which were characterised via SEM/EDX, XPS and thermogravimetric analysis (TGA). Under partially-optimised conditions, >90% of ruthenium was recovered in ca. 8 hours.

Finally, the electroreduction of nickel was studied from two electrolytes: 0.5 mM nickel(II) sulfate or nickel(II) chloride with the corresponding ammonium electrolyte. Reductive impacts were observed in the presence of 20 pM carbon black for both electrolytes. Upscaled long-term impact experiments were conducted and low-level nickel deposits were confirmed via SEM/EDX and inductively coupled plasmon/ mass spectrometry (ICP-MS).

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List of Abbreviations

AgNPs	Silver nanoparticles
CBNPs	Carbon black nanoparticles
CE	Counter electrode
CF	Carbon fibre
CRM	Critical Raw Material
CV	Cyclic Voltammetry/ Voltammogram
DES	Deep Eutectic Solvents
DVLO	Deraguin Landau Varwey Overbeek
EDL	Electric Double Layer
EDTA	Ethylenediaminetetraacetic acid
EU	European Union
E-waste	Electronic waste
GC	Glassy carbon
HBA	Hydrogen Bond Donor
HBD	Hydrogen Bond Acceptor
ICP-MS	Inductively-Coupled Mass Spectrometry
IHP	Inner Helmholtz Plane
ILs	Ionic Liquids
LSV	Linear-Sweep Voltammetry
NIE	Nano-Impact Electrochemistry
NO _x	Nitrous Oxide
NP	Nanoparticle
OHP	Outer Helmholtz Plane
RE	Reference electrode
SCE	Standard Calomel Electrode
SEE	Single-entity electrochemistry
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SRM	Strategic Raw Materials
UV	Ultraviolet
UV/Vis	Ultraviolet Visible Light Spectroscopy
WE	Working electrode
XPS	X-ray Photoelectron Spectroscopy

Contents

1. Introduction.....	1
1.1 Critical Metals	1
1.1.1 Primary Sources of Critical Metals.....	2
1.1.2 Secondary Sources of Metals	4
1.2 Current Methods of Metal Recovery	6
1.2.1 Pyrometallurgy.....	6
1.2.2 Hydrometallurgy.....	8
1.2.2.1 Ionometallurgy.....	10
1.2.2.2 Bio-hydrometallurgy.....	12
1.2.3 Electrochemical Metal Recovery.....	14
1.3 Fundamentals of Electrodeposition.....	15
1.3.1 Nucleation.....	17
1.4 Electrochemistry Principles	19
1.4.1 Structure of the Double Layer	19
1.4.1.1 Helmholtz Model.....	20
1.4.1.2 Gouy-Chapman Model	22
1.4.1.3 Stern Model	23
1.4.1.4 Grahame Model.....	24
1.4.2 Faradaic and Non-Faradaic Processes	25

1.4.3 Mass Transport.....	26
1.4.3.1 Diffusion	26
1.4.3.2 Convection	27
1.4.3.3 Migration.....	27
1.4.4 Electrochemical Cell	29
1.4.5 Nernst Equation	30
1.4.6. Electrochemical Techniques	32
1.4.6.1 Cyclic Voltammetry	32
1.4.6.2 Linear Sweep Voltammetry	34
1.4.6.3 Reversible and Irreversible Behaviour	34
1.4.6.4 Chronoamperometry.....	36
1.4.7. Microelectrodes	37
1.4.7.1 Micro-arrays.....	40
1.4.8 Kinetics	42
1.5 Nano-Impact Electrochemistry	44
1.5.1 Direct Impacts.....	45
1.5.2 Indirect Impacts	46
1.5.2.1 Electrocatalysis Applications	46
1.5.2.2 Nanomaterial Fabrication via Impacts	47
1.5.3 Experimental Set-up and Limitations	48
1.6 Aims and Objectives	50

1.7	References.....	52
2.	Experimental	60
2.1	Materials and Solution Preparation	60
2.1.1	DLS of CB nanoparticles.....	60
2.2	Electrochemistry	60
2.2.1	Working Electrodes.....	61
2.2.1.1	Fabrication of Carbon Fibre Microelectrodes.....	61
2.2.1.2	Fabrication of Graphite Plate Electrodes	61
2.2.1.3	CB-modified GC Voltammetry	62
2.2.2	Nano-Impact Electrochemistry.....	62
2.2.2.1	Analysis of Impact Electrochemical Data.....	62
2.2.2.2	Long-Term Impact Experiment	63
2.3	Material Characterisation of metal-modified CB nanoparticles.....	63
2.3.1	SEM/EDX.....	63
2.3.2	TGA	63
2.3.3	ICP/MS	64
2.3.4	XPS	64
2.4	References.....	64
3.	Redox Electrochemistry of Mn(II) via Carbon Black Nanoparticle Impacts.....	65
3.1	Abstract.....	65
3.2	Introduction	65

3.3 Experimental	68
3.4 Results and Discussion.....	70
3.4.1 Nano-Impact Experiments	76
3.5 Conclusions	88
3.6 References.....	89
4. Electrochemical Recovery of Ruthenium via Carbon Black Nano-Impacts	95
4.1 Abstract.....	95
4.2 Introduction	95
4.3 Experimental	98
4.3.1 Chemicals.....	98
4.3.2. Electrochemistry	98
4.3.3 Characterisation of Carbon Black and Ru-modified CB	100
4.3.4. Recovery Experiment	101
4.4 Results and Discussion.....	102
4.4.1 Nano-Impact Experiment	109
4.4.2 Ruthenium Recovery from Low Concentration of RuCl_3	117
4.5 Conclusions	122
4.6 References.....	122
5. Electroreduction of Nickel on Carbon Black via Nano-Impact Electrochemistry in Ammonium Sulfate and Chloride Electrolytes	127
5.1 Abstract.....	127
6.2 Introduction	127

5.3 Experimental	129
5.4 Results and Discussion.....	131
5.4 Nano-Impact Experiments.....	138
5.4.1 Long-Term Impact Experiment	142
5.5 Conclusions	145
5.6 References.....	146
6. Conclusions.....	149
6.1 Future Work	151

List of Figures

Figure 1.1: Eutectic formation in a two component phase diagram, adapted from²⁸.

Figure 1.2: Scheme for the mechanism of formation of metal deposits on an electrode, adapted from literature.⁶⁰

Figure 1.3: Schematic of the Helmholtz model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

Figure 1.4: Schematic of the Gouy-Chapman model of the electrical double layer showing the potential drop across the electrode/ solution interface as a function of the D , the distance from the electrode surface, adapted from⁶².

Figure 1.5: Schematic of the Stern model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

Figure 1.6: Schematic of the Grahame model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

Figure 1.7: Three-electrode cell consisting of a working electrode (WE), counter electrode (CE) and reference electrode (RE). The solution is degassed with a nitrogen stream.

Figure 1.8. A) Applied potential as a function of time for a generic cyclic voltammetry experiment, adapted from⁶⁷. B) Cyclic voltammogram showing the reversible reduction of a 5 mM ruthenium hexamine trichloride and 0.1 M solution, at a scan rate of 100 mV s^{-1} .

Figure 1.9. A) Applied potential as a function of time for a linear voltammetry. **B)** Simulated linear sweep voltammogram for a 3mm working electrode.

Figure 1.10. A) Potential-time profile for a chronoamperometry experiment. **B)** Typical chronoamperogram as a function of current over time at a planar macroelectrode.

Figure 1.11: Planar and spherical diffusion to an electrode, where r_e is the radius. Arrows represent the electroactive species diffusing to the electrode. A) Large macro electrode where

planar diffusion dominates. B), C) Progressively smaller microelectrodes where planar diffusion no longer dominates and D) Diffusion to a spherical electrode.

Figure 1.12: Simulated LSV for a 9 μm working microelectrode.

Figure 1.13: Four categories (A-D) of diffusion profile which a sphere on a plane in a micro-array arrangement may belong to.

Figure 1.14: Free energy plot for a simple one-electron of a species O(aq) .

Figure 3.1: Cyclic voltammograms (—) conducted in 20 mM K_2SO_4 and (---) conducted in 20 mM K_2SO_4 and 0.5 mM MnSO_4 , respectively, for (A) reductive scans and (B) oxidative scans. Both CVs were recorded using a bare 33 μm carbon fibre working electrode at a scan rate of 100 mV s^{-1} . A dashed red line (---) is used to indicate the onset potential at $\pm 5.0 \text{ pA}$.

Figure 3.2. Graphs showing (A) the average Mn/CB ratio based on weight percent obtained via SEM/ EDX analysis at $2000\times$ for GC tips removed from the post-chronoamperometric solution (containing 10 mM MnSO_4 and 20 mM K_2SO_4) across various potentials and (B) the integrated charge (Q / mC) from the respective chronoamperograms.

Figure 3.3. A) Photograph of a GC electrode with an electrodeposited Mn film (chronoamperogram conducted at -1.6 V vs SCE). B) SEM image at a magnification factor of 2000 of the deposited film. C) Photograph of a GC electrode with an electrodeposited Mn film (chronoamperogram conducted at $+1 \text{ V vs SCE}$). D) SEM image at a magnification factor of 2000 of the deposited film.

Figure 3.4. (A) Representative 30 s chronoamperogram conducted in a solution containing 0.5 mM MnSO_4 and 20 mM K_2SO_4 solution with a 9 μm CF electrode held at -1.6 V vs SCE before (i) and after (ii) the addition of 5 pM carbon black nanoparticles with an inset example of two zoomed in different impacts indicating different particle-electrode interactions. (B) Integrated charge (Q / fC) from impact events from -1.4 to -1.6 V vs SCE with bracketed

numbers indicating the number of impacts analysed at the respective potential. (C) Calculated coverage of manganese on carbon black. and 0.5 mM MnSO_4 with the addition of 500 pM carbon black nanoparticles.

Figure 3.5 A shows a representative 30 s chronoamperogram conducted in a solution containing 0.5 mM MnSO_4 and 20 mM K_2SO_4 with a 9 μm CF electrode held at +0.90 V vs SCE before (i) and after (ii) the addition of 5 pM carbon black nanoparticles with an inset of different zoomed in impact events. Figure 4B shows the integrated charge (Q / fC) from impact events ranging from a potential of +0.40 to +0.90 V vs SCE.

Figure 3.6 shows an SEM image of modified CB particles at a magnification factor of A) 40 and B) 1200. The chronoamperometry scan was conducted at -1.6 V vs SCE.

Figure 3.7 shows the EDX mapping of the modified CB particles deposited at -1.6 V vs SCE.

Figure 3.8: SEM image of Mn/CB deposited at +0.5 V vs SCE.

Figure 3.9: EDX Mapping of electrodeposited Mn oxide on graphite plate electrode held at +0.7 V vs SCE.

Figure 3.10: Raman spectrum of i) the unmodified graphite plate electrode and ii) the graphite plate electrode with electrodeposited Mn species.

Figure 3.11 shows the XPS spectra of 0.5 V vs SCE modified CBNP consisting of A) High resolution Mn 2p XPS spectrum with cumulative peak fit shown in grey. Core level $2p_{3/2}$ peak fitting for Mn(III) shown in (—) and (—) for Mn(IV) with their corresponding satellite peaks shown in (—) and (—) respectively. Core level $2p_{1/2}$ peak fitting for Mn(III) shown in (—) and (—)

Figure 3.12 A) Peak fitting for Mn(III), B) peak fitting for Mn(IV) and C) peak fitting for Mn(III) and Mn(IV) with the absence of satellite peaks.

Figure 4.1 (A) Reductive segment of a cyclic voltammogram performed using an unmodified GC electrode (—) in 10 mM KCl and 10 mM HCl as a control and with the addition of 1 mM

RuCl_3 for the unmodified GC electrode (---) and drop cast CB-modified GC electrode (•••) showing ruthenium reduction. (B) Anodic segment of CV performed using an unmodified GC electrode (—) in 20 mM KCl as a control experiment and with the addition of 1 mM RuCl_3 for the unmodified GC electrode (---).

Figure 4.2: Reductive CV segment conducted using a 3 mm GC working electrode in a solution containing 1 mM RuCl_3 , 20 mM KCl and 0.1 M K_2HPO_4 / 0.1 M KH_2PO_4 buffer solution.

Figure 4.3: Variance of scan rate for CVs conducted using a bare GC electrode in a solution containing 1 mM RuCl_3 and 20 mM KCl.

Figure 4.4: Logarithmic plot of peak current vs scan rate for oxidation peak where $\log_{10}(I) = 0.88\log_{10}(v) - 7.30$ and $R^2 = 0.96$.

Figure 4.5 (A) shows a representative chronoamperogram performed by holding a 9 μm CF microelectrode at -0.5 V vs SCE in a solution containing 1 mM RuCl_3 , 10 mM KCl and 10 mM HCl with and without the presence of 25 pM CB NPs. (B) shows an enlarged impact event at 1.535 s. (C) is a plot of the average charge passed per impact event (Q/fC), and (D) is a plot of the corresponding coverage of ruthenium on carbon black equivalent to a monolayer. Error bars represent the standard deviation of replicate measurements at each applied potential.

Figure 4.6. (A) shows a representative chronoamperogram performed by holding a 9 μm CF microelectrode at 0.5 V vs SCE in a solution containing 1 mM RuCl_3 and 20 mM KCl with and without the presence of 25 pM CB. **(B)** shows a plot of charge passed for impact (Q/pC) vs potential. Error bars represent the standard deviation of replicate measurements at each applied potential.

Figure 4.7: SEM/EDX Analysis of Ru-modified CB NP (-0.5 V vs SCE).

Figure 4.8: TGA thermogram of the 5 hr Ru-modified carbon nanoparticles.

Figure 4.9. (A) High resolution Ru3p XPS spectra of -0.5 V vs SCE modified CB particles showing the core level fitting for RuO₂ in blue and red lines. (B) Wide XPS scan of Ru-modified CB nanoparticles.

Figure 4.10. (A) Calibration curve at 320 nm. (B) Representative UV/Vis spectrum for RuCl₃(aq) solution.

Figure 4.11: UV/Vis spectrum of [Ru(H₂O)₆]³⁺ redrawn from Cady and Connick.⁴⁸

Figure 4.12: UV/Vis spectrum of [RuCl(H₂O)₅]²⁺ redrawn from Cady and Connick.⁴⁸

Figure 4.13: UV/Vis spectrum of [RuCl₂(H₂O)₄]⁺ redrawn from Fine⁴⁹ showing the cis-isomer (yellow) and trans-isomer (green).

Figure 4.14: UV/Vis spectrum of [RuCl₃(H₂O)₃] redrawn from Fine⁴⁹ showing the mer-isomer (orange) and fac-isomer (purple).

Figure 4.15: Percentage of Ru recovered (%) from solution using (A) 2.5 nM, (B) 5 nM and (C) 10 nM carbon black nanoparticles for 1, 2 and 3 L min⁻¹ nitrogen flow rates. Error bars represent the percentage uncertainty due to the y-intercept of the calibration curve.

Figure 5.1: Reductive segments of cyclic voltammograms performed using a 3 mm diameter unmodified GC electrode in (---) 20 mM (NH₄)₂SO₄ and (—) with the addition of 0.5 mM NiSO₄ solution at a voltage scan rate of 100 mV s⁻¹. Figure 1B: Reductive segments of cyclic voltammograms performed using a 3 mm diameter unmodified GC electrode in (---) 20 mM NH₄Cl and (—) with the addition of 0.5 mM NiCl₂ solution at a voltage scan rate of 100 mV s⁻¹.

Figure 5.2 A) Variance of scan rate vs peak current conducted in a solution containing 0.5 mM NiSO₄ and 20 mM (NH₄)₂SO₄. B) Logarithmic plot of peak current vs scan rate where the equation of the line is $\log_{10}(I) = 0.76\log_{10}(v) + 1.40$ and $R^2 = 0.99$.

Figure 5.3 A) Variance of scan rate vs peak current conducted in a solution containing 0.5 mM NiCl₂ and 20 mM NH₄Cl. B) Logarithmic plot of peak current for first reductive peak vs scan rate where the equation of the line is $\log_{10}(I) = 0.74\log_{10}(v) + 0.45$ and $R^2 = 0.99$ C)

Logarithmic plot of peak current for first reductive peak vs scan rate where the equation of the line is $\log_{10}(I) = 0.87\log_{10}(v) - 4.75$ and $R^2 = 0.99$.

Figure 5.4 A) Representative chronoamperogram by holding a 9 μm CF microelectrode at -0.7 V vs SCE in a solution containing 0.5 mM NiSO_4 and 20 mM $(\text{NH}_4)_2\text{SO}_4$ with i) and without ii) the addition of carbon black (20 pM) with an inset of a zoomed in impact. B) Charge passed (Q / fC) for impacts events with the number of peaks analysed indicated in brackets. C) The corresponding coverage of Ni on CB relative to a monolayer.

Figure 5.5 A) Representative chronoamperogram by holding a 9 μm CF microelectrode at -0.5 V vs SCE in a solution containing 0.5 mM NiCl_2 and 20 mM NH_4Cl with i) and without ii) the addition of carbon black (20 pM) with an inset of a zoomed in impact. B) Charge passed (Q / fC) vs potential, with the number of peaks analysed indicated in brackets. C) Corresponding coverage of Ni on CB relative to a monolayer calculated from charge passed per impact (Q / fC).

Figure 5.6: SEM images of A) Impacted CB NPs from NiSO_4 at -0.9 V vs SCE and B) Impacted CB NPs from NiCl_2 at -0.9 V vs SCE.

Figure 5.7: A) SEM image of impacted CB NPs from NiSO_4 at -0.9 V vs SCE, B) and C) Carbon and nickel EDX mapping of the particles, respectively. D) SEM image of impacted CB NPs from NiCl_2 at -0.9 V vs SCE, E) and F) Carbon and nickel EDX mapping of the particles, respectively.

Figure 5.8: A) Graphite plate electrode held at -0.9 V vs SCE in a solution containing NiSO_4 and $(\text{NH}_4)_2\text{SO}_4$. B) Graphite plate electrode held at -0.9 V vs SCE in a solution containing NiCl_2 and NH_4Cl .

List of Tables

Table 1.1: 2023 List of Critical Raw Materials for the EU, adapted from.¹

Table 3.1: Standard electrode potentials, standard free energies, and Gibbs energy at 298 K, pH 7.

Table 3.2 shows the manganese content for unmodified CB nanoparticles, the sample held at -1.6 V, +0.5 V, and +0.7 V vs SCE during chronoamperometry.

Table 3.3: Raman Shift values obtained from spectrum in Figure 3.10 compared to literature values for α -MnO₂, β -MnO₂, γ -MnO₂ and MnOOH. Assignment of shifts are given in the text.

Table 4.1: Calculated Equilibrium Concentrations of 1 mM RuCl₃ in 10 mM KCl and 10 mM HCl.

Table 4.2: Aqueous equilibria and their corresponding standard potentials.

Table 4.3: Parameters used for the irreversible Randles- Sèvčík equation.

Table 4.4: Estimated peak currents for both processes.

Table 4.5: Parameters used for the sphere on a plane calculation.

Table 4.6: Expected peak heights of impact spike for different electron-reduction processes.

Table 4.7: SEM Image of agglomerated CBNP obtained from chronoamperogram performed at -0.5 V vs SCE in a solution containing 500 pM CB NP, 1 mM RuCl₃, 10 mM KCl and 10 mM HCl to the left. The table displays the ruthenium content determined by SEM/EDX and TGA analysis for the unmodified CB NP and sample held at -0.5 V vs SCE.

Table 5.1: Parameters used to calculate the peak current for NiSO₄ and NiCl₂ reduction processes.

Table 5.2: Parameters used to calculate the peak current for NiSO₄ and NiCl₂ reduction processes.

Table 5.3: *Calculated equilibria concentrations for 0.5 mM NiCl₂ and 20 mM NH₄Cl solution*

Table 5.4: *SEM/EDX and ICP-MS characterisation of unmodified and impact modified CB NP.*

List of Publications

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Chapter 4: M.E. Keal, L. Clewlow, E. Roberts, N. V. Rees, *Electrochim. Acta*, 2024, **507**, 145185.

1. INTRODUCTION

1.1 Critical Metals

The global rise in metal consumption is being driven by a growing population, the transition to renewable energy technologies, and the expanding demand for infrastructure development, all of which necessitate significant amounts of metals. Metals possess attractive physical and chemical properties such as electrical conductivity, malleability, corrosion resistance, variable oxidation states and high catalytic activity. Metals are naturally occurring finite resources with varying levels of abundance and accessibility, extracted through mining and ore processing.

Recognising the importance and challenges associated with metal supply, the European commission periodically publishes a list of critical raw materials every three years, with the most recent list from 2023 provided in Table 1.1.¹ This list comprises 34 critical raw materials (CRMs) in addition to 17 strategic raw materials (SRMs). Critical raw materials (CRMs) are defined by two main criteria. Firstly, the economic importance of the metal is considered in terms of the end-use applications and value added. The second criterion is related to the supply risk which is the likelihood of a disruption in the European Union's (EU's) supply of a material, dependent on both the concentration of the primary supply and the EU's reliance on imports. While manganese and nickel are highlighted as SRMs which are essential in the production of strategic products related to the green energy transition, digital technology and defence, they do not meet the thresholds for CRMs. Meanwhile, ruthenium, one of the platinum group metals, is classified as a CRM.

Table 1.1: 2023 List of Critical Raw Materials for the EU, adapted from.¹

2023 Critical Raw Materials		2023 Strategic Raw Materials	
Aluminium/ bauxite	Helium	Bismuth	Magnesium
Antimony	Niobium	Boron	Manganese
Arsenic	Phosphate rock	Cobalt	Natural graphite
Baryte	Phosphorus	Copper	Nickel
Beryllium	Scandium	Gallium	Silicon metal
Coking coal	Strontium	Germanium	Titanium metal
Feldspar	Tantalum	HREE	Tungsten
Fluorspar	Vanadium	Lithium	
Hafnium	Platinum group metals	LREE	

1.1.1 Primary Sources of Critical Metals

Mining CRMs and SRMs involves the extraction of valuable minerals and metals from the earth, a process that significantly impacts both the environment and human communities. Environmentally, mining operations can lead to deforestation, soil erosion, and contamination of water sources with heavy metals and chemicals used in extraction processes.^{2,3} This pollution can harm local ecosystems, affecting plant and animal life. Additionally, mining contributes to air pollution through the release of dust and emissions from machinery. On a social level, mining can disrupt local communities, often leading to displacement and adverse health effects due to exposure to pollutants⁴ however, it can also provide the local community with employment opportunities and contribute to the local economy. While mining is crucial for obtaining materials essential for modern technology and infrastructure, its environmental and social costs necessitate the development and implementation of more sustainable and responsible mining practices. The follow section covers mining

practices specific to the three metals investigated in this thesis: manganese, nickel and ruthenium.

Manganese is the 12th most abundant metal in the Earth's crust amounting to approximately 0.1 wt%. Its primary uses lie in steelmaking and batteries. Its principal ore is pyrolusite (MnO_2), however it exists as further ores such as braunite (a manganese silicate), psilomelane (a manganese oxide) and rhodochrosite (MnCO_3). Extraction occurs primarily in South Africa, accounting for 29% of global extraction, followed by Australia (16%), Gabon (14%), China (9%) and Ghana (6%).⁵ Many other countries are heavily reliant on imports for manganese; for example, the EU sources 97% of its supply from external producers.⁵

Nickel also has uses predominantly in batteries and steelmaking. It occurs mainly in geological environments of magmatic sulfides and in laterites. These mines are geographically limited to Indonesia and the Philippines accounting for 26% and 14% of the production of nickel ores globally with further ores produced in Russia (10%) and New Caledonia (9%).⁶ This, again, means many other countries, such as the UK and those in the EU, are heavily reliant on imports of nickel.

The demand for manganese and nickel is expected to rise dramatically in the battery industry, due to the supply constraints and rising costs associated with other metal components such as cobalt. This could potentially lead to the substitution of cobalt with metals such as manganese and nickel. This increased demand coupled with the UK and EU's reliance on imports creates a significant supply risk. Furthermore, the energy intensive requirements for mining further necessitates the need for improved recycling processes for these two metals. At present, only ca. 9% of manganese is

recycled in the EU; whereas for nickel this recycling rate is slightly higher at 42% in the EU, perhaps owing to its higher market value.^{5,6}

Ruthenium is one of the platinum group metals (PGMs), which all have very similar chemical properties whilst their physical properties may vary. In general, they show high catalytic activity, very high resistance to corrosion and oxidation, very high melting point and excellent electrical conductivity. The mining activities of PGMs are concentrated in a few countries; in particular, ruthenium is mostly produced in South Africa accounting for 93.5% of global production.⁷ Ruthenium is primarily used in the electronics sector and chemical processes such as the production of nylon and the chlor-alkali process. Additionally, in the transition to green energy, ruthenium oxide catalysts are being increasingly used for green hydrogen production. The market price of ruthenium has risen significantly in the past ten years from \$72/troy oz (May 2014) to \$430/troy oz (May 2024) due to a sustained demand, constrained supply and increasing interest in this metal in both chemical and electrochemical processes.⁷ Thus, it is imperative to find sustainable recycling processes for this precious metal to meet future demand.

Due to the aforementioned issues with primary extraction of these metals, it is imperative to consider other more sustainable sources of metals such as secondary sources (e.g., e-waste).

1.1.2 Secondary Sources of Metals

Secondary sources of metals are derived from post-consumer products, scrap materials or waste, rather than being extracted directly from natural ore deposits. One significant source of secondary metals is electronic waste (e-waste) which includes discarded, surplus, obsolete or broken electrical and electronic appliances. E-waste

can be broadly divided into six main categories: temperature exchange equipment (e.g., refrigerators, air conditioners), screens and monitors (e.g., televisions, monitors, tablets), lamps, large equipment (e.g., washing machines, dishwashers), small equipment (e.g., kettles, toasters, radios) and small IT equipment (e.g., mobile phones, routers, printers).^{8,9}

According to a report published by the United Nations Institute for Training and Research, the world generated 62 billion kg of e-waste in 2022.⁹ However, only 13.8 billion kg of waste was formally collected and recycled globally in an environmentally sound manner.⁹ This significant gap between the waste generation and recycling rate highlights the need for more sustainable practices. Recovering metals from secondary sources such as e-waste is becoming increasingly important due to adverse environmental impacts of mining and concerns over the future stability of metal supply.

The composition of e-waste varies depending on the type of equipment but mainly consists of metals (50%) and plastics (20%), with the remainder being alloys, composite materials, glass and concrete.⁹ Among these metals, iron/steel, aluminium and copper are typically present in higher amounts, whereas precious metals such as gold, silver and platinum group metals are present in lower quantities but can still be viably recovered due to their high value.

Improper disposal and inadequate waste management of e-waste can have severe effects on the environment and economic consequences through the loss of high-value resources.^{8,9} Additionally, it can pose significant health and safety risks to operators and nearby inhabitants of recycling/ disposal sites. For example, when small electronic equipment is disposed of with normal household waste, they can end up incinerated or in landfill sites without proper recycling. These processes lead to

significant losses of high-value metals and the potential generation of harmful emissions. In high income well-developed countries, legislation is often in place to prevent such disposal of e-waste but this is not always the case in lower income countries. Furthermore, many high to middle income countries still export a significant volume of e-waste to lower income countries with inadequate waste management infrastructure, exacerbating the problem.

Both primary and secondary metal extraction processes generate waste solutions that contain low concentrations of critical or strategic raw materials. These low concentrations arise due to inefficiencies in mining and recycling processes. The main challenge lies with recovering metals from such waste solutions as currently used recovery techniques, such as pyrometallurgy and hydrometallurgy, are not effective for such low concentrations of metals, necessitating the need for costly pre-concentration steps.

1.2 Current Methods of Metal Recovery

1.2.1 Pyrometallurgy

Most metal recovery focuses on the use of metallurgy which, in simple terms, is the extraction metals from their ores and modifying the metals for use. Pyrometallurgy is one type of metallurgy used to recover both nonferrous and precious metals from electronic waste.¹⁰ The process typically involves heating the electronic waste to elevated temperatures ranging from 800 - 1200 °C to reduce/ extract metals in processes known as smelting, combustion and pyrolysis.¹⁰ Smelting is a traditional process used on an industrial scale to recover a range of metals. Both copper and lead smelting are used industrially but copper smelting is preferred due to environmental issues associated with the toxic fumes released from lead.¹¹

During smelting, Pb, Sn, Sb and other precious metals mix with the copper rich phase and this is cast into an anode.¹¹ The anode is further purified through electrorefining, in which copper from the anode dissolves in solution and deposits at the cathode.¹² The undissolved metals form an anodic slime which can be processed further to separate these metals using hydrometallurgical methods. Note, Fe and Al are not recovered, but are instead oxidised and collected in slag,¹² along with any other inorganic components. Due to the high temperatures used, any additional materials present such as polymers and other organics, which decompose at lower temperatures, are efficiently removed during the process or can be used as fuel.¹³

Despite the typically high yield of metals recovered from pyrometallurgy, some losses can occur when there is a high inorganic component present.¹⁴ As inorganic components usually end up in the slag, a large proportion of inorganics can lead to a high volume of slag.¹⁴ A larger slag volume can lead to losses of metals which is particularly problematic in the case of spent lithium-ion batteries, leading to losses of metals like Li, Mn and Al.¹⁴ Further disadvantages exist related to environmental concerns and the overall sustainability of the process. Due to the high temperatures required during smelting, the process is highly energy intensive resulting in high operational costs. Furthermore, harmful secondary pollutants such as sulfur dioxide, carbon dioxide and polybrominated dibenzo-p-dioxins and dibenzofurans are generated.¹⁵ These pollutants require specific treatment to avoid release to environment and can pose significant health risks to operators.

1.2.2 Hydrometallurgy

Hydrometallurgy is a further technique to extract metals from pre-treated electronic waste using chemical separation methods. It requires lower temperatures ranging from room temperature to 200 °C and therefore relatively modest energy requirements in comparison to pyrometallurgical methods.¹⁶ Typically, hydrometallurgical processes consist of two main steps: chemical leaching of the metals with lixiviants followed by subsequent extraction from the leachate via precipitation, solvent extraction, electrowinning and ion exchange.¹⁷ Chemical leaching is predominantly achieved with acids¹⁸ but complexing agents such as cyanide, thiourea, thiosulfate and halides (I, Br, Cl, F) are also utilised, dependent on the metal present. Other methods such as leaching with chelating agents like EDTA or etching with FeCl₂ or CuCl₂ have been investigated but are not commonly used in industry due to their poor economic viability.

For precious metal recovery, removal of any base metals like Cu is required to pre-concentrate the sample to improve selectivity while reducing contamination [18]. Acid leaching can then be carried out using reagents like sulfuric acid, hydrochloric acid and nitric acid. The ability of an acid to leach (dissolve) metal depends on both the strength and concentration of the acid. The electrochemical reduction potential of the metal can be a predictor of how easily it can be oxidised (dissolved) in solution. For instance, weak dilute acids can leach Zn (-0.74 V vs SHE for Zn²⁺/Zn) and Fe (-0.44 V vs SHE for Fe²⁺/Fe) but fail to leach Cu (+0.159 V vs SHE for Cu²⁺/Cu) and precious metals like Ag (+0.80 V vs SHE for Ag⁺/Ag) and Au due to their more positive reduction potentials.¹⁹

In order to leach precious metals such as Ag and Au, strong acids such as concentrated nitric acid and aqua regia, or weak acids, with the addition of oxidising agents (O₂, H₂O₂, Cl₂, Cu²⁺ and Fe³⁺) to improve the reaction kinetics, are required.

The corrosive and volatile nature of nitric acid and aqua regia make the use of these reagents unsuitable for industrial-scale reactors both from a practical and economic standpoint.¹⁷ Furthermore, these acids can present significant health risks to operators handling them, as well as the environmental issues such as the generation of NO_x emissions and acidic waste which must be treated properly before its release. In addition, aqua regia exhibits poor selectivity and will dissolve nearly all base and precious metals (e.g Cu, Pb, Zn, Ni, Au, Pt, Pd).

Alternative acids such as sulfuric acid, which is commonly used with H₂O₂, can be used but still suffer from issues relating to waste management and the requirement of relatively high concentrations, high pressure and longer leaching time for precious metals.²⁰

For this reason, many studies are suggesting a two-step process of leaching base metals such as Cu with inorganic acids under relatively mild conditions as the first step, followed by alternative lixiviants for precious metal recovery such as cyanide, thiourea, thiosulfate and halides.²¹ Historically, cyanide leaching has been utilised industrially for gold and silver recovery.¹⁸ However, thiourea and thiosulfate are preferable due to the toxic nature of cyanide. Recent studies have indicated recovery rates as high as 99% of Au are possible with thiourea.²² Ferric sulfate can be used as an oxidant in conjunction with thiourea for Au recovery.²³

Thiosulfate is another alternative to cyanide and benefits from lower environmental toxicity, lower corrosion rates, low cost and high selectivity.²⁴ However, due to its instability in an acidic medium, leaching must be conducted in a pH ranging from 9 to 10.5.²⁵ Compared to thiourea, the leaching rate is relatively slow but can be improved

with the addition of Cu^{2+} and ammonia, which form a complex that catalyses the leaching process.²⁶

1.2.2.1 Ionometallurgy

Ionometallurgy has emerged as a promising alternative to pyrometallurgy and hydrometallurgy offering enhanced efficiency, lower energy consumption, and reduced environmental impact compared to traditional methods. This is achieved through the selective extraction and processing of metals using Ionic Liquids (ILs) and Deep Eutectic Solvents (DES). In recent years, the research focus has shifted dramatically from ILs to DES due to their more cost-effective and straightforward synthesis, which involves mixing components in specific molar ratios.²⁷ DES are defined as a mixture of two or more compounds, a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), with a lower melting point than the individual components.²⁸ When the two components are mixed in a specific molar ratio, these components reach a eutectic point, as shown in Figure 1.1.²⁸

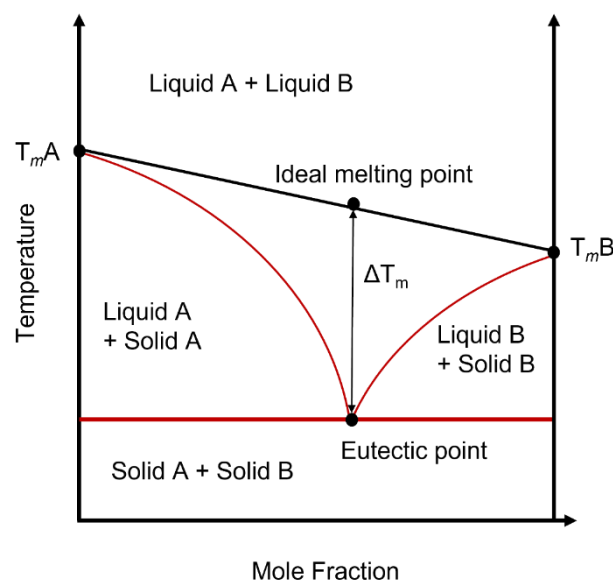


Figure 1.1: Eutectic formation in a two component phase diagram, adapted from²⁸.

DESs were first reported by Abbott *et al.* in 2003 with choline chloride and urea, although they were not specifically referred to as DES until later.²⁹ Since this seminal work, extensive studies have demonstrated the solubility of metal oxides,³⁰⁻³¹ metal sulfides and metal chalcogenides³² in DES and the separation of these complex mixtures via electrochemistry. Redox catalysts such as FeCl₂ and CuCl₂ in DES have also been shown to successfully dissolve metals directly from electrical waste such as printed circuit boards,³³ thermoelectric generators³⁴ and photovoltaic cells.³⁵ The electrochemistry of DES has the advantages of a wider potential window than aqueous systems, as well as avoiding the formation of passivating oxy- and hydroxy-compounds due to the absence of water.

Despite the promising applications of these solvents in the recovery of base and precious metals, several challenges need to be addressed before industrial-scale application is feasible. One of the main drawbacks of DES is the high viscosity of these solvents which can lead to poor mass transport and conductivity.³⁶ To mitigate this, water has been added to DES to improve mass transport^{37,38} and modify the double layer structure³⁹ although care must be taken as to not affect the metal speciation. Alternative methods to improve the mass transport of DESs, which avoid the undesired water chemistry, include the utilisation of forced convection such as ultrasound.³⁶⁻⁴⁰

Another obstacle is the cost of DES. While they are significantly cheaper than other ionic liquids, they remain relatively expensive compared to aqueous solvents.²⁸ Therefore, in order to be economically feasible, energy requirements and the need for chemical additives should be reduced to offset the cost of the solvent.

Additionally, although DES are often presented as “green” and environmentally benign, their environmental impact and safety should not be overlooked. Predicting

the ecotoxicity of DES is challenging due to the variability of the individual components, and some reports have raised concerns regarding the biodegradability and toxicity of DES mixtures.^{27,41,42}

Finally, due to this being a relatively new area of research, DES lack reference databases of metal speciation data and known reduction potentials making their electrochemical behaviour somewhat more challenging to predict. Some research, such as studies using techniques such as Extended X-ray Absorption Fine Structure (EXAFS), has provided insights into metal speciation^{43,44} but this remains limited due to the expense and accessibility of such techniques. Sometimes UV/Vis can be sufficient but this not always the case.

1.2.2.2 Bio-hydrometallurgy

Bio-hydrometallurgical metal recovery is a further greener alternative to pyrometallurgy and hydrometallurgy that can operate under mild conditions without the use of complex machinery, thus reducing process costs. Bio-hydrometallurgy, specifically bioleaching, utilises microorganisms to recover and purify metals from secondary waste sources in aqueous solutions. Various factors influence the recovery rate of metal such as the choice of microbe, pH, temperature, aeration and nutrients.

Generally speaking, bioleaching occurs via iron-oxidising and sulfur-oxidising microbes which naturally occur in the waters of former mine sites.⁴⁵ The metabolites of these two microbes, ferric ions (Fe^{3+}) and protons (via sulfuric acid), attack metal sulfides to aid their dissolution and release into solution. These processes are proposed to occur via two different pathways known as contact and non-contact leaching.

In contact leaching microbes attach themselves directly to the mineral surface and the dissolution of metal sulfides takes place at the interface between the mineral and microbes. This space is filled with an extracellular polymeric substance matrix containing polysaccharides, proteins, lipids and nucleic acids which both aids adhesion to the metal surface⁴⁶ and creates a favourable microenvironment that traps enzymes and ferric ions (Fe^{3+}) involved in the dissolution of the metal.⁴⁶⁻⁴⁸ Although, the exact mechanism of this process is still an active area of research.

Conversely, in non-contact bioleaching the microbes facilitate the generation of ferric ions and sulfuric acid which aid the dissolution of the metal. The mechanism of leaching depends on the leaching solution. It is also possible for these processes to occur concurrently in a further process known as cooperative leaching in which free-living microbes oxidise sulfur produced by microbes in contact with the metal.⁴⁵

This method is industrially applied to the primary extraction of low-grade metal sulfide ores. However, non-sulfide ores can also be treated with other microbes and fungi through the production of organic acids and complexing agents to attack and solubilise the metals respectively. These principles have been more recently applied to recovery of technology critical metals found in electronic waste such as printed circuit boards,^{49,50} lithium-ion batteries⁵¹ and photovoltaic cells⁵² but is still in the early stages of research.

Despite the lower environmental impact of bio-hydrometallurgy compared to other hydrometallurgical methods, its slow dissolution kinetics and therefore longer operational times remain somewhat undesirable.⁵³ However, as this process is fairly low-cost, it is more economically feasible for low-concentration waste solutions and low-grade ores than other metallurgical processes such as smelting with high

operational costs. Various attempts to accelerate leaching times have been applied such as the use of voltage to improve electron transfer reactions,⁵⁴ applying a weak magnetic field,⁵⁵ ultrasound⁵⁶ and ultraviolet (UV) light⁵⁷ to induce mutations with the bacteria. However, most of these attempts have had limited success with only UV light showing some improvement in the leaching times. Furthermore, there are some concerns with the toxic chemicals created with this process.

1.2.3 Electrochemical Metal Recovery

Electrochemical metal recovery encompasses several well-known techniques, namely, electroplating, electrowinning and electrorefining for both metal recycling and purification. These processes benefit from several advantages over the previously described recovery techniques. Firstly, unlike pyrometallurgical and hydrometallurgical techniques, such as high purity of recovered metals, selective recovery, scalability and versatility, energy efficiency and cost effectiveness as it does not require elevated temperatures and pressures.⁵⁸ Most importantly, electrochemical recovery can minimise the amount of waste produced, reducing the need for disposal and enabling a circular economy.⁵⁸

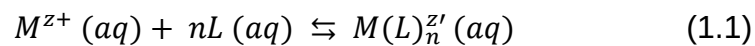
Electrorefining is primarily used to purify metals which have already been extracted or recovered through the previously described techniques. It involves placing the impure metal as an anode and by passing an electric current, the pure metal is deposited onto the cathode. Any impurities collect at the bottom as anode sludge. This process is utilised in the industrial production of high-purity metals such as copper, nickel and lead, from usually impure feedstocks. However, as this process still requires pyrometallurgical and hydrometallurgical techniques to extract and prepare the metal for electrorefining, it is often energy intensive and can involve significant chemical inputs.

Electrodeposition, on the other hand, is the most traditional metal recovery technique. The simplest experimental consists of an electroplating bath in which an inert anode and cathode are placed. By passing an electric current, metal ions in aqueous solution (electrolyte) are reduced onto a cathode to produce a coherent film, layer or bulk material. By optimising the electrolyte composition and operating parameters such as current density, pH, additives and temperature the metal deposit can be tailored for specific applications such as corrosion prevention or decorative purposes.

The main challenge of this technique lies in the recovery of metals from dilute solution where the electrodeposition is often limited by mass transfer.⁵⁹ To mitigate these effects, gas sparging can be employed or electrolyte can be pumped through the cell. Alternatively, a rotating disk electrode can be utilised to increase mass transfer rates by enhancing the convective flow of electrolyte across the electrode surface.

1.3 Fundamentals of Electrodeposition

Metal cations exist in aqueous solution with a surrounding solvation shell, as described by the equilibrium in equation 1.1. The nature of this solvation shell is dependent on the composition of the electrolyte and concentration of the solution.



Where M^{z+} is the metal cation with a charge $z +$ in solution, L represents a ligand (e.g., H_2O , Cl^- etc), n is the number of ligands involved in the complexation of the metal cation, $M(L)_n^{z'}$ is the metal-ligand complex and z' reflects the new charge after ligand interaction.

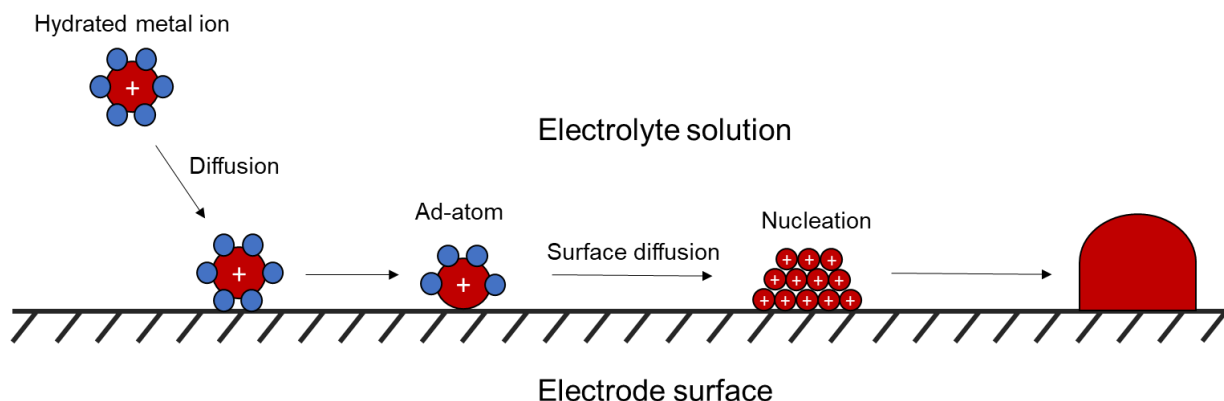


Figure 1.2: Scheme for the mechanism of formation of metal deposits on an electrode, adapted from literature.⁶⁰

The electrodeposition mechanism of metals from aqueous solution consists of a number of stages as illustrated in Figure 1.2.⁶⁰ This process, also known as electrocrystallisation, occurs as follows. The first stage involves the diffusion of solvated metal ions from the bulk solution to the electrode surface via diffusion, migration and convection. As the ions approach the electrode surface reaching the Helmholtz double layer, they shed part of their solvation sheath but retain some charge. The intermediate species are referred to as ad-ions. These ad-ions are highly unstable and move rapidly across the electrode surface via surface diffusion to incorporate into a growing crystal lattice. This typically occurs at surface defects, kinks or step-edges where they can integrate into the lattice structure. Once, incorporated they become ad-atoms and accumulate to form thermodynamically stable crystalline nuclei. The formation of coherent metallic layer requires achieving a critical nucleation size.^{60,61}

To drive electrocrystallisation, an overpotential must be applied to the electrode, which is defined as the difference between the applied potential and equilibrium potential (E_{eq}):

$$\eta = E - E_{eq} \quad (1.2)$$

As metal deposition is a Faradaic process in which metal ions are electrochemically reduced, it adheres to Faraday's law which describes the relationship between the mass deposited at the electrode surface to the charge passed:

$$m = \frac{M}{nF} Q \quad (1.3)$$

where m is the mass of deposited material, M is the molar mass, n is the number of electrons transferred, F is the Faraday constant and Q is charge.

Charge can be expressed as the integral of fixed current, over time^{60,62}:

$$Q = \int I . dt = I t \quad (1.4)$$

1.3.1 Nucleation

Nucleation refers to the initial formation of metal nuclei, and once these nuclei have formed, the subsequent crystal growth depends on the rate of both processes, which in turns influences the morphology of the metal deposit.⁶⁰ The nuclei can either be two or three-dimensional dependent on the interaction between the substrate and deposited metal species. As mentioned previously, a critical size of nuclei must be reached to become thermodynamically stable and grow further. For both 2D and 3D nuclei, this critical size is related to the overpotential and molar surface free energy, as shown in equations 1.5 and 1.6.⁶⁰

$$r_c = - \frac{\gamma M}{nF\rho\eta} \quad (1.5)$$

$$r_c = - \frac{2M\gamma}{nF\eta} \quad (1.6)$$

Where r_c is the critical nucleus radius. γ is the molar surface free energy, M is the molecular weight of the deposit, n is the number of electrons transferred, F is the Faraday constant, ρ is the density of the deposit and η is the overpotential applied.

It can be inferred from these equations that an increase in overpotential results in a decrease in the critical size required, meaning that at higher overpotentials a small growth of small nuclei forming a fine-grained polycrystalline deposit is expected.

The rate of nucleation is dependent on thermal fluctuations in the system as shown in equation 1.7.⁶⁰

$$B = F \exp\left(-\frac{\Delta G_c}{kT}\right) \quad (1.7)$$

Where B is the rate constant of nucleation, F is the pre-exponential factor, ΔG_c is the Gibbs critical energy of clusters formation. It is accepted that nucleation is a first-order reaction [66] and therefore the rate at which new nuclei form is directly proportional to the number of sites available for nucleation:

$$N(t) = N_0[1 - \exp(-Bt)] \quad (1.8)$$

where N_0 is the initial number of active sites, B is the nucleation rate constant and t is time.

If $Bt > 1$, the number of active sites is equal to the number of initial active sites and is referred to as instantaneous nucleation, resulting the slow growth of nuclei on a small number of active sites.^{60,61} Conversely, if the nucleation rate constant is very small (i.e. $Bt \approx 1$) then the number of active sites is equal to N_0Bt and in this case the number of nuclei increases over time. This is referred to as progressive nucleation and corresponds to fast growth of nuclei on many active sites, as the electroreduction proceeds.^{60,61}

Chronoamperometry, a technique later detailed in section 1.4.6.3, can be used to experimentally determine which mode of nucleation is taking place. This is achieved by fitting the mathematic models, first derived by Scharifker and Hills,⁶³ which describe instantaneous and progressive nucleation, respectively:

$$\frac{i^2}{i_m^2} = \frac{1.9542}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m} \right) \right] \right\}^2 \quad (1.9)$$

$$\frac{i^2}{i_m^2} = \frac{1.2254}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m} \right)^2 \right] \right\}^2 \quad (1.10)$$

where i_m and t_m are the current and time coordinates of the peak.

1.4 Electrochemistry Principles

1.4.1 Structure of the Double Layer

To understand electron transfer reactions, the nature of the electrode/ electrolyte interface must be considered. This interface disrupts the electrolyte solution due to the interactions between the solid electrode and electrolyte differing significantly to those occurring solely in the solution. For electrodes under potentiostatic control, the charge results in strong interactions between the ions in solution and the electrode surface, giving rise to the formation of a region known as the electrical double layer. There are various models used electrical double layer. The main models include the Helmholtz model, Gouy-Chapman model, Stern model and Grahame model which are described below.^{62,64-66}

1.4.1.1 Helmholtz Model

The Helmholtz model is one of the oldest and simplest models used to describe the electrical double layer. The basic concept is that when a metal electrode is immersed in an electrolyte solution, it acquires a charge density (q^m) due to an excess or deficiency of electrons at the electrode surface. To maintain electroneutrality, the charge of the electrode must be balanced with an equal but opposite charge in solution (q^s), as represented in equation 1.11.⁶²

$$-q^m = q^s \quad (1.11)$$

This balancing charge in solution arises from the redistribution of ions at the interface. Ions are either electrostatically attracted or repelled by the charged electrode, leading to an excess of either cations or anions that forms a rigid monolayer close to the electrode surface. The ions in this monolayer are situated at a minimum distance from the electrode, limited by their solvation shell, and this distance is referred to as the Outer Helmholtz Plane (OHP). In this model, the excess charge of the electrode is balanced completely by the ions located at the OHP, and the potential drop occurs solely over the region between the electrode and OHP. This double layer is equivalent to an electrical capacitor in which two layers of charge are separated by a fixed distance. A schematic of the Helmholtz model is shown in figure 1.3.

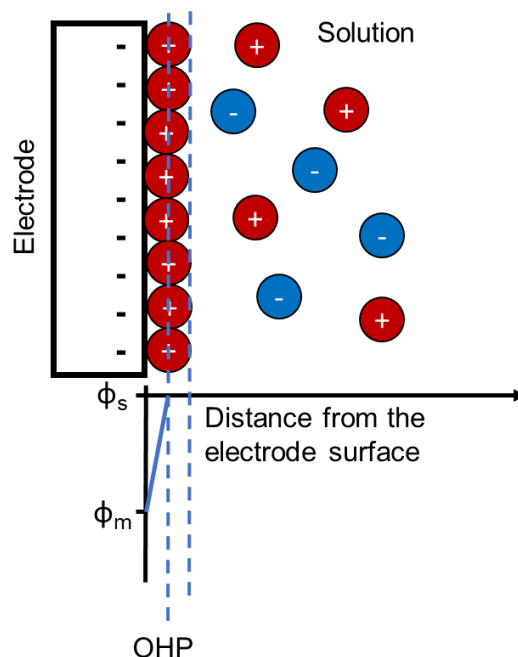


Figure 1.3: Schematic of the Helmholtz model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

Despite the Helmholtz model providing a basis for subsequent models, it is highly simplified and therefore has some limitations. It does not take into account the way in which the metal ions are distributed close to the electrode surface, due to the combined effects of electrostatic attraction and random Brownian motion. Consequently, this model does not accurately reflect the actual charge distribution for dilute electrolytes but it does provide a reasonable approximation for high concentration electrolytes.⁶²

1.4.1.2 Gouy-Chapman Model

The Helmholtz model was later refined by Gouy and Chapman who incorporated the effect of random Brownian motion, which disperses the metal ions, into their model. As a result, there is a loss of order near the electrode surface and the concentration of metal ions decreases in an exponential manner with increasing distance from the electrode surface. Ions are assumed to be point charges and the population of cations and anions can be described by Poisson-Boltzmann equations.^{65,66} The charge density is no longer exclusively found in the OHP but instead confined to a diffuse layer in which most of the charge is still found close to the electrode surface but some charge is held further away. As a result, the potential drop occurs exponentially over the diffuse layer.

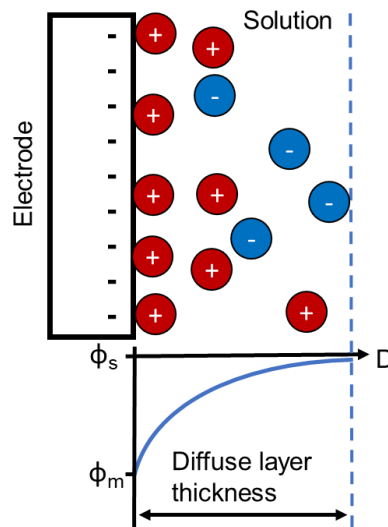


Figure 1.4: Schematic of the Gouy-Chapman model of the electrical double layer showing the potential drop across the electrode/ solution interface as a function of the D , the distance from the electrode surface, adapted from⁶².

The change in potential across the diffuse layer, δV_{diff} , is given by:

$$\delta V_{diff} = \sqrt{\frac{2RT}{\epsilon} \sum_{i=1}^s c_i \left[\exp\left(-\frac{z_i F \phi}{RT}\right) - 1 \right]} \quad (1.12)$$

where R is the gas constant, T the absolute temperature, ε the dielectric constant, c_i the metal ion concentration in the bulk solution, z_i the metallic ion charge, ϕ is the total potential difference across the solution side of the double layer and F is the Faraday constant.

Despite being a more accurate description of the double layer for dilute electrolyte solutions, there are still some limitations to the Gouy-Chapman model. The ions are assumed as being point charges with no physical size, when in reality ions occupy finite volumes and this will affect how closely they can approach the electrode and interact with each other; which is particularly pertinent for high concentration electrolyte solutions.⁶⁶ Furthermore, the Gouy-Chapman model does not take into account the solvation shells around ions which can significantly affect ion mobility and distribution.

1.4.1.3 Stern Model

Stern developed the EDL model further by effectively combining the Helmholtz and Gouy-Chapman models, that is assuming that the ions have a minimum distance of approach (the OHP) as well as the formation of a diffuse layer via the Brownian motion of the ions.⁶² A schematic of the model is shown in figure 1.5 where the potential drop is seen experience a sharp drop between the electrode and OHP, which gradually falls to a value of the bulk electrolyte. Although this model is more accurate description of the double layer, it still neglects the effect of solvent and solvated ions.

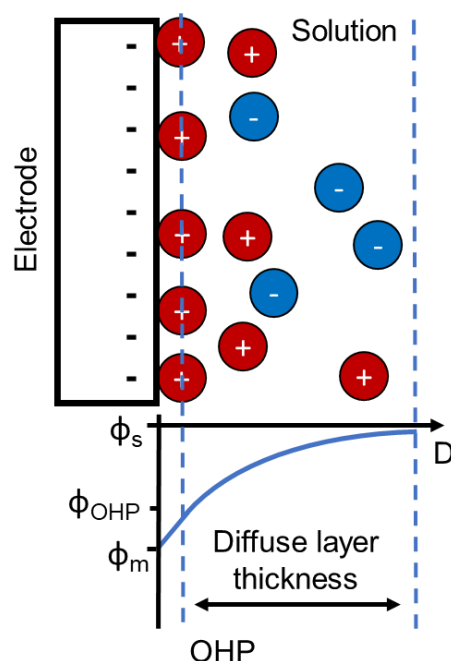


Figure 1.5: Schematic of the Stern model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

1.4.1.4 Grahame Model

In contrast, the Grahame model built upon the Stern model to include the effect of solvent molecules. He proposed that the region closest to the surface was occupied by solvent molecules but it was also possible for ionic or uncharged species to penetrate this region. This could occur if ions did not possess a solvation shell or lost their solvation shell when approaching the electrode surface. These ions are in direct contact with the electrode and said to be “specifically adsorbed”, referred to as such due to the fact only certain ions or molecules are adsorbed; unrelated to their charge in relation to the electrode surface. This closer plane of approach is referred to as the Inner Helmholtz Plane (IHP) and its axis is drawn through the centre of the adsorbed species, as shown in figure 1.6. The Grahame model comprises four regions: the IHP, OHP, diffuse layer and bulk electrolyte solution.

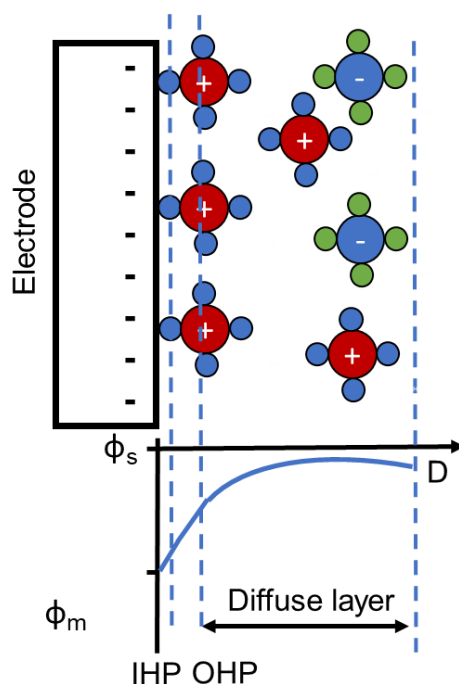


Figure 1.6: Schematic of the Grahame model of the electrical double layer showing the potential drop across the electrode/ solution interface, adapted from⁶².

1.4.2 Faradaic and Non-Faradaic Processes

There are two types of processes which can occur at electrodes: faradaic and non-faradaic processes. The former, faradaic processes, refers to processes in which electrons are transferred across the electrode-electrolyte interface causing oxidation/ reduction processes to occur. These processes are governed by Faraday's law which states the amount of chemical reaction (e.g., the mass of a substance deposited at an electrode) caused by a flow of current is proportional to the charge of electricity passed.⁶⁴ Under certain conditions, there may a range of potentials in which no faradaic processes occur because these reactions are thermodynamically or kinetically unstable.

Conversely, non-faradaic processes refer to capacitive processes in which no charge transfer can occur across the electrode-electrolyte interface; instead, adsorption and

desorption processes can occur. Although there is no charge transferred, external currents can flow when the potential, electrode area or solution composition changes.

1.4.3 Mass Transport

To initiate an electron-transfer process such as metal electrodeposition, a significant overpotential must be applied to shift the potential from equilibrium, resulting in electron flow. For a reaction to proceed, three key processes must occur: reactants must be transported to the electrode surface, the transfer of charge at the electrode surface, and resultant products must be transported away from the electrode surface. Mass transport can occur through three modes: diffusion, convection and migration, each influencing the reaction depending on the specific experimental conditions. The overall rate of the reaction is determined by the slowest step, known as the rate-determining step. When the kinetics of electron transfer are rapid, the reaction rate is controlled by the mass transport of materials to and from the electrode.

1.4.3.1 Diffusion

Diffusion is the process by which particles travel from an area of high concentration to low concentration, driven by a concentration gradient. In the context of electrochemical reactions, this involves the region adjacent to the electrode surface. Diffusion is the mechanism by which reactant ions are transported to this region and reaction products are removed in order to not inhibit the reaction. To quantitatively define diffusion, Fick's first and second law (equation 1.13 and 1.14) can be used.^{62,67} Fick's first law states that the flux of a diffusing species is proportional to the concentration gradient; this is relevant for linear diffusion to planar electrodes. Fick's second law describes how the concentration of diffusing species changes over time.

$$j = -D_B \frac{\partial [B]}{\partial x} \quad (1.13)$$

$$\frac{\partial[B]}{\partial t} = D_B \left(\frac{\partial^2[B]}{\partial x^2} \right) \quad (1.14)$$

where j is the diffusional flux of B, $-D_B$ is the diffusion coefficient and $[B]$ is the concentration of species B.

1.4.3.2 Convection

When a mechanical force acts on the solution, it causes a movement of ions known as convection. There are two types of convection: natural convection and forced convection. Natural convection can be present in any solution and arises from thermal gradients related to the exo- or endothermic nature of the reaction or density differences found between the products near the electrode surface and the ions in the bulk electrolyte solution. Due to the irreproducible nature of natural convection, it is generally undesirable in electrochemical experiments. One method to avoid these effects is to ensure voltametric measurements do not exceed 10-20 s.⁶⁷

Another method is to deliberately introduce forced convection. This is achieved by external forces such as stirring, rotation or vibration of the electrode (e.g., rotating disk electrode) or gas bubbling through solution. The change of concentration due to the movement of solution can be expressed using equation 1.5.^{62,67}

$$\frac{\partial[B]}{\partial t} = -v_x \frac{\partial[B]}{\partial x} \quad (1.15)$$

where $[B]$ is the concentration B and v_x is the velocity.

1.4.3.3 Migration

At the electrode/ electrolyte interface there is an external electric field which exists as a result of the potential drop between the two phases. This electric field can exert an electrostatic force on charged species at the interface, thereby inducing the movement of ions to or from the electrode. This electrostatic force acting on the ion under the

external field is given by equation 1.6.⁶² The migratory flux (j_M) is proportional to the concentration of the species, the electric field and ion mobility.

$$Force = \frac{zF}{N_A} \frac{\partial \phi}{\partial x} \quad (1.16)$$

where F is Faraday constant, N_A is Avogadro's constant and ϕ is the potential drop.

Migration effects can cause the rate of mass transport to vary throughout an electrochemical experiment, making interpretation of experimental data somewhat challenging. To mitigate these effects, a chemically and electrochemically inert background electrolyte solution in high concentration (≥ 0.1 M) is added. The presence of excess ions from the electrolyte can maintain near electroneutrality in the region adjacent to the electrode, thus making migration effects negligible. This background electrolyte is commonly referred to as supporting electrolyte. For aqueous solutions, this is usually potassium chloride or sulfate. Calculations have shown that a concentration of supporting electrolyte 100 times greater than the analyte is sufficient for quantitative analysis.⁶⁸

The addition of a supporting electrolyte has some other advantages such as increasing the solution conductivity making it less resistive to the flow of current. Furthermore, a large excess of supporting electrolyte is able to compress the double layer to 10-20 Å, which enables reagents to be within the electron tunnelling distance, in order to successfully drive the reaction. Finally, the presence of supporting electrolyte is able to maintain a constant ionic strength and therefore constant activity coefficients of the ions which are highly sensitive to ionic strength.

1.4.4 Electrochemical Cell

The simplest electrochemical cell to measure current/ potential characteristics consists of two electrodes. The first electrode is referred to as the working electrode and is where the reaction of interest takes place. The second electrode serves as both a reference and counter electrode to ensure the measurement of the potential drop between the working electrode and solution, $\phi_M - \phi_s$, is precisely defined. When a potential, E , is applied between the working and reference electrode with a finite current flowing between them, the potential can be described by equation 1.17.^{62,67}

$$E = (\phi_M - \phi_s) + iR + (\phi_s - \phi_{REF}) \quad (1.17)$$

where E is the potential, $\phi_M - \phi_s$ is the potential drop between the metal electrode and solution, i is the current, R is resistance and $(\phi_s - \phi_{REF})$ is the potential drop between the solution and reference electrode.

When conducting a voltammetry experiment, the objective is to measure i as a function of changes in the potential drop between the metal electrode and solution. In the case of microelectrodes, the current flowing through the electrode is very small and therefore the term iR can be neglected. Additionally, as the $(\phi_s - \phi_{REF})$ term remains constant, the equation can be simplified to eq. 1.18.

$$E = (\phi_M - \phi_s) + \text{constant} \quad (1.18)$$

In contrast, when using larger macroelectrodes, the current is significantly higher that the iR term can no longer be neglected. This results in a significant iR drop across the electrolyte which can distort the applied potential and make the accurate measurement of the potential drop between the working electrode and solution more challenging.

The use of a supporting electrode can minimise the iR drop to a certain extent but it is common practice to use a three-electrode system in which a third auxiliary electrode which can act solely as the counter electrode, in addition to the working and reference electrodes. The use of a potentiostat to perform electrochemical experiment ensures that current only flows between the working and auxiliary electrode, with no current flowing between the working and reference electrode.

For this reason, the three-electrode system depicted in Figure 1.7 was used throughout this project. The solution was thoroughly degassed with a nitrogen stream prior to electrochemical experiments and all experiments were conducted inside a Faraday cage.

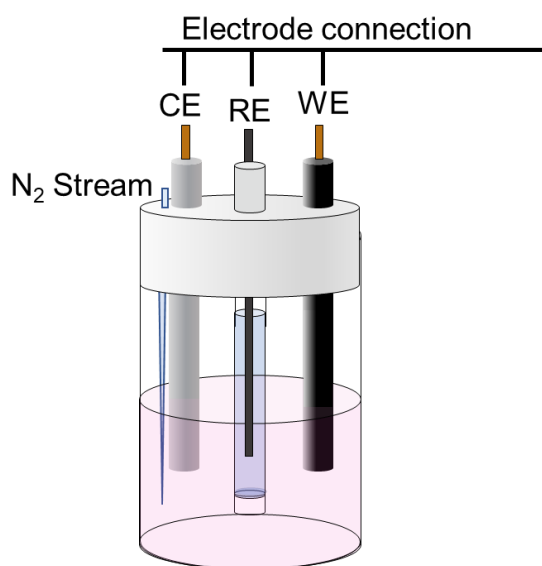
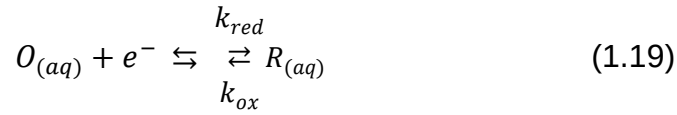


Figure 1.7: Three-electrode cell consisting of a working electrode (WE), counter electrode (CE) and reference electrode (RE). The solution is degassed with a nitrogen stream.

1.4.5 Nernst Equation

For the following redox reaction, **O** is the oxidised species and **R** is the reduced species in solution that are reduced and oxidised at a rate given by k_{red} and k_{ox} respectively (equation 1.19).



At thermodynamic equilibrium, the Gibbs free energy is minimised (Equation 1.20).

$$G_{sys} = 0 \quad (1.20)$$

Under constant temperature and pressure, the change in Gibbs free energy ΔG_{sys} for the reaction is related to the equilibrium constant by:

$$\Delta G_{sys} = -RT \ln k_{eq} \quad (1.21)$$

where R is the gas constant, T is temperature in Kelvin and k_{eq} is the equilibrium constant for the reaction.

Gibbs free energy can also be equated to the cell potential:

$$\Delta G = -nFE \quad (1.22)$$

where n is the number of electrons transferred, F is the Faraday constant and E is the cell potential of the electrode cell.

Under standard conditions, a temperature of 298.15 K, pressure of 1 atm and 1 M concentration solutions, the standard Gibbs free energy, ΔG^0 , is given by equation 1.23.

$$\Delta G^0 = -nFE^0 \quad (1.23)$$

By combining and rearranging equations 1.10 and 1.12, the standard cell potential can be shown to be related to the equilibrium constant:

$$E^0 = \frac{RT}{nF} \ln k_{eq} \quad (1.24)$$

However, for non-standard conditions, the equilibrium constant is replaced by the reaction quotient, Q which is a ratio of the relative chemical concentrations of products and reactants in a reaction mixture. The Gibbs free energy can be given by equation 1.14.

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad (1.25)$$

Since ΔG and ΔG° are related to the cell potential (Equations 1.22 and Eq. 1.23), this equation can be rearranged and written to make the cell potential the subject, giving the Nernst equation⁶⁷:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad (1.26)$$

1.4.6. Electrochemical Techniques

1.4.6.1 Cyclic Voltammetry

The cyclic voltammetry experiment involves applying a potential with changes with time, as shown in figure 1.8A. Typically, the starting potential, E_1 , is chosen so that any reduction/ oxidation processes does not occur and as a result there is only a negligible current flow. The potential is then swept in a linear manner to a second potential, E_2 , so that reduction/oxidation process of interest can occur within the region between E_1 and E_2 . At this point the direction of the scan is reversed and the potential is swept back to its original value.

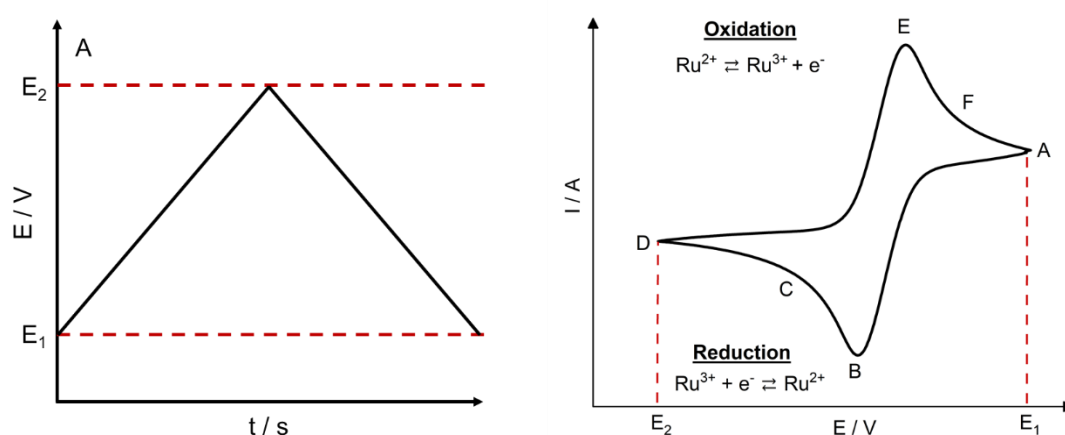


Figure 1.8. A) Applied potential as a function of time for a generic cyclic voltammetry experiment, adapted from⁶⁷. **B)** Cyclic voltammogram showing the reversible reduction of a 5 mM ruthenium hexamine trichloride and 0.1 M solution, at a scan rate of 100 mV s⁻¹.

Figure 1.8B shows a representative voltammogram conducted in a ruthenium hexaammine trichloride solution. As the potential is scanned cathodically from point A to D, the electroreduction of the electroactive species is observed resulting in the steady depletion of Ru³⁺ at the electrode surface and the formation of Ru²⁺. The cathodic peak at C is the maximum current corresponding to the delivery of additional Ru³⁺ via diffusion from the bulk solution, and the generation of Ru²⁺ results in a thicker diffusion layer. This diffusion layer slows down the mass transport of Ru³⁺ to the electrode. Consequently, as the potential is swept more negatively to point D, the current decreases. When the scan direction is reversed and the potential swept in an anodic direction, the Ru²⁺ present at the electrode surface is oxidised back to Ru³⁺, resulting in an analogous anodic peak.

1.4.6.2 Linear Sweep Voltammetry

Linear-sweep voltammetry (LSV) is the simplest voltammetry experiment where the current flowing is recorded with respect to the increasing applied potential. This plot is referred to as a voltammogram and is shown in figure 1.9B for an oxidation process. The potential is swept from E_1 where no faradaic processes can occur to E_2 where the electron transfer is driven rapidly.

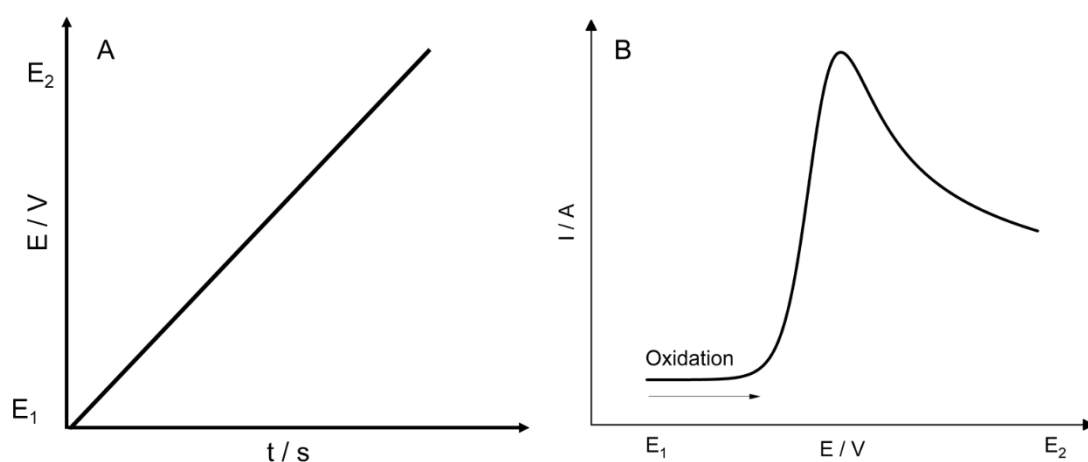


Figure 1.9. A) Applied potential as a function of time for a linear voltammetry. **B)** Simulated linear sweep voltammogram for a 3 mm diameter disc working electrode.

1.4.6.3 Reversible and Irreversible Behaviour

Electrochemical reversibility refers to the rate of electrode kinetics, k^0 , relative to the rate of mass transport, m_T . Reversible processes have 'fast' electrode kinetics (equation 1.27).⁶⁷ Conversely, irreversible processes have 'slow' electrode kinetics (equation 1.28).⁶⁷

$$k^0 \gg m_T \quad (1.27)$$

$$k^0 \ll m_T \quad (1.28)$$

The electrochemical reversibility of a system can be evaluated experimentally from the peak-to-peak separation (ΔE_{pp}) in a CV of the cathodic and anodic peak, as shown in equation 1.29.⁶⁷

$$\Delta E_{pp} = E_p(anodic) - E_p(cathodic) \quad (1.29)$$

In the case of the reversible-redox couple, such as ruthenium hexaammine trichloride (as shown in figure 1.9B), the peak-to-peak separation is around 59 mV at 298 K; this is significantly higher in the case of irreversible processes.

The reversibility of the redox couple can also be evaluated by the difference between the peak potential and $E_{\frac{1}{2}}$ half the peak current for the forward peak (equations 1.30-32).⁶⁷

Reversible system:

$$\left| E_p - E_{\frac{1}{2}} \right| = 2.2 \frac{RT}{F} \quad (1.30)$$

Irreversible system:

$$\left| E_p - E_{\frac{1}{2}} \right| = 1.9 \frac{RT}{\alpha F} \quad (1.31)$$

Irreversible oxidation:

$$\left| E_p - E_{\frac{1}{2}} \right| = 1.9 \frac{RT}{\beta F} \quad (1.32)$$

where E_p is the peak potential, $E_{\frac{1}{2}}$ is the potential at half the peak current, R is the gas constant, T is temperature, F is Faraday constant, α is the transfer coefficient and β is the symmetry factor.

For both reversible and irreversible processes, a square root dependence of peak current with scan rate is observed from the Randles–Ševčík equation, for a one-electron reduction at 298.15 K (equation 1.33 and 1.34).⁶⁷

Reversible:

$$i_p = 2.69 \times 10^5 AD^{1/2}[A]_{bulk}v^{1/2} \quad (1.33)$$

Irreversible:

$$i_p = 2.99 \times 10^5 \sqrt{\alpha} D^{1/2}[A]_{bulk} A v^{1/2} \quad (1.34)$$

Where A is the area of the electrode, D is the diffusion coefficient, $[A]_{bulk}$ is the concentration of the analyte, v is the scan rate and α is the transfer coefficient.

1.4.6.4 Chronoamperometry

Chronoamperometry is a further technique used to probe electrochemical reactions. In this experiment, the applied potential is stepped instantaneously from E_1 where no current flows to E_2 (Figure 1.10A). The resulting current response, referred to as a chronoamperogram, is shown in figure 1.10B. Initially, a large current is detected due to the high concentration of reactants which falls over time due to the reactants being consumed, and the process becomes mass-transport controlled. The decay of current over time can be described by the Cottrell equation (equation 1.35).^{62,67}

$$I = \frac{nFA\sqrt{D}c^*}{\sqrt{\pi t}} \quad (1.35)$$

Where n is the number of electrons transferred in the electrode reaction, F is the Faraday constant, D is the diffusion coefficient, c^* is the bulk concentration of analyte and t is time.

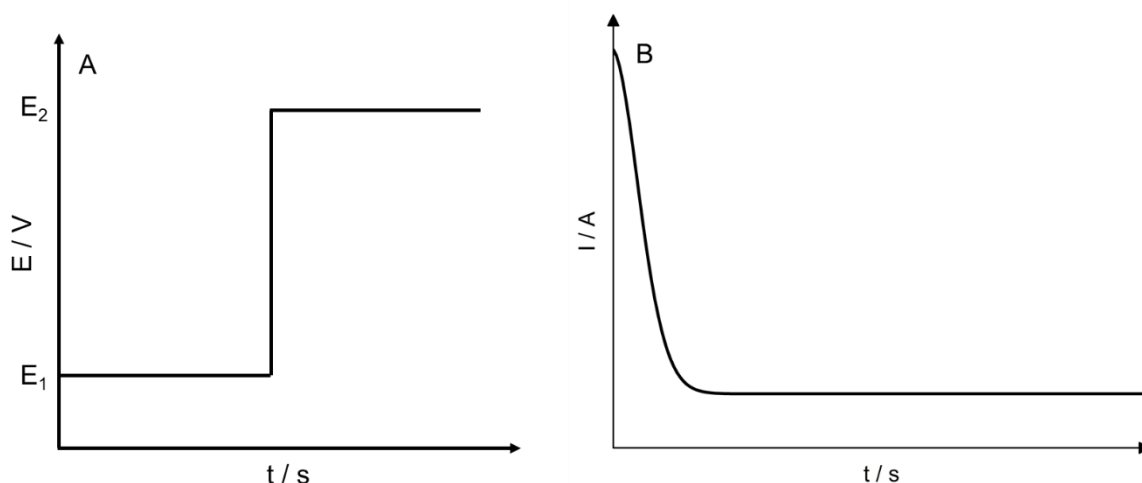


Figure 1.10. **A)** Potential-time profile for a chronoamperometry experiment. **B)** Typical chronoamperogram as a function of current over time at a planar macroelectrode.

1.4.7. Microelectrodes

Microelectrodes refer to electrodes in which at least one of the dimensions are microns or sub-microns; typically, less than $25\ \mu\text{m}$.⁶⁷ Unlike macroelectrodes, which exhibit linear diffusion of electroactive species to the electrode surface, microelectrodes with sufficiently small radii exhibit radial diffusion. Figure 1.11 illustrates these diffusion modes as a function of electrode radius. Due to this radial diffusion, mass transport of reactants to a microelectrode surface occurs rapidly, leading to a quick establishment of the steady-state mass transport regime. Consequently, the voltammetry of microelectrode differs from that of macroelectrodes; steady-state conditions are reached more rapidly in microelectrodes, whereas macroelectrode feature peaks due to mass transport limitations (Figure 1.12).

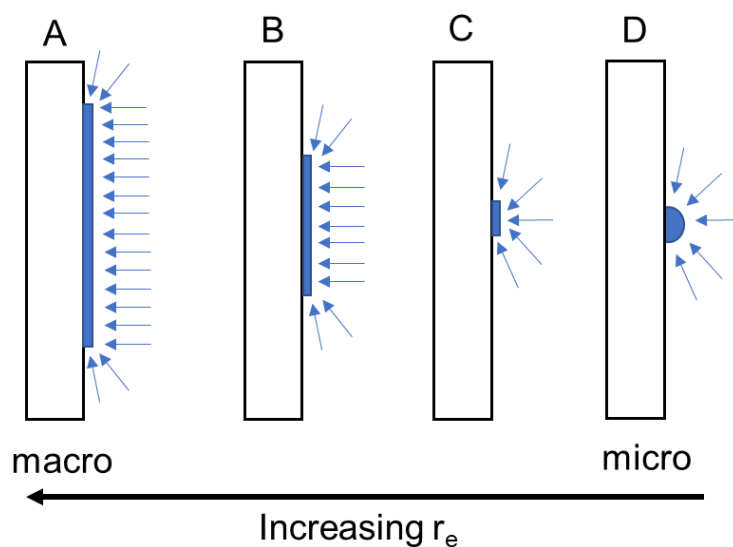


Figure 1.11: Planar and spherical diffusion to an electrode, where r_e is the radius. Arrows represent the electroactive species diffusing to the electrode. A) Large macro electrode where planar diffusion dominates. B), C) Progressively smaller microelectrodes where planar diffusion no longer dominates and D) Diffusion to a spherical electrode.

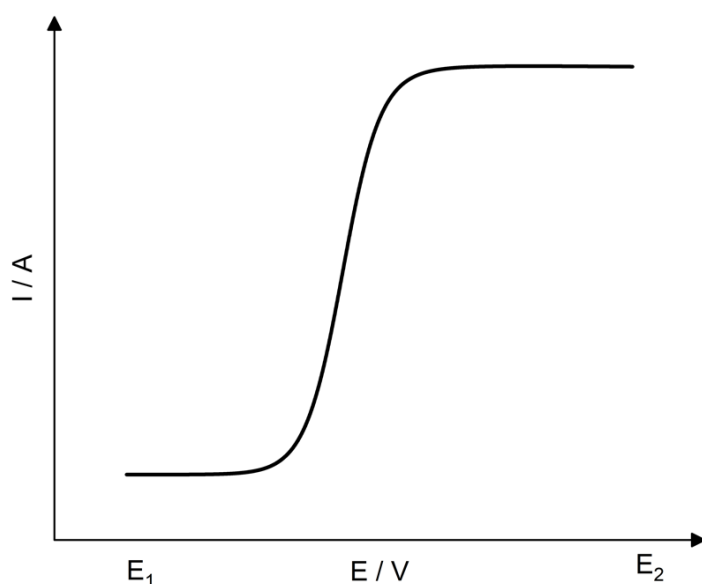


Figure 1.12: Simulated LSV for a $9\ \mu\text{m}$ working microelectrode.

In mathematical terms, the diffusion regime of microelectrodes can be described by a modified version of Fick's second law. This modification accounts for the geometry

and radius of the electrode. For spherical and hemispherical electrodes, the diffusion equations are given by:⁶⁹

Spherical:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad (1.36)$$

Hemispherical:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \quad (1.37)$$

where r is the radius of the electrode.

At short times, the diffusion layer around a spherical electrode is relative compared to the electrode's radius. In this case, the diffusion regime can be approximated as linear and shows Cottrellian behaviour (equation 1.24). Conversely, at longer times, the diffusion layer grows larger relative to the electrode radius, leading to a more rapid flux of reactants to the electrode surface. As the reaction proceeds, the diffusion layer thickens due to spherical expansion, allowing the electrode to react with more and more reactants over time. This results in a constant diffusion gradient and the establishment of a steady-state current described by equation 1.27.

$$I_{ss} = 4\pi r_e D F c^* \quad (1.38)$$

Where r_e is the electrode radius, D is the diffusion coefficient, F is the Faraday constant and c^* is the bulk concentration of the electroactive species.

Microelectrodes are suitable in studying reactions with fast electrode kinetics. Furthermore, they have a reduced capacitance due to their small size, which lowers the background current. This is especially important for nano-impact electrochemistry

(discussed later in section 1.5) where the low currents produced are highly susceptible to electrical noise. A high signal-to-noise ratio is required to resolve any impacts.

1.4.7.1 Micro-arrays

Electrodes can be modified with nanoparticles via methods such as drop-casting for various applications. The steady state current of an isolated spherical electrode was given in equation 1.38. The steady-state current for a sphere in contact with a plane (e.g., a nanoparticle during an impact) has a correction factor applied is given by^{70,71}:

$$I_{lim} = 4\pi \ln(2) nFD r_p [A]_{bulk} \quad (1.39)$$

where n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, r_p is the radius of the nanoparticle in contact with electrode and $[A]_{bulk}$ is the concentration of the electroactive species.

Given the associated advantages of using microelectrodes discussed previously, sometimes it is preferable to use up to hundreds and thousands of microelectrodes in parallel which are referred to as micro-arrays. For the case of microelectrodes well-separated by insulating material, individual diffusion layers develop and continue to grow throughout experiments. The resultant voltammetry is dependent on the size of individual diffusion layers relative to the radius of the microelectrode itself and the size of the diffusion layers relative to the separation between the microelectrodes in the array. There are four categories in which the diffusion profile can correspond to, as illustrated in figure 1.13.

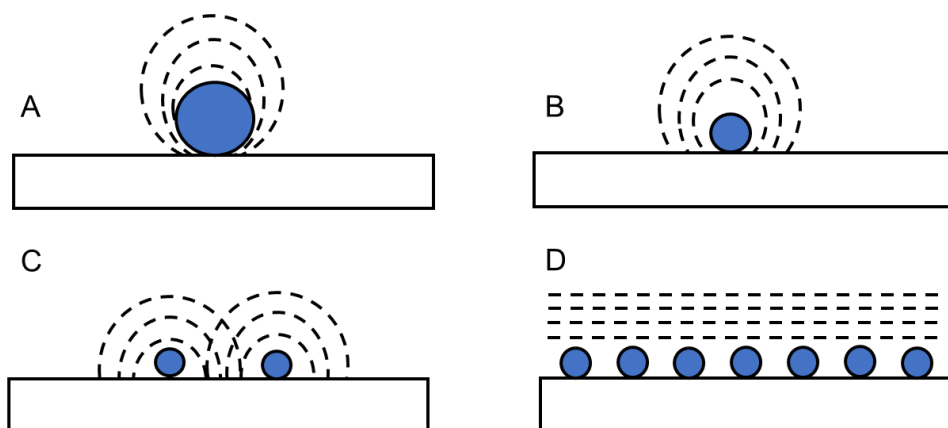


Figure 1.13: Four categories (A-D) of diffusion profile which a sphere on a plane in a microarray arrangement may belong to.

For category 1 (1.13A), during a short timescale (i.e., fast voltage scan rates), the diffusion layer is significantly smaller than the radius of the spherical electrode and is isolated to individual nanoparticles. Consequently, peaks are observed during voltammetry similar to the response of a macroelectrode. For category 2 (1.13B), during a longer timescale (i.e., slow voltage scan rates), the diffusion layer becomes larger than the radius of the spherical electrode and steady-state behaviour is observed at isolated nanoparticles. For category 3 (1.13C), the individual nanoparticle-modified microelectrodes are spaced more closely together. As a result, the diffusion layers become partially overlapped and the voltametric response is an intermediate between category 2 and 4. For category 4 (1.13D), the diffusion layer is significantly larger than the separation between individual nanoparticle-modified microelectrodes. This results in significant overlap between the diffusion layers and linear diffusion is observed. Assuming the array is macroscale, the entire array acts as a single macroelectrode and exhibits peak-shaped responses in voltammetry. For microscale arrays, a steady-state voltammogram with a limiting current is observed.

1.4.8 Kinetics

For a given overpotential, the magnitude of current flow is dependent on the charge transfer between the solution species and electrode (kinetics), and mass transport. At low overpotentials, where the applied potential deviates slightly from the equilibrium potential, the current flow is limited by the charge transfer kinetics at the electrode which is significantly slower than the mass transport of reactants and products to and from the electrode surface. For an electrochemical reaction, electron transfer can proceed in both the forward (reductive) and reverse (oxidative) directions, as shown in equation 1.8.

The current for the cathodic and anodic counterparts can be given by the following equations:

$$I_c = -nFAk_{red}[O]_0 \quad (1.40)$$

$$I_a = nFAk_{ox}[R]_0 \quad (1.41)$$

where n is the number of electrons transferred, F is the Faraday constant, A is the electrode area, k_{red} and k_{ox} are the rate constants for the reductive and oxidative reactions, respectively and $[O]_0$ and $[R]_0$ are the initial concentrations of species at the electrode surface.

The net current flow is equal to the sum of cathodic and anodic currents (equation 1.42) and as a result can be written as equation 1.43.

$$I = I_a + I_c \quad (1.42)$$

$$I = nFA(k_{ox}[R]_0 - k_{red}[O]_0) \quad (1.43)$$

It is assumed that electron transfer reactions can be described using a transition state model (figure 1.14). This involves the reactants overcoming an energy barrier via a transition state to become the product. Transition state theory predicts that the rate of reduction and oxidation reactions can be related to the Gibbs energy of activation using the Arrhenius equation, respectively⁶²:

$$k_{red} = A \exp\left(\frac{-\Delta G_{red}^{\ddagger}}{RT}\right) \quad (1.44)$$

$$k_{ox} = A \exp\left(\frac{-\Delta G_{ox}^{\ddagger}}{RT}\right) \quad (1.45)$$

Where A is the frequency factor that accounts for the rate of collision of an electroactive species with the surface, $-\Delta G_{red}^{\ddagger}$ and $-\Delta G_{ox}^{\ddagger}$ are the Gibbs energy of activation and R is the gas constant and T is temperature.

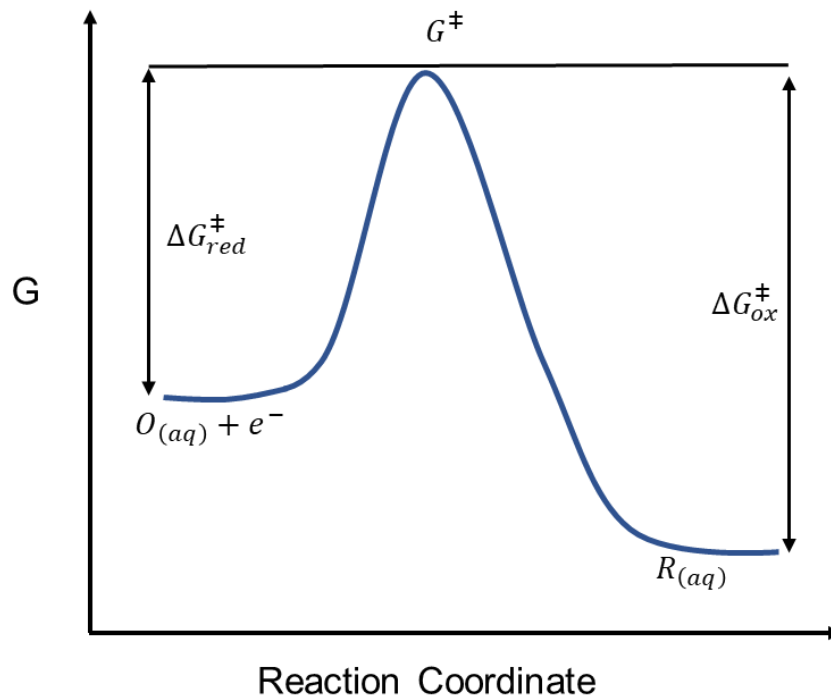


Figure 1.14: Free energy plot for a simple one-electron of a species $O(aq)$.

Equations 1.33 and 1.34 describe the rate of the reduction and oxidation processes at a single interface, whereas in reality, electrochemical reactions are influenced by the interfacial potential difference. The effect of the overpotential applied is included, with the introduction of new rate constants k_{red}^0 and k_{ox}^0 which are independent of n ⁶²:

$$k_{red} = k_{red}^0 \exp\left(\frac{-\alpha n F \eta}{RT}\right) \quad (1.46)$$

$$k_{ox} = k_{ox}^0 \exp\left(\frac{\beta n F \eta}{RT}\right) \quad (1.47)$$

where α is the transfer coefficient, β is the symmetry factor, n is the number of electrons transferred, F is the Faraday constant, η is the overpotential applied, R is the gas constant and T is the temperature.

By substituting, equations 1.44 and 1.45 into 1.43, the Butler-Volmer equation is formed which shows how current varies with the overpotential and transfer coefficient:

$$j = j_o \left[\exp\left(\frac{\beta n F \eta}{RT}\right) - \exp\left(\frac{-\alpha n F \eta}{RT}\right) \right] \quad (1.48)$$

Where j is the current density and j_o is the exchange current density.

1.5 Nano-Impact Electrochemistry

The term single-entity electrochemistry (SEE) in simple terms refers to studying “one thing at a time” using electrochemical methods.⁷² Within SEE, the subfield nano-impact electrochemistry (NIE), ambiguously referred to in the literature as several names, including “single entity nano impact electrochemistry”, “particle-impact electrochemistry”, “impact electrochemistry”, “nanoparticle collision electrochemistry” and “stochastic collision electrochemistry” has rapidly expanded in recent years.⁷³ Nano-impacts were initially observed by Micka in 1956 who studied the cathodic peaks resulting from the collisions of insoluble HgS, PbS and Ag₂O particles with a mercury

electrode.⁷⁴ Similarly, later in 1969, Jones and Kaye observed anodic peaks when studying stirred solutions of activated charcoal in 0.1 M KCl.⁷⁵ These initial findings were explored further by Moller in 1971⁷⁶ who demonstrated the first practical applications of NIE, which was later refined by Holland and Feinerman.^{77,78} A rotating turntable was utilised to reduce silver bromide particles upon contact with a platinum needle electrode, thus allowing the grain size of the particles to be determined.

However, this field did not receive significant attention again until nearly twenty-five years later. In 1995, Heyrovský published a series of papers concerning the collisions of colloidal particles of various semi-conductors (SnO_2 , TiO_2 , Fe_2O_3) with a mercury electrode.⁷⁹⁻⁸² Although the focus was not made on recording individual impact events, instead the ensemble current response was observed from the catalytic reduction of protons at the impacting particles. Since this seminal work, the focus has shifted to studying the response of single particle collisions. Impact experiments were first pioneered by Xiao, Bard, Scholz and Compton's group.⁸³⁻⁸⁹

1.5.1 Direct Impacts

This technique involves the addition of electroactive nanoparticles (NPs) into an electrolyte solution that can randomly collide with an inert polarised electrode. When the electrode is held at a suitable potential, the nanoparticle can be directly reduced/oxidised (typically referred to as “direct” impacts).

Initial experiments concerning “direct” impacts involved the (destructive) oxidative impacts resulting from silver nanoparticles (AgNPs) colliding with a carbon fibre electrode.^{90,91} Analysis of the resultant transient signals produced were shown to elucidate a range of information, such as nanoparticle size and agglomeration distributions showing applications in the environmental monitoring of AgNPs in

seawater media.^{92,93} Subsequent work by Zhou *et al.* extended this study to gold nanoparticles demonstrating the particle size could be determined using similar methods.⁹⁴ Additional investigations by Haddou *et al.* explored copper and nickel nanoparticles, revealing details about the slow, irreversible oxidation kinetics of these metals.^{95,96} Mixtures of nanoparticles were also investigated, revealing silver and nickel nanoparticles could be individually distinguished from their oxidative transient signals.⁹⁷ This study provided size distributions of both particles as well as demonstrating the ability to estimate unknown concentrations of nanoparticles by fitting the cumulative number of transient events over time to an integrated chronoamperogram.⁹⁷ Since these initial experiments, the direct impacts for various other aqueous and organic systems have been studied.⁹⁸⁻¹⁰⁰

1.5.2 Indirect Impacts

1.5.2.1 Electrocatalysis Applications

Work on “indirect” impacts, also referred to as catalytic amplification, has demonstrated the use of impacting NPs as “nanoelectrodes” for surface reactions such as the reduction of protons and hydrazine oxidation. This was first demonstrated by Xiao and Bard who studied proton reduction at single platinum nanoparticles impacting a carbon fibre ultramicroelectrode.⁸⁶ Analysis of the reductive transient peaks allowed for the study of the dynamics of the process and information about the heterogeneous electron-transfer kinetics at the single-particle level. This pioneering work set the stage for using nano-impact electrochemistry as a powerful tool in electrocatalysis, allowing researchers to probe catalytic reactions at a single-particle level.

The conventional electrochemical characterisation to evaluate catalyst performance via drop-casting on a macroscopic electrode surface is not only time-consuming, but there is a level uncertainty regarding the accuracy of this method due to particles

potentially undergoing aggregation, degradation, and deactivation, as well as problems arising from the drop-casting method itself.¹⁰¹⁻¹⁰³ In contrast, NIE exhibits several advantages. Firstly, by studying reactions at a single particle level, a more accurate structure-activity relationship can be correlated compared to ensemble measurements in which the averaged response of particles, which could be a different size, shape, or possess different catalytic activity, is used.¹⁰⁴ This is of particular importance for increasingly used bimetallic nano-catalysts where the core and shell layers can have distinct contributions to catalytic activity.¹⁰⁵ Furthermore, NIE typically does not involve any additives, meaning that the full surface of the nanocatalyst can be considered electroactive. This, in turns, allows for a more accurate calculation of useful properties such as current densities and turnover frequency.¹⁰¹ The ease of this technique provides the potential to rapidly screen catalysts with high-throughput measurements of tens or hundreds of NPs within a few minutes, leading to more efficient nanoelectrocatalyst design.¹⁰⁶

1.5.2.2 Nanomaterial Fabrication via Impacts

Another application of indirect impacts is the fabrication of different nanoparticle architectures. Conventional approaches to nanoparticle synthesis through chemical reduction often face challenges such as contamination of reducing agents within the nanoparticle batch, complexities in monitoring the reduction process, and the time-consuming nature of size analysis.¹⁰⁷ In contrast, NIE has recently emerged as a promising technique offering the unique ability to combine in-situ synthesis or modification of a nanoparticle with simultaneous nanoparticle characterisation, as well as in-situ electrocatalyst performance evaluation (if desired). A number of methods of NIE-facilitated nanoparticle synthesis¹⁰⁷ and modification methods via doping,^{108,109} electrodeposited metal layers¹¹⁰⁻¹¹² and the fabrication of bimetallic NPs¹⁰⁶ have been

presented in the literature. However, most of these methods lack in-situ electrocatalyst performance testing and hence still rely on subsequent ensemble measurements.

The Compton group reported metal deposition under impact onto metallic NPs, specifically the bulk and underpotential deposition of cadmium onto silver nanoparticles and the deposition of zinc onto zinc nanoparticles.¹¹⁰⁻¹¹² Since these first reports, this area has expanded with recent focus on metal deposition on non-metallic nanoparticle supports, which has the potential to be applied to the recovery of metals from waste solutions whilst simultaneously generating in-situ (electro)catalysts. So far, this has been achieved for copper deposition onto fly-ash cenospheres¹¹³ and palladium onto carbon black.¹¹⁴ In particular, the study of palladium deposition on carbon black by Oladeji *et al.*¹¹⁴ showed a (non-optimised) metal recovery rate of 86% after 26 h, and these Pd-modified carbon black NPs were shown to catalyse both HER and Suzuki-coupling.

Although nano-impact electrochemistry is a well-established technique for electrocatalysis and various other applications, its use in metal recovery remains in its infancy with only two known examples in the literature, copper and palladium^{113,114} as mentioned previously. Therefore, this thesis aims to extend this research by investigating further commercial and critical metals typically found in low-concentration waste solutions, assessing the viability of this technique for their recovery.

1.5.3 Experimental Set-up and Limitations

For the aforementioned nano-impact experiments, some experimental factors are different to conventional electrochemical experiments and therefore need to be considered. For conventional electrochemical experiments a high concentration of supporting electrolyte is required to reduce the Ohmic drop and subsequently

compress the double layer. However, in the case of impacts, the high ionic environment can cause agglomeration or aggregation of nanoparticles. This is due to the fact many particles possess a charged coating and according to Deraguin Landau Verwey Overbeek (DLVO) theory, the presence of electrolyte causes agglomeration due to the contraction of the double layer surrounding each particle and the resultant decreased repulsion.¹¹⁵ To mitigate these effects, a lower concentration of electrolyte is typically used¹¹⁶ or an alternative is to use particles with steric stabilisation through the use of a polymer coating.¹¹⁷

Moreover, due to the fact that this technique operates on the single-particle level, background currents are very small, typically ranging from pA to nA, meaning that these signals are highly susceptible to electrical noise. Many commercial potentiostats are often not able to resolve impact signals successfully due to their high signal-to-noise ratio meaning that some impact signals are “lost” in the noise reduction settings, which typically cannot be adjusted. Attempts have been made to improve the signal-to-noise ratio of nano-impact experiments by using specialised Faraday cages or employing very high gain amplifiers with low-bandwidth electronic filtering.¹¹⁸ However, the use of electronic filtering can cause significant distortion to the impact signal, often leading to an inaccurate peak height and duration; therefore, the interpretation of such parameters should be treated with caution.¹¹⁹

In addition to the choice of potentiostat, the working electrode selection is also of paramount importance to minimise electrical noise. In general, the smaller the electrode, i.e. ones with a smaller capacitance, have improved signal-to-noise ratios allowing better resolution of individual impact events.¹²⁰ However, as the size of the electrode decreases so does the probability of observing an impact and hence the frequency is lower. The impact frequency is proportional to the nanoparticle diffusion

coefficient and concentration.¹¹⁶ This can be a particular issue when the study involves large/ and or low concentration of nanoparticles.

Furthermore, due to the stochastic nature of impact collisions, they can be difficult to control. This can mean multiple particles can collide with the electrode at the same time, potentially leading to overlapping signals, which can be hard to distinguish and successfully analyse, and hence many studies employ very low concentrations of particles in order to lower the probability of this. Other researchers have employed an “impinging jet” technique to mitigate this issue.^{122,123} In this set-up, a jet of fluid containing nanoparticles is directed towards the working electrode. The flow of the jet can be carefully controlled to regulate the velocity and concentration of particles as they approach the electrode, thus reducing the randomness of collisions and lowering the likelihood of simultaneous impacts.

As a final consideration, current analysis techniques typically employ peak search functions in software, but for complex and irregular peak shapes some manual input can be required, which can introduce human bias. Researchers have started to develop automated analysis tools that use machine learning to speed up analysis time and eliminate human bias,¹²⁴ but this is currently not a commonly used practice.

1.6 Aims and Objectives

Metals play a pivotal role in society, with their rapidly increasing consumption driven across a range of industries. However, the mismanagement of electronic waste represents a pressing challenge, causing severe environmental damage and posing significant risks to human health. Furthermore, metals are a finite resource and thus the recovery of critical and strategic raw materials such as manganese, nickel and ruthenium are imperative for their sustainable use. Current recovery technologies such

as pyrometallurgy, hydrometallurgy, ionometallurgy and bio-hydrometallurgy are associated with severe environmental impacts due to their energy intensive processes and large volumes of toxic waste generated. Moreover, these techniques are not well-suited to low-concentration metal solutions typically found in wastewater, necessitating costly pre-concentration steps.

In contrast, electrochemical methods of metal recovery have become increasingly attractive due to their relatively modest energy requirements and reduced environmental impact. Among these, nano-impact electrochemistry has recently emerged as a promising approach with distinct advantages compared to other electrochemical techniques. It benefits from high rates of mass transport to the nanoparticles and suffers less from the fouling of a single electrode by using high numbers of nanoparticles onto which the target metal can be electrodeposited.

The overall aim of this project is to investigate the electrodeposition of critical metals using nano-impact electrochemistry, as a means of recovering metals from low concentration solutions.

In order to achieve this aim, the following objectives will be carried out. The first step is to investigate the electrodeposition of the metal on carbon surfaces to establish a suitable potential window for subsequent impact experiments. Following this, nano-impact experiments will be performed to confirm the metal is able to deposit on the nanoparticle via impacts. To produce a sufficient volume of modified carbon black nanoparticles to characterise the deposited metal, the impact experiment needs to be upscaled. Characterisation of these nanoparticles can be achieved through techniques such as scanning electron microscopy/ energy dispersive x-ray analysis

(SEM/EDX), x-ray photoelectron spectroscopy (XPS) and inductively-coupled plasma/mass spectrometry (ICP-MS).

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2. EXPERIMENTAL

2.1 Materials and Solution Preparation

All chemicals and materials were purchased commercially and used as received without further purification unless otherwise stated; specific chemicals and materials will be detailed in the relevant results chapters. All solutions were made using ultrapure water of resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$ (MilliQ, Millipore). All glassware was cleaned thoroughly by soaking overnight in Decon 90 (10%), rinsing with ultrapure water, followed by soaking overnight in 0.1 M sulfuric acid solution (Honeywell, 98%) and rinsing with ultrapure water. A suspension of carbon black XC-72 nanoparticles (Fuel Cell Store) was prepared in ultrapure water by sonicating in an ultrasonic bath for 1 hr.

2.1.1 DLS of CB nanoparticles

The hydrodynamic diameter of carbon black XC-72 nanoparticles was determined using Dynamic Light Scattering (DLS) using a Malvern Zetasizer instrument. An aliquot of the carbon black suspension was taken after 1 hr sonication and diluted accordingly. The suspension was placed inside a folded capillary zeta cell (Malvern Panalytical) for analysis.

2.2 Electrochemistry

All experiments were conducted in a standard three-electrode cell inside a Faraday cage. The cell consisted of a saturated calomel reference electrode (SCE), working electrode and graphite counter electrode (5 mm, Goodfellow Cambridge Ltd). All solutions were thoroughly degassed for with nitrogen (oxygen free, BOC gases plc) before experiments and a nitrogen atmosphere was maintained throughout. For

standard electrochemical measurements, an Autolab128 N potentiostat (Metrohm-Autolab BV, Netherlands) was used controlled by a PC with Nova 2.1 software.

2.2.1 Working Electrodes

All working electrodes were polished thoroughly using alumina suspensions of 1, 0.3, and 0.05 μm sequentially on microcloth pads (all from Buehler Inc). The working electrodes used were glassy carbon (GC) electrode (diameter: 3mm) and 33 μm carbon fibre (CF) microelectrode purchased from and IJ Cambria Ltd respectively. Some electrodes used were fabricated in house, as detailed below.

2.2.1.1 Fabrication of Carbon Fibre Microelectrodes

Carbon fibre microelectrodes were made by connecting pitch-derived carbon fibre (Goodfellow Cambridge Ltd) to silver wire using silver conductive paste (RS Pro) and dried in an oven at 60 °C. The wire and carbon fibre were then coated in epoxy resin and allowed to cure overnight. The resulting electrodes were calibrated in a solution of hexaammineruthenium trichloride (Sigma Aldrich, 98%).

2.2.1.2 Fabrication of Graphite Plate Electrodes

Graphite plate electrodes were made by cutting a 2.5 x 2.5 cm square of graphite purchased from Amazon. A silver wire was connected to the graphite using silver conductive paste (RS pro) and this was dried in the oven at 60 °C. The graphite was covered in Araldite epoxy resin and allowed to cure overnight. The resulting electrodes were calibrated in a solution of hexaammineruthenium trichloride (Sigma Aldrich, 98%).

2.2.1.3 CB-modified GC Voltammetry

For CB-modified GC voltammetry, the GC electrode was prepared using a drop-cast method in which 5 μL of a 5 nM aqueous suspension of carbon black was added to a polished GC surface and allowed to dry under nitrogen.

2.2.2 Nano-Impact Electrochemistry

For nano-impact experiments, a three-electrode cell was used with a saturated calomel reference electrode, carbon fibre microelectrode (diameter: 33 μm , 9 μm or array) and graphite counter electrode. The SCE reference electrode was placed inside a glass frit to avoid nanoparticle contamination. The glass frit was prepared by flame-sealing a molecular sieve (Sigma Aldrich, 4Å) in the end of a Pasteur pipette. The glass frit was filled with saturated KCl (Sigma Aldrich, 98%).

Chronoamperometry (duration: 30 s) was conducted in a bespoke low-noise potentiostat controlled by a PC using PyFemto software,¹ with a sampling rate of 100 kHz. The solution was used typically 0.5 -1 mM metal salt with a total of 20 mM supporting electrolyte with and without the presence of carbon black suspension (5-25 μM) was used.

2.2.2.1 Analysis of Impact Electrochemical Data

Unless stated otherwise, impact electrochemical data were analysed following electronic filtration (digital) at 250 Hz in order to improve the signal-to-noise ratio and facilitate analysis. The design of the potentiostat is such that charge is conserved by the filter.² Impact spikes were analysed by using OriginPro 2021 software for spike identification and integration: the baseline was set using the filtered data in short time sections, and the peak search was automated based on a threshold criterion that the

spike height should be at least 80% of the that of the largest spike signal, in order to give confidence that random noise signals were not included in the analysis.

2.2.2.2 Long-Term Impact Experiment

The long-term impact experiment was conducted by performing a 5 hr chronoamperogram inside a 500 mL three electrode cell consisting of a fritted saturated calomel reference, graphite plate working electrode (area: 6.25 cm²) fabricated (as described previously) and graphite counter rods (Alfa-Aesar). A larger concentration of 5 nM of carbon black suspension was used to increase the frequency of impacts. The solution was kept under constant agitation using pre-saturated nitrogen (BOC gases, oxygen-free). The post-chronoamperometric solution was filtered and washed under vacuum using Anodisc 47 filter paper with a pore size of 0.02 µm and diameter of 47 mm. The resulting filter cake was dried at 40 °C.

2.3 Material Characterisation of metal-modified CB nanoparticles

The resulting filter cake consisting of metal-modified CB particles was analysed using various methods detailed below.

2.3.1 SEM/EDX

For SEM/EDX analysis, the metal-modified nanoparticles were attached to an SEM stub using carbon paper and examined using a Hitachi TM3030 Plus electron microscope was used in backscattering mode.

2.3.2 TGA

Thermogravimetric analysis (TGA) (sample mass of approximately 10 mg) was performed using NETZSCH TG 209 F1 in an aluminium oxide crucible at a heating

rate of 10 °C min⁻¹ from 25 to 900 °C under nitrogen purging (10 mL min⁻¹) and compressed air (50 mL min⁻¹).

2.3.3 ICP/MS

For the ICP-MS analysis, aqua regia was used to dissolve three samples. These samples were then diluted using ultrapure water to obtain 1% aqua regia at a concentration of 1 ppm (CB content), and filtered with 0.45µm syringe filters (Fisher Scientific). A Nexion 300X ICP-MS (Perkin Elmer) instrument was used for analysis with a limit of detection of 10 ppt. A calibration curve was produced ranging from 1 ppb to 1 ppm and was used to calculate the metal concentration.

2.3.4 XPS

For the XPS characterization, the samples were analysed (by Dr Long Jiang at Nanoscale and Microscale Research Centre (nmRC), University of Nottingham) using a Kratos Liquid Phase Photoelectron Spectrometer (LiPPS, in dry sample mode) with monochromated Al K α X-ray source (1486.6eV) operated at 10 mA emission current and 12 kV anode potential (120W). Data processing was conducted using CASA XPS software (version2.3.20) for Shirley background subtraction, and peak deconvolution was conducted using a Voigt lineshape function on OriginPro2021.

2.4 References

1. C. Batchelor-McCauley C, J. Ellison, K. Tschulik, P. L. Hurst, R. Boldt and R. G. Compton, *Analyst*. 2015, **140**, 5048-5054.
2. A. V. Oladeji, J.M. Courtney, M. Fernandez-Villamarin, N. V. Rees, *J. Am. Chem. Soc.*, 2022, **144**, 18562-18574.

3. REDOX ELECTROCHEMISTRY OF MN(II) VIA CARBON BLACK NANOPARTICLE IMPACTS

3.1 Abstract

The field of impact electrochemistry, namely, electrochemical processes occurring at nanoparticles during collisions with a substrate electrode, has recently been applied to the recovery of commercially important metals. In this study, the reduction and oxidation of solution Mn(II) were observed on carbon black particles during nano-impacts, with the onset potentials of the reduction and oxidation processes in good agreement with solution voltammetry. The formation of Mn(0) and MnO₂ was confirmed via scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) analysis and X-ray photo-electron spectroscopy (XPS) analysis. Coverages of between 0.2 and 0.6 monolayer equivalents were obtained for the reductive deposition of Mn, whereas for the anodic deposition of MnO₂, a more complex picture was found due to the oxidation pathway from Mn(II) to MnO₂.

3.2 Introduction

The recovery of commercially important metals from waste and/or recycling streams is imperative for their sustainable use as well as minimizing harmful environmental and health hazards associated with disposal. Current recovery methods such as ion exchange,¹ chemical precipitation,² and adsorption/biosorption are generally not economically viable for low concentrations of such metals as they involve costly preconcentration and separation steps.³ These processes are energy-intensive, involve consumption of considerable amounts of reagent, and can generate secondary pollutants.^{4,5} Electrochemical techniques would appear well-suited to metal recovery, with methods such as electrowinning and electrodeposition boasting selective metal

recovery in high purity with a reduced solvent and energy consumption compared to metallurgical methods.^{6,7} However, these techniques usually require a high aqueous metal ion concentration at the industrial scale which is not often the case in waste effluent streams where there are trace concentrations of commonly found heavy metals.⁸

Using nano-impact electrochemistry to recover metal species has numerous advantages compared to other electrochemical methods in that it has a high rate of mass transport to the nanoparticles and lessens the fouling of a single electrode by providing high numbers of particles onto which the target metal can be electroreduced.⁹ This technique involves the introduction of nanoparticles into the solution (containing an inert supporting electrolyte and analyte), which then move under Brownian motion and can randomly collide with the electrode;¹⁰⁻¹⁴ although convection can be applied if required.¹⁵⁻¹⁷ When the working electrode is held at a suitable potential, the particles themselves can either be reduced or oxidized or upon collision the nanoparticles can provide a surface where the oxidation/reduction of a species in solution can take place.¹⁰ It is this latter impact experiment that is relevant to metal deposition, where metal ions in solution can be reduced onto the impacting nanoparticle during the collision. Here, we assume that during impacts, the metal is reduced onto the particle itself; however, when the working electrode and particles are the same material (e.g., carbon), competition can occur between these two materials, and there is a possibility of metal ions being reduced/oxidized on the electrode surface during “impact”.

Analysis of the resulting transient signals can determine a range of information including nanoparticle size, concentration, and charge transfer kinetics of a system.¹⁸⁻

²⁹ In the context of metal recovery, there are few reports concerning the

electrodeposition of metals using nano-impact electrochemistry, and until recently, these were limited to metal nanoparticle cores only.³⁰⁻³² More recently, the electrodeposition of copper onto fly-ash cenospheres and palladium on carbon black has been reported as well as the fabrication of bimetallic catalysts.^{9,33,34}

Manganese is a commercially significant metal used in applications such as batteries and steelmaking.^{35,36} If manganese is left untreated in wastewater, it can cause detrimental health effects, in severe cases leading to “manganism” affecting the central nervous system.³⁷ Current recovery methods of manganese from battery waste rely on metallurgical techniques^{38,39} following an initial physical separation step⁴⁰: a technique such as nano-impact electro-chemistry may be advantageous in terms of efficiency, as it can simplify the recovery process.³³

The bulk electrodeposition of Mn has been well-studied in the literature, primarily in sulfate and chloride solutions.⁴¹⁻⁴³ Despite the higher current efficiency observed when using chloride baths, it is conventionally produced from manganese(II) sulfate/ammonium sulfate solutions to avoid the formation of Cl₂ gas and due to the corrosive nature of the solution.⁴⁴ Ammonium sulfate acts as both an electrolyte and buffer in these solutions,⁴⁴ and it has been speculated that it prevents the formation of insoluble manganese hydroxides during electrodeposition by promoting the formation of soluble ammonium complexes.^{45,46} However, chemical analysis of manganese deposited in the presence of (NH₄)₂SO₄ still results in the presence of oxides and hydroxides.^{47,48}

Another commonly used additive is selenium dioxide which has been shown to inhibit the hydrogen evolution reaction (HER) through the reduction of Se(IV) to Se(0) on the electrode surface, altering its morphology and electrochemical properties such that the

HER overpotential was increased.^{49,50} However, in addition to the toxic nature of SeO_2 , it also results in contamination of the manganese deposits, and precipitation of these compounds in the electrolyte can prove problematic.⁵¹ Organic additives such as carboxylic acids and polyacrylamide have also been tested to improve the crystallinity of deposits with limited success.⁵²

In order to determine whether the nano-impact method maybe a candidate for the recovery of aqueous Mn(II) , this study investigates the deposition of oxidation and reduction products (MnO_2 and Mn) from manganese(II) sulfate solution at neutral pH on carbon black particles (CB, nominal diameter 50 nm) without the use of any additives. Scaled-up deposition experiments were conducted to generate sufficient deposited materials for characterization, and the reduction product was confirmed by X-ray photoelectron spectroscopy (XPS) to Mn(0) on CB, and the product of the oxidative impacts was found to be predominantly $\alpha\text{-MnO}_2$ and MnOOH on CB by Raman spectroscopy and XPS. The oxidative deposition products are found to reflect the complex mechanism of the formation of MnO_2 .

3.3 Experimental

The following chemicals were purchased and used without further purification: manganese(II) sulfate monohydrate (99%, Sigma-Aldrich), potassium sulfate (99%, Sigma-Aldrich), and Vulcan XC-72R carbon black (Fuel Cell Store). All solutions were made using ultrapure water (with a resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$). Solutions were thoroughly degassed using nitrogen (oxygen-free, BOC Gases plc), and a nitrogen atmosphere was maintained throughout experiments. A three-electrode cell arrangement was used for all electrochemical experiments consisting of a standard calomel electrode (SCE, saturated with KCl) as the reference electrode, a graphite rod (5 mm, Goodfellow Cambridge Ltd.) as the counter electrode, and either a carbon fibre

microelectrode (diameters: 9, 33 μm , and array) or a glassy carbon (diameter: 3 mm) macroelectrode as the working electrode. The 9 μm and array working electrodes were made in-house using pitch-derived carbon fibre (Goodfellow Cambridge Ltd.), while the 33 μm carbon fibre electrode was purchased from IJ Cambria Ltd. The glassy carbon (GC) electrode was made in-house using glassy carbon rod purchased from Alfa Aesar. All of the working electrodes were prepared by polishing on microcloth pads with alumina suspensions of 1, 0.3, and 0.05 μm sequentially (all from Buehler Inc.). Unless otherwise stated, the reaction solution consisted of 0.5 mM MnSO_4 and 20 mM K_2SO_4 . All standard electrochemical experiments were conducted using an Autolab 128N potentiostat (Metrohm-Autolab BV, Netherlands) controlled by a PC with Nova 2.1 software. For impact experiments, the solution had carbon black nanoparticles (number concentration of 5 pM) added to it. The carbon black (CB) suspension was sonicated for 30 min before use. Chronoamperograms (duration of 30 s) were conducted using the same three-electrode cell as described previously in a bespoke low-noise potentiostat controlled by a PC with PyFemto software.⁹ Impact electrochemical data were analysed following electronic filtration (digital) at 250 Hz to improve the signal-to-noise ratio and facilitate analysis. Impact spikes were analysed by using OriginPro 2021 software for spike identification and integration: the baseline was set using the filtered data in short time sections, and the peak search was automated based on a threshold criterion that the spike height should be at least 80% of the that of the largest spike signal, in order to give confidence that random noise signals were not counted.

Long-term impact experiments were performed in the solution stated above with the addition of higher-concentration carbon black nanoparticles (500 pM). The three-electrode cell used consisted of a saturated SCE reference electrode in a separate

fritted compartment, graphite plate electrode (diameter: 2.5 cm) as the working electrode, and graphite rods (Alfa Aesar) as the counter electrode. The post-chronoamperometric solution was filtered and washed under vacuum using Anodisc 47™ filter paper with a pore size of 0.02 μm and a diameter of 47 mm, and the resulting filter cake was dried at 40 °C.

For the XPS characterization, the samples were analysed (at NMRC, University of Nottingham) using a Kratos Liquid Phase Photoelectron Spectrometer (LiPPS, in dry sample mode) with monochromated Al K α X-ray source (1486.6 eV) operated at 10 mA emission current and 12 kV anode potential (120 W). Data processing was conducted using CASAXPS software (version 2.3.20) for Shirley background subtraction, and peak deconvolution was conducted using a Voigt lineshape function on OriginPro 2021. For scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) analysis, GC tips were removed post-chronoamperometric scan from the plating solution, attached to carbon tape, and examined using a Hitachi TM3030 Plus electron microscope. For Raman spectroscopy analysis, a Renishaw inVia microscope with a 532 nm laser was used. All data were processed using a combination of Microsoft Excel and OriginPro 2021.

3.4 Results and Discussion

To study the electrodeposition of manganese on carbon, cyclic voltammetry was conducted using a 33 μm carbon fibre working electrode. An onset potential has been defined as a sufficiently negative or positive potential to generate a current response [9], although it can be a controversial parameter due to the range of ways in which it can be defined, many of which are (semi)arbitrary and occasionally have limited physical meaning.⁵³ In this case, a current of ± 5.0 pA has been used to define the onset potential, based on the observed faradaic currents in both the cathodic and anodic

processes (see Figure 3.1). First, a cyclic voltammogram (CV) was recorded in a solution of 20 mM K₂SO₄ at a voltage scan rate of 100 mV s⁻¹, scanning negatively (cathodically) from 0 V (vs SCE) as a control experiment (see Figure 1A). Then, the CV was repeated in a solution containing 0.5 mM MnSO₄ and 20 mM K₂SO₄, and the reduction of Mn(II) was observed (equation 3.1) with an onset potential of -1.44 V (vs SCE) as shown in Figure 3.1A and in good agreement with the literature.⁴⁴

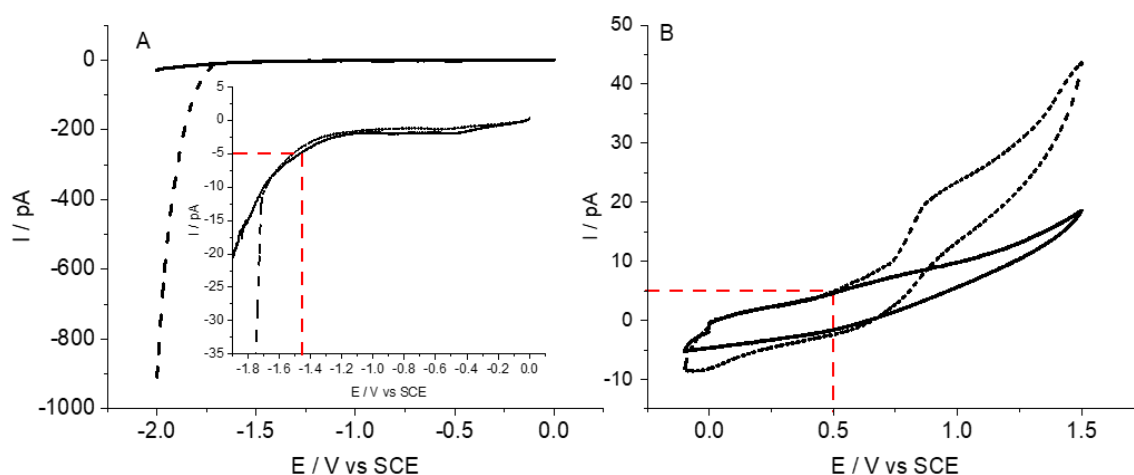
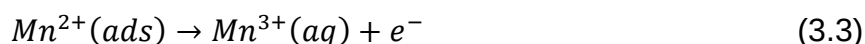
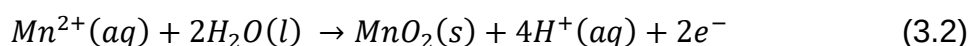


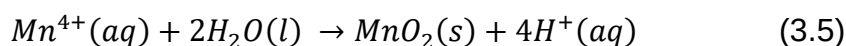
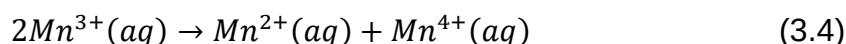
Figure 3.1: Cyclic voltammograms (—) conducted in 20 mM K₂SO₄ and (---) conducted in 20 mM K₂SO₄ and 0.5 mM MnSO₄, respectively, for (A) reductive scans and (B) oxidative scans. Both CVs were recorded using a bare 33 μm diameter carbon fibre working electrode at a scan rate of 100 mV s⁻¹. A dashed red line (---) is used to indicate the onset potential at ± 5.0 pA.

Next, the electrode was thoroughly polished and then scanned in the same degassed solution in the positive (anodic) direction. An oxidative process was observed, and Figure 4.1B shows the result of these CV scans in 20 mM K₂SO₄ and 0.5 mM MnSO₄/20 mM K₂SO₄ solutions at a scan rate of 100 mV s⁻¹. The onset potential of the oxidation, according to the previous definition, was observed at +0.48 V (vs SCE) in good agreement with the literature⁵⁴ corresponding to the oxidation of Mn²⁺(aq) to

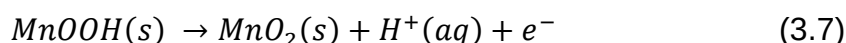
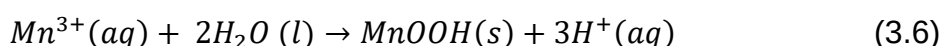
produce MnO_2 , as illustrated in the overall equation 3.2 below.⁵⁵ However, it has been reported that it is unlikely to occur directly and instead occurs via a multistep reaction. The first step in this mechanism is the oxidation of adsorbed Mn^{2+} ions on the electrode surface to Mn^{3+} (equation 3.3), followed by either disproportionation to produce Mn^{2+} and Mn^{4+} (equation 3.4) or hydrolysis to produce an intermediate $MnOOH$ (equation 3.6) depending on the stability of the Mn^{3+} ion in solution. At pH 7, Mn^{3+} is shown to be thermodynamically unstable with respect to disproportionation. Equations 3.5 and 3.7 involving the precipitation of MnO_2 are reported to be kinetically slow.⁵⁵⁻⁶⁰



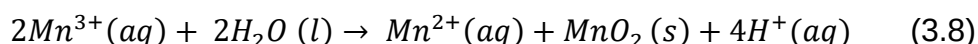
Disproportionation pathway:



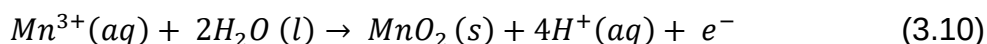
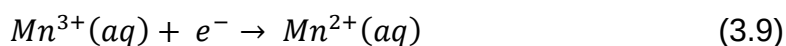
Hydrolysis pathway:



The disproportionation of Mn^{3+} in aqueous solution occurs via the overall equation (4.8):¹



This equation is the combination of the following two half equations:



The standard Gibbs energy ΔG^0 can be calculated from the standard electrode potential E^0 via:

$$\Delta G^0 = -nFE^0 \quad (3.11)$$

where n = number of electrons transferred and $F = 96485 \text{ C mol}^{-1}$

For non-standard conditions, the Gibbs energy ΔG can be calculated from:

$$\Delta G = \Delta G^0 + RT \ln \frac{[Mn^{2+}][H^+]^4}{[Mn^{3+}]^2} \quad (3.12)$$

where R is $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, and the activities of each species have been approximated to concentrations.

Table 3.1: Standard electrode potentials, standard free energies, and Gibbs energy at 298 K, pH 7.

Reaction Equation	E^0 / V	ΔG^0 / kJ mol ⁻¹	ΔG / kJ mol ⁻¹
$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$	+ 1.542 [61]	-149.0	-
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	+ 1.224 [61]	-	-
$Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + e^-$	+ 0.905	-86.84	-
$2Mn^{3+}(aq) + 2H_2O(l) \rightarrow Mn^{2+}(aq) + MnO_2(s) + 4H^+(aq)$	-	-235.8	-141.1

Note the summation of ΔG^0 for reaction equations 3 and 1 gives ΔG^0 for the overall reaction (eqn 3.8). ΔG_m for the overall reaction (equation 3.8) has a negative value, indicating Mn^{3+} is thermodynamically unstable with respect to disproportionation.

The electrodeposition of manganese and manganese dioxide on carbon working electrodes was further investigated using SEM/EDX analysis to establish a potential window to use in the impact electrochemistry experiments. A chronoamperometric experiment was conducted in a degassed solution containing 20 mM potassium sulfate and 10 mM manganese sulfate for 5 min at various potentials between -1.6 and +1.0

V (vs SCE). The tip of the GC working electrode was then analysed using SEM/EDX. Figure 4.2 A shows the average manganese-to-carbon ratio obtained using EDX analysis at a magnification of 2000 $\times$. Significant levels of manganese were observed at overpotentials negative of -1.45 V (vs SCE), consistent with the onset potential for Mn(II) reduction. Significant levels of manganese were also observed at overpotentials positive of $+0.8$ V (vs SCE). A small amount of manganese was observed at potentials between $+0.5$ and $+0.8$ V (vs SCE), which is consistent with the onset potential for Mn(II) oxidation as previously stated. The resulting charge from integration of the chronoamperograms is shown in Figure 3.2B.

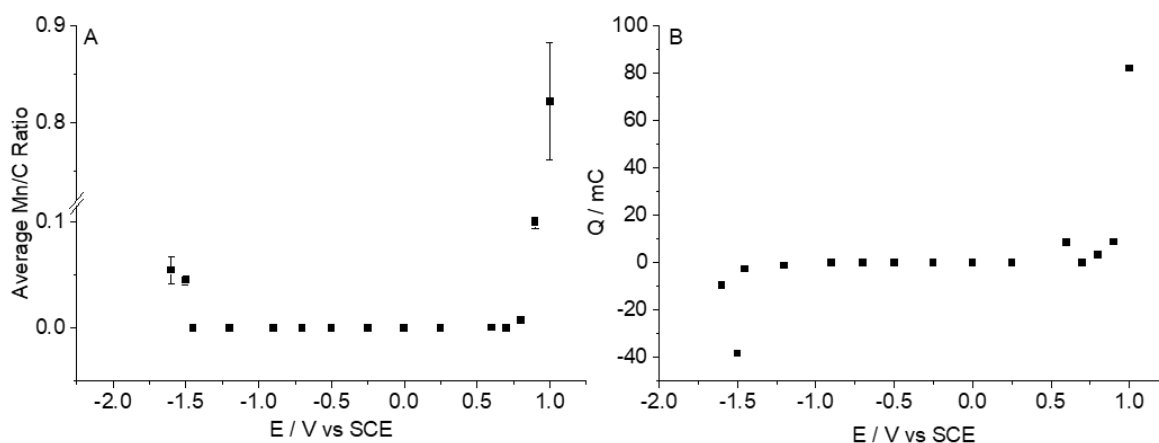


Figure 3.2. Graphs showing (A) the average Mn/CB ratio based on weight percent obtained via SEM/ EDX analysis at 2000 $\times$ for GC tips removed from the post-chronoamperometric solution (containing 10 mM MnSO_4 and 20 mM K_2SO_4) across various potentials and (B) the integrated charge (Q / mC) from the respective chronoamperograms.

Photographs and SEM images of the GC electrodes were obtained at a magnification of 2000 $\times$ at these two potentials, showing a needle-type structure for the electrode held at -1.6 V vs SCE and a continuous film with some defects for the electrode held at $+1.0$ V vs SCE (see Figure 3.3).

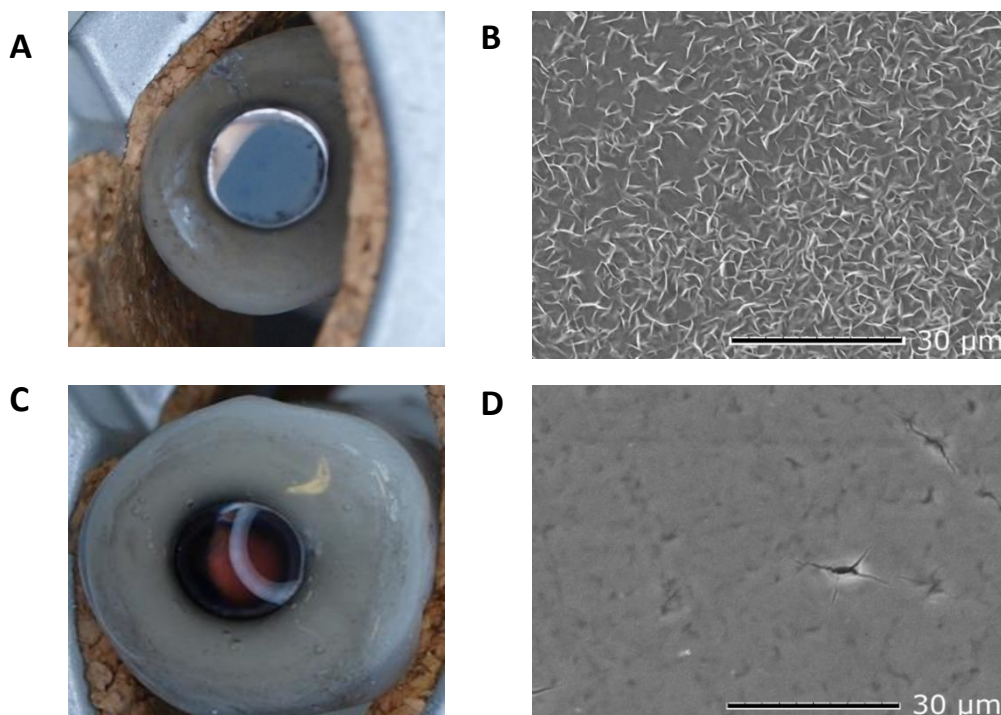


Figure 3.3. A) Photograph of a GC electrode with an electrodeposited Mn film

(chronoamperogram conducted at -1.6 V vs SCE). B) SEM image at a magnification factor of 2000 of the deposited film. C) Photograph of a GC electrode with an electrodeposited MnO₂ film (chronoamperogram conducted at $+1$ V vs SCE). D) SEM image at a magnification factor of 2000 of the deposited film.

3.4.1 Nano-Impact Experiments

To determine whether impacts could be detected due to manganese reduction and oxidation processes, chronoamperometry was conducted with and without the addition of carbon black (5 pM) in a solution containing 0.5 mM MnSO₄ and 20mM K₂SO₄ at a series of potentials from $+0.9$ to -1.6 V (vs SCE). Impact experiments were performed at potentials from -1.4 to -1.6 V (vs SCE) to observe the reduction process (eq 3.1). Impacts were observed with an onset potential of -1.45 ± 0.01 V (vs SCE), in good agreement with Figure 3.1, and a plot of the charge passed (Q / fC) is given in Figure 3.4 along with a typical chronoamperogram. It is noted that a variety of spike forms are present from single sharp features to larger “step on, step off”-type signals, indicating a range of impact durations and particle–electrode interactions^{33,62} as

shown in Figure 4.3A. Figure 4.3B shows the variation in charge passed per impact with potential and the onset potential of ca. -1.45 V (vs SCE). The charge was calculated using the following equations (3.13 - 3.17).

$$S_{CB} = 4\pi r^2 \quad (3.13)$$

$$N_{Mn} = \frac{Q}{ez} \quad (3.14)$$

$$N_{mono} = 0.7405 \frac{S_{CB}}{\pi r^2} \quad (3.15)$$

$$N_{mono} = \frac{S_{CB}}{ab} \quad (3.16)$$

$$\theta = \frac{N_{Mn}}{N_{mono}} \times 100\% \quad (3.17)$$

where S_{CB} is the surface area of 1 carbon black particle, r is the atomic radius of the Mn atom = 129 Å [58], N_{Mn} is the number of Mn atoms, Q is the charge passed in impact events, e is the electronic charge, z is the number of electrons transferred, N_{mono} is the number of Mn atoms in one monolayer, a/b are lattice parameters of MnO_2 = 9.68 Å [59] and θ is the calculated coverage.

The apparent trend of the lowering in mean charge passed per impact as overpotential increases is due to some data points skewing the mean hence the large overlapping error bars. Impact experiments are often subject to significant variation due to the multiple factors that contribute to the range of charges measured at each potential, such as the number of measurements, the size of impacting particle (single vs aggregated), the shape of the impact signal (sharp single spikes vs “bursts” of spikes vs step on–step off spikes), and other reactions that may occur on the particles at those potentials (e.g., hydrogen evolution etc.). The calculated coverage (Figure 3.4C) at all potentials was found to be less than monolayer indicating slow kinetics for manganese reduction.

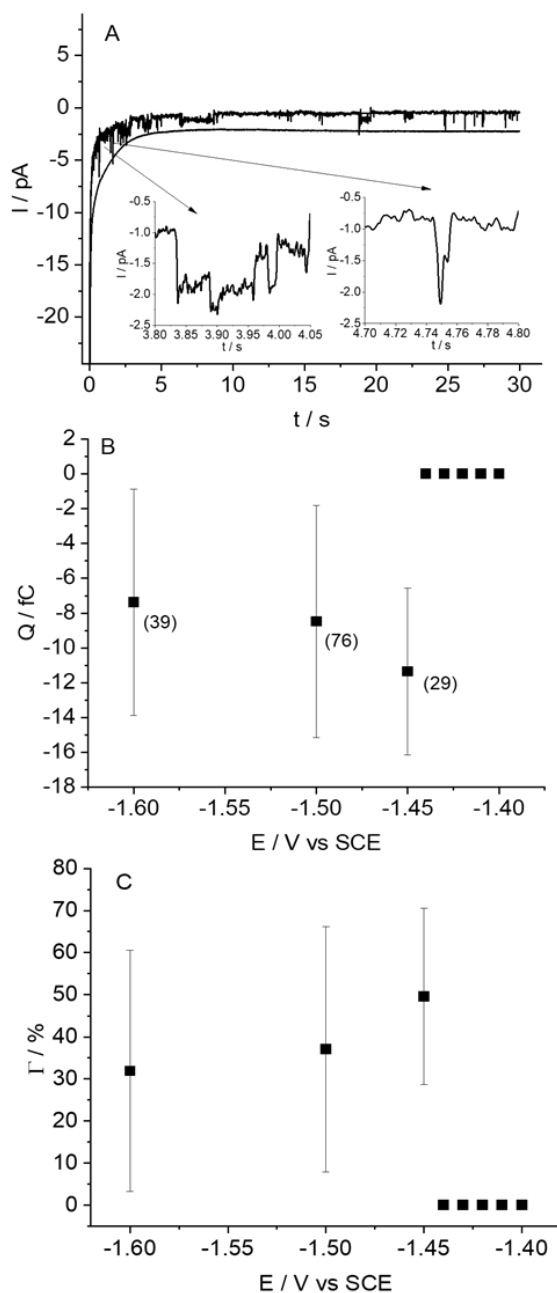


Figure 3.4. (A) Representative 30 s chronoamperogram conducted in a solution containing 0.5 mM MnSO_4 and 20 mM K_2SO_4 solution with a 9 μm diameter CF electrode held at -1.6 V vs SCE before (i) and after (ii) the addition of 5 pM carbon black nanoparticles with an inset example of two zoomed in different impacts indicating different particle-electrode interactions. (B) Integrated charge (Q / fC) from impact events from -1.4 to -1.6 V vs SCE with bracketed numbers indicating the number of impacts analysed at the respective potential. (C) Calculated coverage of manganese on carbon black. and 0.5 mM MnSO_4 with the addition of 5 pM carbon black nanoparticles.

Analogous impact experiments were conducted between +0.40 and +0.90 V vs SCE to investigate the oxidation of Mn(II), and these results are shown in Figure 3.5. The onset of oxidative spikes was observed at $+0.50 \pm 0.01$ V (vs SCE) also in good agreement with Figure 3.1. An example of a typical chronoamperogram is shown in Figure 3.5 A, along with the integrated average charges of the oxidative impacts (Figure 3.5 B).

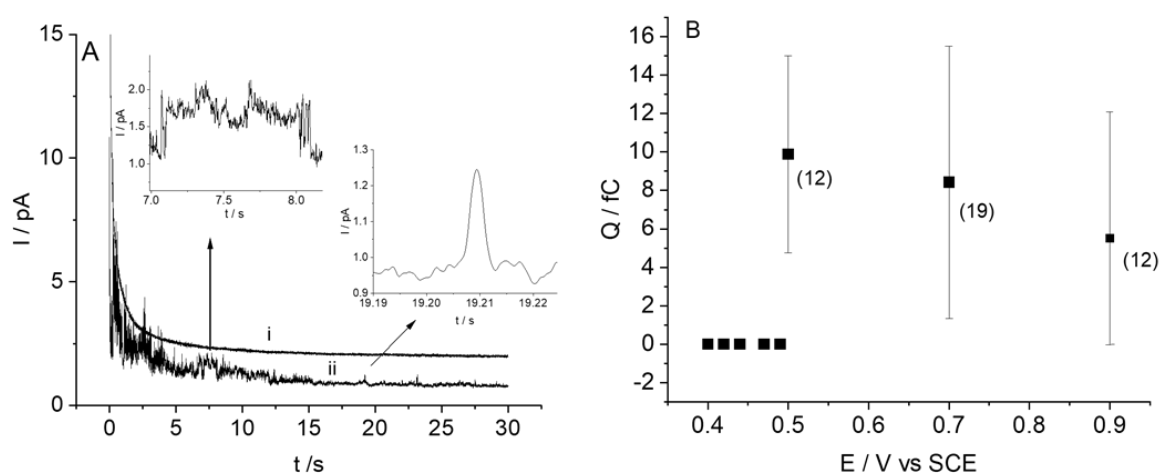


Figure 3.5 A shows a representative 30 s chronoamperogram conducted in a solution containing 0.5 mM MnSO_4 and 20 mM K_2SO_4 with a 9 μm diameter CF electrode held at +0.90 V vs SCE before (i) and after (ii) the addition of 5 pM carbon black nanoparticles with an inset of different zoomed in impact events. Figure 3.5B shows the integrated charge (Q / fC) from impact events ranging from a potential of +0.40 to +0.90 V vs SCE.

To obtain direct evidence of Mn deposition on the carbon black nanoparticles, the experiment was scaled up to a 500 mL cell and a 5 hr chronoamperogram was recorded at a potential of -1.60 V vs SCE, as this provided a significant overpotential compared to the onset potential of -1.44 V (vs SCE). A three-electrode cell consisting of a saturated SCE (KCl) reference electrode encased in a separate fritted compartment, a graphite plate working electrode and graphite rod as the counter electrode was used in a solution containing 20 mM K_2SO_4 and 0.5 mM MnSO_4 with

the addition of 500 pM carbon black nanoparticles. The reaction solution was thoroughly de-oxygenated and kept under constant agitation with nitrogen gas to maintain an oxygen-free solution, prevent sedimentation of the carbon black suspension, and increase the number of impact events. After the experiment, the solution was filtered and dried at 40 °C to yield the modified carbon black particles, which were analysed using SEM/EDX which revealed the presence of deposited manganese in an average carbon to manganese to carbon weight percent ratio of 0.030 ± 0.007 as displayed in table 3.2. An SEM image of modified CB NP deposited at -1.6 V vs SCE is shown in Figure 3.6 and EDX mapping of the particle shown in Figure 3.7. In addition to the manganese deposit, EDX detected the presence of aluminium presumably due to the working electrode preparation as well as potassium and sulfate covering the particles, presumably due to residual electrolyte.

Table 3.2 shows the manganese content for unmodified CB nanoparticles, the sample held at -1.6 V, +0.5 V, and +0.7 V vs SCE during chronoamperometry.

CB NP Samples	SEM EDX Average Weight% Ratio Mn/CB / 10^{-3}
unmodified	0
-1.6 V vs SCE	30 ± 7
+0.5 V vs SCE	20 ± 7
+0.7 V vs SCE	0.3 ± 0.2

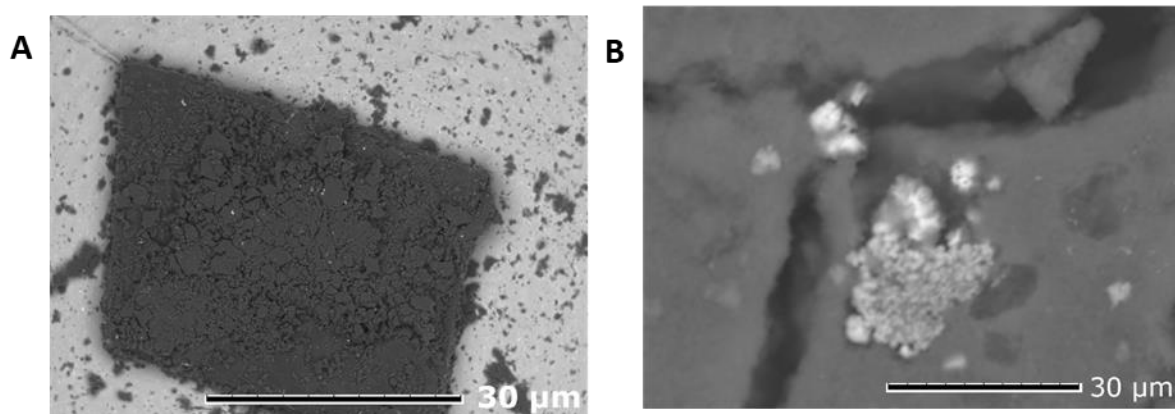


Figure 3.6 shows an SEM image of modified CB particles at a magnification factor of A) 40 and B) 1200. The chronoamperometry scan was conducted at -1.6 V vs SCE.

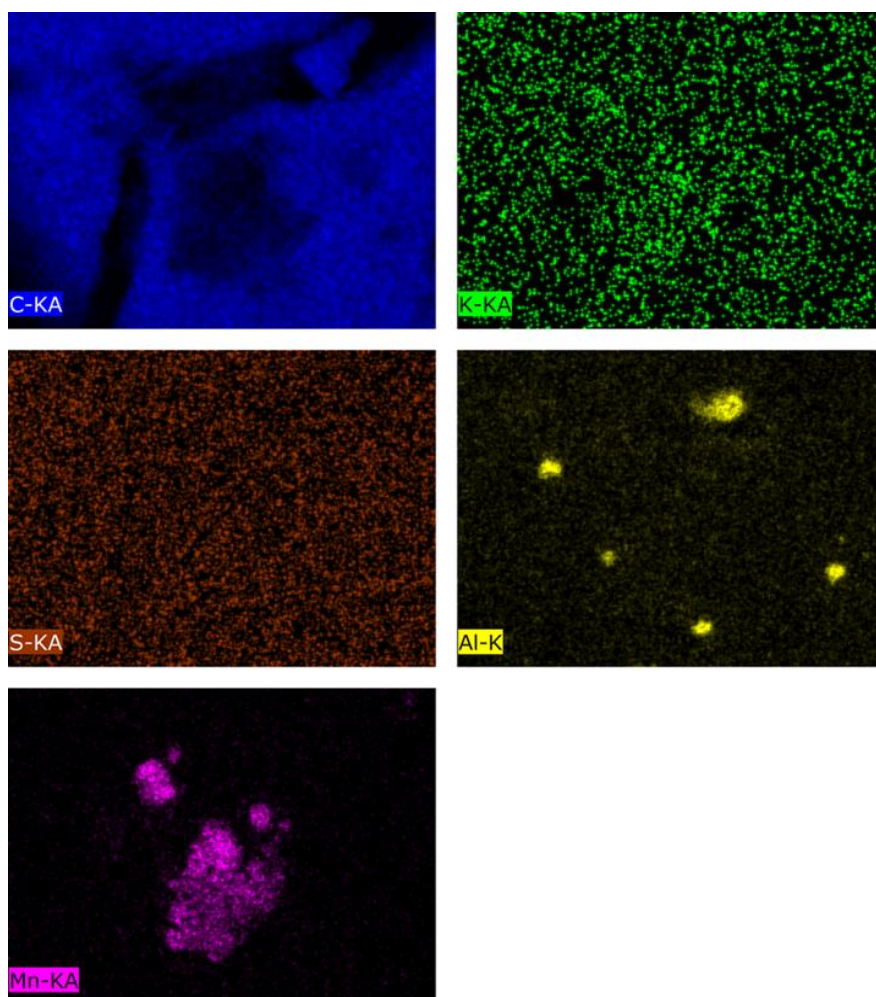


Figure 3.7 shows the EDX mapping of the modified CB particles deposited at -1.6 V vs SCE.

The upscaled experiment was repeated for the manganese oxidation process using potentials of +0.50 V (onset of oxidative spikes), and +0.70 V vs SCE. Following the filtration of the solution, the SEM/ EDX analysis of the resulting carbon black powder surprisingly revealed manganese deposited at +0.50 V with only trace detected at +0.70 V (see table 3.1). An SEM image of the modified CB NP particles is shown in Figure 3.8. We postulate that this is due to the complex non-equilibrium pathways of MnOx formation on the nanoscale⁶³⁻⁶⁸ which often involve metastable states such as α -, β -, γ -MnOOH. DFT calculations reported by Ceder *et al.*⁶⁵ suggests that the above oxidizing potentials of +0.50 and +0.70 V (vs SCE) would correspond to metastable states of β -MnOOH and γ -MnOOH/MnO₂ (rutile) respectively. The picture is further complicated by the stability of the states being dependent on size (surface energy) as well as pH and potential⁶⁵, which suggest that MnOOH and MnO₂ species may not be stable at sizes below several nm. We conclude that the significant decrease in the amount of Mn detected from impacts recorded at +0.5 V to +0.7 V (vs SCE) indicates the interplay between the kinetics of the Mn(II) oxidation, with the relative stability of the metastable oxyhydroxide and oxide species as nucleating nanoclusters at the two potentials.

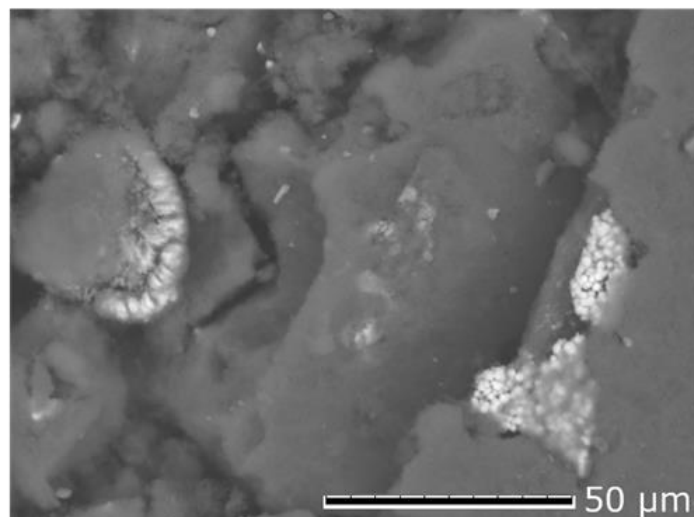


Figure 3.8: SEM image of Mn/CB deposited at +0.5 V vs SCE.

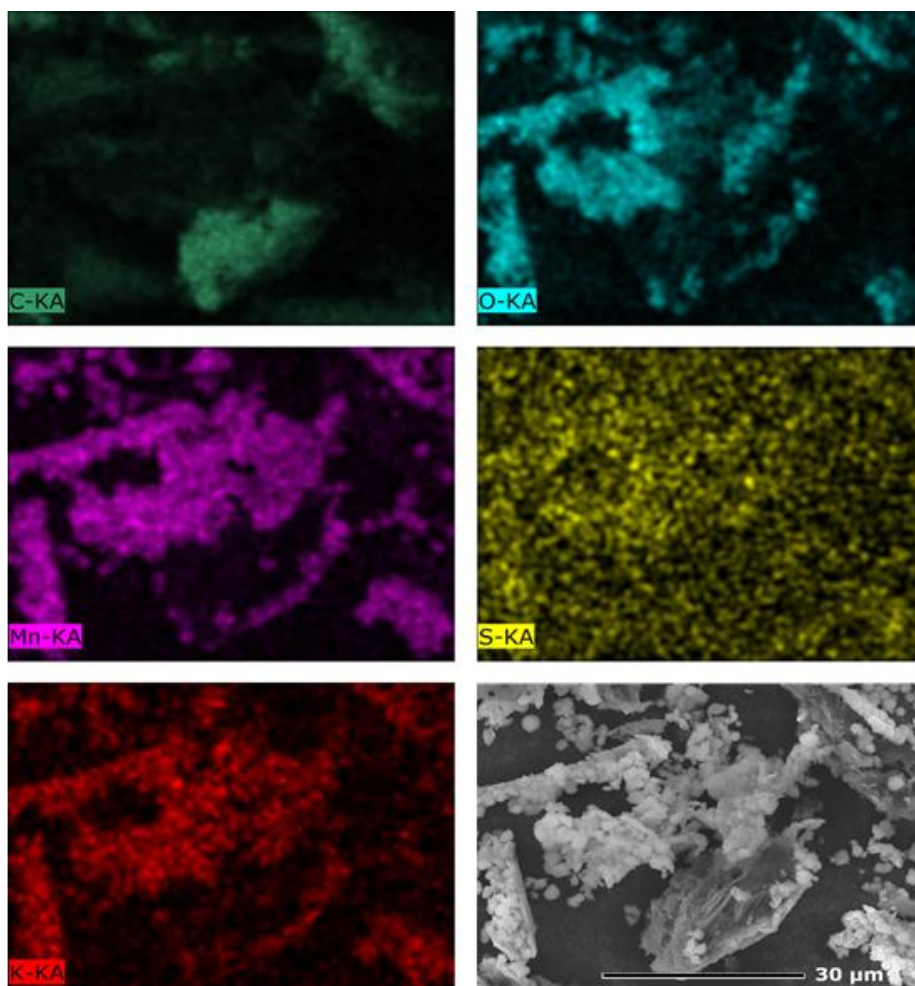


Figure 3.9: EDX Mapping of electrodeposited Mn oxide on graphite plate electrode held at +0.7 V vs SCE.

At very low overpotentials (i.e., close to the onset potential for observation of current spike signals), a black deposit was observed on the graphite electrode surface, which was confirmed to contain manganese and oxygen via SEM/EDX (figure 3.9), suggesting deposition of MnOx had preferentially occurred on the substrate electrode. There was also the presence of potassium and sulfate detected, presumably from the electrolyte solution.

Raman spectroscopy was used to provide evidence on the identity of the MnOx species, due to its use in characterising manganese oxides.⁷⁰⁻⁷⁵ The Raman spectrum of the substrate electrode surface (figure 3.10) exhibited 4 strong bands at 138, 501, 575 and 654 cm^{-1} as well as weaker bands at 301 cm^{-1} , 746 cm^{-1} , 610 cm^{-1} and broad feature at 187 cm^{-1} . No peaks were present in the spectrum of the unmodified graphite plate electrode (see figure 3.10) in the chosen range (100-1000 cm^{-1}) indicating that the peaks were due to an electrodeposited manganese species and not due to the graphite electrode.

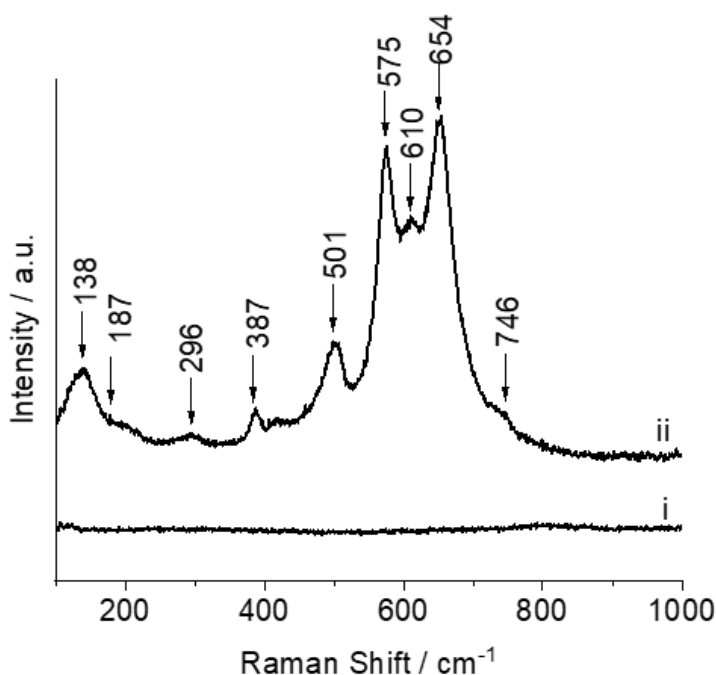


Figure 3.10: Raman spectrum of i) the unmodified graphite plate electrode and ii) the graphite plate electrode with electrodeposited Mn species.

Table 3.3 shows the tabulated Raman signals of the recorded spectrum (figure 3.10) compared to literature values for shifts corresponding to that of α , β , and γ forms of MnO_2 .^{70,72-74} The recorded Raman spectrum exhibits all the peaks reported in literature corresponding to α - MnO_2 (187, 387, 577 and 654 cm^{-1}). The latter two bands (577 and 654 cm^{-1}) correspond to the two symmetric vibrations of Mn-O characteristic of α - MnO_2 .⁷⁰ The sharp band exhibited at 387 cm^{-1} is due to the Mn-O bending vibration.^{72,73} It is reported that the formation of the crystal phase of MnO_2 is largely dictated by the potassium concentration; the α - MnO_2 (2×2) tunnel can be stabilised by K^+ ions present in the K_2SO_4 supporting electrolyte which may explain the formation of this crystal phase.⁷¹

Table 3.3: Raman Shift values obtained from spectrum in Figure 3.10 compared to literature values for α - MnO_2 , β - MnO_2 , γ - MnO_2 and MnOOH . Assignment of shifts are given in the text.

	α - MnO_2 Raman Shift / cm^{-1}			β - MnO_2 Raman Shift/ cm^{-1}	γ - MnO_2 Raman Shift/ cm^{-1}	MnOOH Raman Shift/ cm^{-1}
Experimental Raman Shift / cm^{-1}	70	72	73	74	70	70
746	649	640	636	750	770	625
654	582	585	574	667	658	560
610	-	515	-	538	582	530
575	392	386	387		527	494
501	185	184	183.2		494	389
387					278	359
296						285
187						259
138						148

In addition to these peaks, the spectrum exhibits weaker shifts at 138 cm^{-1} , 301 cm^{-1} , 501 cm^{-1} , 610 cm^{-1} and 746 cm^{-1} which do not correspond with bands observed in the $\alpha\text{-MnO}_2$ Raman spectra presented in the literature.^{70,72,73} Some of these remaining peaks (138 cm^{-1} , 301 cm^{-1} , 501 cm^{-1} and 746 cm^{-1}) are present in $\beta\text{-MnO}_2$ [74], $\gamma\text{-MnO}_2$, and MnOOH ⁷⁰ Raman spectra (see table 3.4), in addition to peaks in similar positions to that of $\alpha\text{-MnO}_2$ which may lead to some potential overlapping of peaks in the spectra. We postulate the electrodeposited species is therefore predominantly $\alpha\text{-MnO}_2$ with small amounts of $\beta\text{-MnO}_2$ $\gamma\text{-MnO}_2$, and unreacted MnOOH consistent with the previously described hydrolysis pathway for the mechanism of the oxidation of manganese dioxide (see equation 3.6 and 3.7).⁵⁵

To attempt to prevent deposition on the electrode, the upscaled experiment was repeated at the lower potential of $+0.50\text{ V}$ (vs SCE), that is, corresponding to the onset potential of MnO_2 deposition. The dried carbon particles were analysed first using SEM/EDX revealing an average weight percent ratio of manganese to carbon of 0.020 ± 0.007 (see table 3.3). XPS was used to elucidate the identity of the electrodeposited species. The Mn $2p$ spectrum is displayed in figure 3.11 in which spin-orbit coupling is observed as expected resulting in a doublet consisting of a $2p_{3/2}$ peak centred at a binding energy of 639.4 eV which is twice the intensity of the $2p_{1/2}$ peak centred at 650.6 eV . In addition to these two peaks, a small broad feature is observed to the left of the $\text{Mn}2p_{3/2}$ and $\text{Mn}2p_{1/2}$ peak at 640.1 eV and 651.7 eV respectively which could indicate the presence of “shake-off” satellite peaks; a feature commonly observed in Mn $2p$ spectra⁷⁵ arising from a core electron being removed completely by photoionisation. The assignment of the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks can be somewhat

ambiguous due to the small difference in binding energies observed for Mn(III) and Mn(IV).⁷⁵⁻⁷⁸

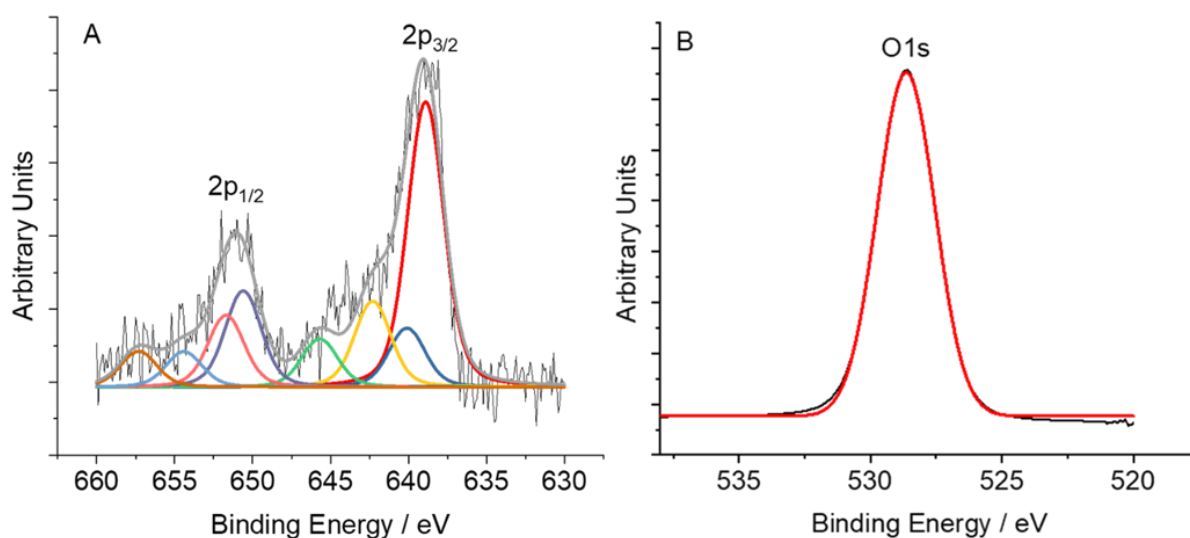


Figure 3.11 shows the XPS spectra of 0.5 V vs SCE modified CBNP consisting of A) High resolution Mn 2p XPS spectrum with cumulative peak fit shown in grey. Core level $2p_{3/2}$ peak fitting for Mn(III) shown in (—) and (—) for Mn(IV) with their corresponding satellite peaks shown in (—) and (—) respectively. Core level $2p_{1/2}$ peak fitting for Mn(III) shown in (—) and (—) for Mn(IV) with their corresponding satellite peaks shown in (—) and (—) respectively. B) High resolution O1s level with peak fitting shown in (—).

For this reason, the deconvolution of the four peaks was conducted for a number of possible scenarios consisting of the sole presence of Mn(III) or Mn(IV) and the combination of these two species with and without the presence of the satellite peaks. The best fit ($R^2 = 0.929$) was achieved for the presence of Mn(III) and Mn(IV) peaks with satellite peaks (figure 3.12). This is consistent with the MnOOH and MnO₂ species observed previously on the graphite substrate electrode using Raman spectroscopy (fig 3.10 and table 3.4). Furthermore, the O 1s spectra (fig 6B) exhibits a broad peak centred at a binding energy of 529 eV which is indicative of O²⁻ present.⁷⁸

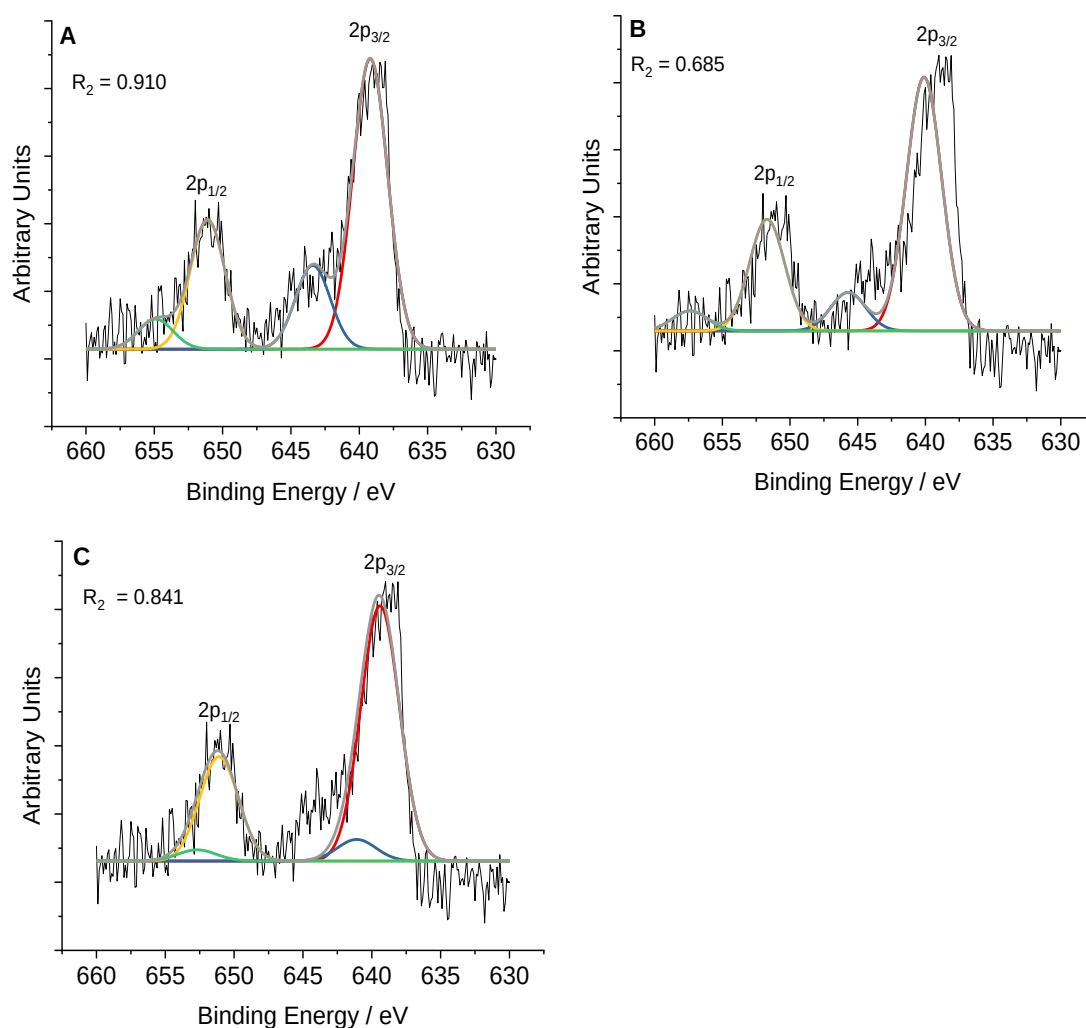


Figure 3.12 A) Peak fitting for Mn(III), B) peak fitting for Mn(IV) and C) peak fitting for Mn(III) and Mn(IV) with the absence of satellite peaks.

3.5 Conclusions

Microelectrode studies and macroelectrode studies on GC indicated that the onset for Mn(II) reduction and oxidation agrees well with literature. Using impact electrochemistry, Mn(II) reduction and oxidation onto carbon black nanoparticles were demonstrated, where the switch on potential aligns with previously observed onset potentials (-1.44 V vs SCE and +0.5 V vs SCE) respectively. The upscaled impact experiment gave direct evidence for Mn deposition on carbon black shown by SEM/

EDX analysis. Lower than expected amounts of MnO₂ were found on the CB NPs, in addition to some intermediate species, which we postulate was due to the mechanism of oxidation of Mn(II). For the development of this method for depositing metals, the use of carbon black particles with a carbon substrate electrode limits the efficiency of deposition/recovery: alternative electrode materials with higher overpotentials for the reduction of the metal of interest should be used to achieve better selectivity in the deposition (i.e. depositing wholly onto the CB particles and not the substrate electrode). Ideally these materials should also have high overpotentials for the hydrogen evolution reaction, and current work is underway to explore the fabrication and use of alternative materials (such as BDD) as microelectrodes for use in this way.

3.6 References

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4. ELECTROCHEMICAL RECOVERY OF RUTHENIUM VIA CARBON BLACK NANO-IMPACTS

4.1 Abstract

The recovery of ruthenium from low-concentration solutions poses a significant challenge due to its scarcity and rising economic value, and nano-impact electrochemistry has emerged as a promising method for efficient recovery of critical metals from solution through deposition during impacts of non-metallic nanoparticles.¹⁻

³ In this study, we investigate the redox chemistry of ruthenium on carbon black via the impact technique and demonstrate the ability to recover ruthenium from solution. The reduction (electrodeposition) and oxidation of Ru(III) ions in solution onto carbon black nanoparticles can be observed during nano-impacts with the respective onset potentials of these redox processes agreeing with those obtained from solution voltammetry. Upscaled experiments focusing on the electroreduction process, led to the formation of RuOx deposits, confirmed through scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) analysis, X-ray photoelectron spectroscopy (XPS) analysis, and thermogravimetric analysis (TGA). Under partially-optimised conditions, >90% recovery of Ru(III) from a 1 mM solution was achieved in ca. 8 hours.

4.2 Introduction

Platinum group metals (PGMs) play a pivotal role in modern society for use in catalysts for industrial and automotive applications as well as providing sustainable solutions to energy production (e.g., fuel cells). PGMs (Pt, Pd, Ru, Ir and Rh), have been identified as being critical materials by the European Commission.⁴ Despite traditional PGM catalysts mainly containing platinum and/or palladium, recent emphasis is being

placed on “minor PGMs” (e.g., ruthenium) as being key metals in the energy transition to net zero emissions.⁵ This is reflected in the price of ruthenium which has risen significantly in the past ten years from \$72.00/troy oz (May 2014) to \$430/troy oz (May 2024) due to a sustained demand, constrained supply and increasing interest in this metal in both chemical and electrochemical processes.⁵ Primary uses of ruthenium include catalysts for chemical processes such as the production of feedstocks for nylon synthesis⁶ as well as electrical and electronic applications. Furthermore, ruthenium is an electrocatalyst for long-established electrochemical processes such as the chlor-alkali process,⁶ hydrogen evolution,⁷ oxygen evolution⁸ as well as in ruthenium/platinum based electrocatalysts for direct methanol fuel cells (DMFCs).⁹⁻¹²

The current ruthenium supply is adequate to meet demand for this critical metal, however the development of recovery and recycling methods is imperative for its continued sustainable use. At present, only 5-15% of ruthenium is being recycled providing just 11% of its current demand.^{13,14} Recovery of ruthenium from solution is heavily reliant on hydrometallurgical techniques which consume large volumes of expensive and often toxic solvents, and face issues related to limited selectivity and low purity¹⁵⁻¹⁷ and so electrochemical methods for recovery have become increasingly attractive due to reduced solvent and energy consumption.¹⁸ However, a high aqueous metal ion concentration is required at the industrial scale which is not often the case in waste effluent streams where there are trace concentrations of heavy metals.

The electrodeposition of ruthenium from aqueous solutions is not well-reported in the literature¹⁹ and is mainly from nitrosyl salts and nitric acid solutions.^{20,21} Some work has been reported on deposition from RuCl_3 in deep eutectic solvents and ionic liquids which can control the speciation of the Ru species and limit hydrogen evolution due to the wider potential window of these solvents.²² However, these processes often utilise

high concentrations of Ru^{3+} (40 mM), and elevated temperatures (70-80 °C), as well as requiring the use of harmful additives such as sulfamic acid.²² Conversely, the electrodeposition of ruthenium dioxide is widely reported but often lacks mechanistic details²³⁻²⁵ as more emphasis is placed on the performance of this material as an electrocatalyst and supercapacitor.^{24,26,27} Therefore, it is of interest to study the electrodeposition of these two species from low concentration aqueous chloride solution for applications in waste solution treatment.

The use of nano-impact electrochemistry is one alternative technique to recover low concentration metal species from solution, and can utilise non-metal¹⁻³ as well as metal core particles.²⁸⁻³¹ It benefits from high rates of mass transport to the nanoparticles and suffers less from the fouling of a single electrode by using high numbers of nanoparticles onto which the target metal can be electrodeposited.

“Recovery impact experiments” in which metals are recovered from low concentration metal solutions via deposition under “impact” onto carbon supports have been recently reported^{2,3} as a long-term upscaled version of the previously described impact experiment. Unlike conventional impact experiments, these systems use a high concentration of nanoparticles and are constantly agitated with nitrogen to both enhance mass transfer as well as maintaining the carbon black suspension during the extended time period. Furthermore, a larger working electrode is typically employed to increase the frequency of impacts.

In order to determine whether the nano-impact method may be a candidate for the recovery of aqueous Ru(III) , this study investigates the deposition of Ru(0) and RuO_2 from ruthenium(III) chloride solution at pH 2 and pH 7 respectively on carbon black (CB) particles (XC-72, 30-60 nm).³² A scaled-up deposition experiment was conducted

to generate sufficient deposited material for characterisation, and the reduction product was confirmed by X-ray photoelectron spectroscopy (XPS) as RuO₂ on CB.

4.3 Experimental

4.3.1 Chemicals

All chemicals were used as received unless otherwise stated, namely ruthenium(III) chloride hydrate (99.99%, Thermo Scientific), potassium chloride (99.0 – 100.5%, Alfa Aesar), hydrochloric acid (37.0%, Honeywell) and 50 nm carbon black XC-72 nanoparticles (Fuel Cell Store). All solutions were made using ultrapure water of resistivity ≥ 18.2 M Ω cm (MilliQ, Millipore).

4.3.2. Electrochemistry

Electrochemical experiments were conducted in a three-electrode setup inside a Faraday cage. Prior to each experiment, all solutions were thoroughly degassed with nitrogen (oxygen-free, BOC Gases plc), and a nitrogen atmosphere was maintained throughout. The working electrodes employed were a glassy carbon (GC, 3 mm diameter, BASI Inc.) electrode and carbon fibre (CF) microelectrodes (9 μ m, made in house using pitch-derived carbon fibre from Goodfellow Cambridge Ltd.). The working electrodes were polished with alumina suspensions of 1, 0.3, and 0.05 μ m on microcloth pads (all from Buehler Inc.), used sequentially. A saturated KCl calomel electrode (SCE, BASI Inc.) was used as the reference electrode, and a graphite rod (Goodfellow Cambridge Ltd.) was used as the counter electrode. During impact experiments, the reference electrode was placed in a glass fritted compartment to prevent nanoparticle contamination. A bulk solution of CB nanoparticles was prepared and sonicated for 1 hr before use and an aliquot (26 μ L) was taken to achieve the desired nanoparticle (NP) concentration of 25 pM. Unless otherwise stated, the

solution used was 1 mM ruthenium(III) chloride with 10 mM potassium chloride and 10 mM hydrochloric acid.

The speciation of 1 mM ruthenium(III) chloride, 10 mM KCl and 10 mM HCl was calculated using equilibrium constants from Fine and Connick³³ as shown in Table 4.1. Due to the lack of data available for the first reaction, it was assumed the starting complex of ruthenium chloride in solution was $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$. The predominant species being $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ in agreement with literature.³⁴

For standard electrochemical experiments, an Autolab 128N (Metrohm UK) was used, controlled via a PC running Nova 2.1 software. For impact experiments, a previously described bespoke low-noise potentiostat was used, controlled via a PC running PyFemto software.³⁵ All data was processed using a combination of Microsoft Excel and OriginPro 2023. Electrochemical impact data was analysed following electronic (digital) filtration at 250 Hz to improve the signal-to-noise ratio and facilitate analysis. Impact spikes were analysed by using OriginPro 2024 software for spike identification and integration.

For the long-term impact experiments, a chronoamperogram was performed in a 500 mL cell with a higher carbon black particle concentration of 500 pM for 5 hours. A large graphite plate working electrode (area: 6.25 cm²) was used along with a saturated SCE reference encased in a glass fritted compartment and a graphite rod as the counter electrode. The solution was constantly agitated with pre-saturated nitrogen at a volumetric flow rate of 1 L min⁻¹ to inhibit agglomeration of the CB particles and to increase the frequency of impact events. The modified CB particles were filtered using Whatman® Anodisc 47™ filter paper and the resulting filter cake was dried at 40 °C.

Table 4.1: Calculated Equilibrium Concentrations of 1 mM RuCl₃ in 10 mM KCl and 10 mM HCl.

	K/ mol ⁻¹ dm ³	Species	Calculated Equilibrium Concentration / mol dm ⁻³	Species in solution / %
[Ru(H ₂ O) ₆] ³⁺ + Cl ⁻ ⇌ [RuCl(H ₂ O) ₅] ²⁺ + H ₂ O	Data unavailable	[RuCl(H ₂ O) ₅] ²⁺	-	-
[RuCl(H ₂ O) ₅] ²⁺ + Cl ⁻ ⇌ [RuCl ₂ (H ₂ O) ₄] ⁺ + H ₂ O	30.0 ³³	[RuCl ₂ (H ₂ O) ₄] ⁺	6.00 × 10 ⁻⁴	100
[RuCl ₂ (H ₂ O) ₄] ⁺ + Cl ⁻ ⇌ [RuCl ₃ (H ₂ O) ₃] + H ₂ O	2.7 ³³	[RuCl ₃ (H ₂ O) ₃]	3.24 × 10 ⁻⁵	-
[RuCl ₃ (H ₂ O) ₃] + Cl ⁻ ⇌ [RuCl ₄ (H ₂ O) ₂] ⁻ + H ₂ O	0.8 ³³	[RuCl ₄ (H ₂ O) ₂] ⁻	5.18 × 10 ⁻⁷	-
[RuCl ₄ (H ₂ O) ₂] ⁻ + Cl ⁻ ⇌ [RuCl ₅ (H ₂ O)] ²⁻ + H ₂ O	0.14 ³³	[RuCl ₅ (H ₂ O)] ²⁻	1.45 × 10 ⁻⁹	-
[RuCl ₅ (H ₂ O)] ²⁻ + Cl ⁻ ⇌ [RuCl ₆] ³⁻ + H ₂ O	0.1 ³³	[RuCl ₆] ³⁻	2.90 × 10 ⁻¹²	-
		[Cl ⁻]	2.00 × 10 ⁻²	
		[RuCl ₃]	1.00 × 10 ⁻³	

4.3.3 Characterisation of Carbon Black and Ru-modified CB

Dynamic Light Scattering (DLS) was conducted to determine the hydrodynamic diameter of the carbon black nanoparticles using a Malvern Zetasizer instrument. For

Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (SEM/EDX) analysis, Ru-modified CB particles were attached to carbon tape and analysed using a Hitachi Tabletop 3030 Plus microscope using a backscattering mode. For X-ray Photoelectron Spectroscopy (XPS) analysis, samples were analysed using a Kratos Liquid Phase Photoelectron Spectroscopy (LiPPS) with a monochromated Al K α X-ray source (1486.6 eV) operated at 10 mA emission current and 12 kV anode potential (120 W). The analysis chamber pressure was greater than 5×10^{-9} Torr. Pass energy was 160 eV for wide scans and 20 eV for high resolution scans. Wide scans were run with a step size of 0.5 eV and high-resolution scans were run with a step size of 0.1 eV. Data processing was carried out using CASAXPS software (version 2.3.20) with Kratos sensitivity factors (RSFs) to determine atomic % values from the peak areas. Thermogravimetric analysis (TGA) (sample mass of approximately 10 mg) was performed using NETZSCH TG 209 F1 in an aluminium oxide crucible at a heating rate of 10 °C min⁻¹ from 25 to 900 °C under nitrogen purging (10 mL min⁻¹) and compressed air (50 mL min⁻¹).

4.3.4. Recovery Experiment

To analyse and optimise the rate of recovery experiments were performed as above for 8 hours at different N₂ flow rates using different concentrations of carbon black. A 5 mL aliquot was taken at regular time intervals and placed inside a quartz cuvette (path length: 10 mm) for UV/Vis spectroscopy using a Cecil 7500 Double Beam UV/Visible spectrophotometer. A calibration curve was generated with a 1 – 40 ppm ruthenium(III) chloride solution in ultrapure water. The samples were then analysed and the concentration of ruthenium was calculated from the calibration curve.

4.4 Results and Discussion

Initial experiments were conducted to study the electrodeposition of ruthenium on carbon surfaces. First, a cyclic voltammogram (CV) was recorded using a bare GC electrode (diameter 3 mm) at a voltage scan rate of 100 mV s^{-1} in a degassed solution containing 10 mM KCl and 10 mM HCl, scanning (cathodically) from 0 to -1.2 V vs SCE to act as control experiment. Then, the CV was repeated at the same voltage scan rate in a solution containing 1 mM RuCl_3 and 10 mM KCl and 10 mM HCl using both a bare GC and CB-modified GC electrode. The CB-modified GC electrode was prepared by drop casting 5 μL of 50 nm CB suspension onto a polished GC surface.

Figure 4.1 shows the reductive segments of CV scans showing the deposition of ruthenium on the GC surface (dotted line) and CB-modified (dashed line), with an inset showing the onset potentials for these surfaces. An onset potential has been previously defined as a sufficient potential to generate a current response.³⁶ In this case, a current of -0.1 mA has been used to define the onset potential suggesting that ruthenium deposition occurs on the bare GC surface at -0.55 V vs SCE whereas the CB-modified surface occurs at -0.50 V vs SCE. This would suggest there is a small potential window (ca. 50 mV) in which Ru will deposit solely on the CB particles with minimal deposition on the substrate electrode.

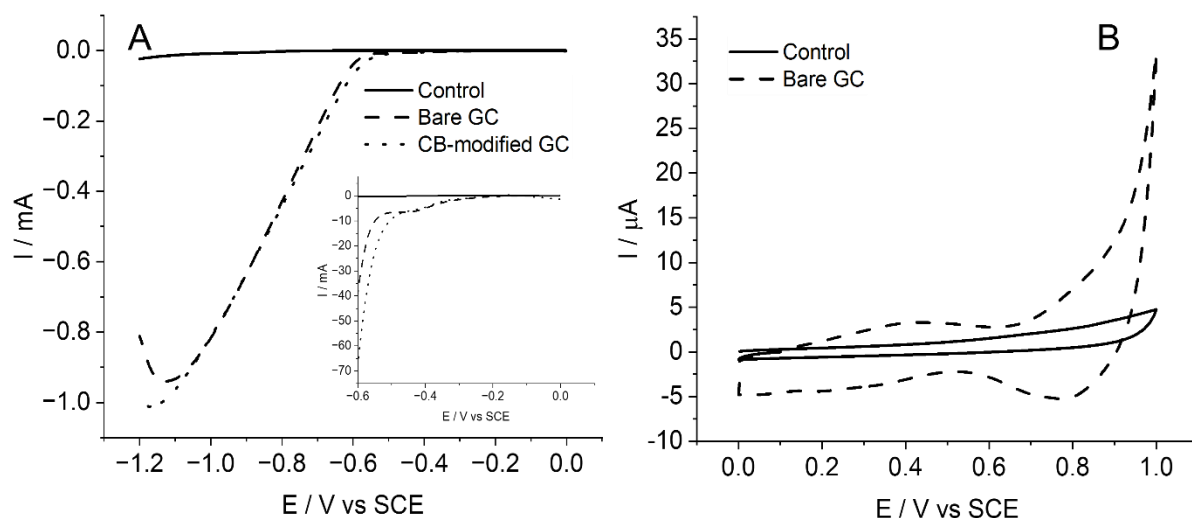


Figure 4.1 (A) Reductive segment of a cyclic voltammogram performed using an unmodified GC electrode (—) in 10 mM KCl and 10 mM HCl as a control and with the addition of 1 mM RuCl_3 for the unmodified GC electrode (- - -) and drop cast CB-modified GC electrode (• • •) showing ruthenium reduction. (B) Anodic segment of CV performed using an unmodified GC electrode (—) in 20 mM KCl as a control experiment and with the addition of 1 mM RuCl_3 for the unmodified GC electrode (- - -).

The mechanism for ruthenium electrodeposition from chloride solution has not been reported in literature, but in the reported case of nitrosyl complexes it occurs via a 2-stage process in which Ru(III) is first reduced to Ru(II) at a potential of -0.04 V vs SCE¹⁸ and then further reduced to Ru(0) at a potential of -0.27 V vs SCE.²¹ For chloro-complexes, a formal reduction potential for Ru(III) to Ru(0) can be estimated based on the available literature thermodynamic data. Literature results for the reduction potentials of Ru(III) to Ru(0) in chloride solutions could not be found, and so an estimated value can be calculated as follows, with knowledge that the principle species in solution is $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$:

Table 4.2: Aqueous equilibria and their corresponding standard potentials.

Aqueous Equilibria	E^0 / V
$Ru^{2+} + 2e \rightleftharpoons Ru$	+0.455 ³⁷
$Ru^{3+} + e \rightleftharpoons Ru^{2+}$	+0.249 ³⁷

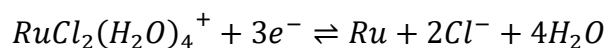
Combining these values, we can calculate the Gibbs energy for the process



To be $\Delta G = -0.249F - 0.910F = -1.159F$

And hence $E^0 = \frac{-1.159F}{-3F} = +0.386 V$

The desired reduction process:



Can therefore be obtained by combining equation 5.1 with the speciation data in table 4.1. The data for the mono-chloro complex is unavailable, hence the calculation is an estimate. In (i), this step will be ignored, resulting in a minimum potential, and in (ii) a representative value of $K = 10^3$ is used to show the relative insensitivity of the result on this first complexation equilibrium.

(i): $\Delta G = +1.159F + RT \ln 30 = +120.3 kJ mol^{-1}$

$$E^0 = \frac{120.3 \times 10^3}{-3F} = -0.415 V$$

Using the Nernst equation to calculate a formal potential:

$$E_f^0 = E^0 - \frac{RT}{3F} \ln \frac{[Cl^-]^2}{[RuCl_2(H_2O)_4]^+}$$

$$E_f^0 = -0.415 - \frac{RT}{3F} \ln \frac{[20 \times 10^{-3}]^2}{[6 \times 10^{-4}]} = -0.412 \text{ V}$$

$$E_f^0 = -0.654 \text{ V vs SCE}$$

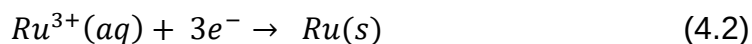
Similarly in the case where a large value is assumed for the first equilibrium in table 4.1 (such that the hexa-aquo ion is not in significant amounts):

$$(ii): \quad \Delta G = +1.159F + RT \ln 30 + RT \ln 10^3 = +137.4 \text{ kJ mol}^{-1}$$

$$E^0 = \frac{137.4 \times 10^3}{-3F} = -0.475 \text{ V}$$

$$E_f^0 = -0.714 \text{ V vs SCE}$$

This would suggest the peak at -1.1 V vs SCE is therefore due to the (electrochemically irreversible) three-electron reduction of Ru(III) to Ru(0):



It is noted that the experimentally observed peak current exceeds the expected peak current (ca -43.6 μA) for this process. This can be ascribed to the ruthenium deposit subsequently catalysing the HER which has been reported in literature.³⁸ In order to calculate the peak current for the possible different ruthenium reduction processes and HER reaction for a 3 mm GC surface, the irreversible Randles-Sèvčík equation was used (equation 4.3). Note the diffusion coefficient was assumed to be that of ruthenium hexaammine trichloride, and the transfer coefficient to be 0.5 due to lack of available data in the literature. The parameters used are shown in Table 4.3 and corresponding estimated peak currents are shown in table 4.4.

$$I_p = 2.99 \times 10^5 n A C D^{1/2} (n' + \alpha_{n'+1})^{1/2} v^{1/2} \quad (4.3)$$

where, n is the total number of electrons transferred, n' is the number of electrons transferred before the rate limiting step, $\alpha_{n'+1}$ is the transfer coefficient for the rate limiting step, A is the electrode geometric area, C the bulk concentration of analyte, D the diffusion coefficient, and v the voltage scan rate.

Table 4.3: Parameters used for the irreversible Randles- Sèvcík equation.

Parameter	Value for Ru-reduction process	Value for HER
A	0.07 cm ²	0.07 cm ²
C	1 x 10 ⁻⁶ mol cm ⁻³	1 x 10 ⁻⁵ mol cm ⁻³
v	0.1 V s ⁻¹	0.1 V s ⁻¹
α	0.5	0.35 ³⁷
D	8.69 x 10 ⁻⁶ cm ² s ⁻¹ ³⁸	9.6 x 10 ⁻⁵ cm ² s ⁻¹ ³⁸
T	298 K	298 K

Table 4.4: Estimated peak currents for both processes.

n	Value for Ru-reduction process / mA	Value for HER / mA
1	0.04	0.46
2	0.09	-
3	0.13	-

In order to deconvolute the peak due to HER and due to ruthenium electrodeposition, the CV was repeated in a pH 7 solution containing 1 mM RuCl_3 , 20 mM KCl and 0.1 M $\text{K}_2\text{HPO}_4/0.1$ M KH_2PO_4 buffer solution (figure 4.2). With a peak current of -0.18 mA, the first reduction wave is ascribed to the three-electron reduction of Ru^{3+} to $\text{Ru}(0)$, suggesting the second onset potential is likely to be HER. A Nernstian shift of 0.295 V is expected due the pH change from 2 to 7.

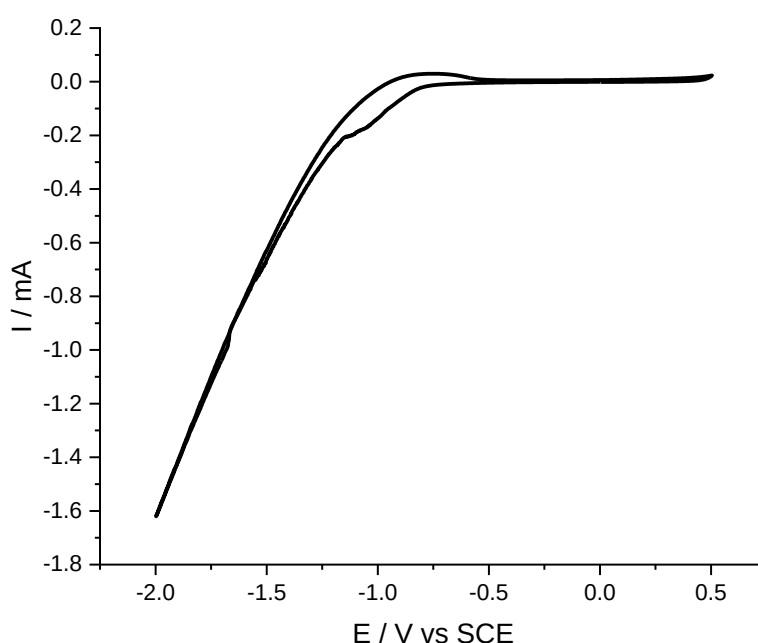
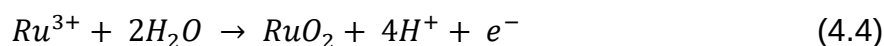


Figure 4.2: Reductive CV segment conducted using a 3 mm diameter GC working electrode in a solution containing 1 mM RuCl_3 , 20 mM KCl and 0.1 M $\text{K}_2\text{HPO}_4/0.1$ M KH_2PO_4 buffer solution.

Next, the electrode was thoroughly polished and analogous scans were conducted in the oxidative region. A GC (diameter 3 mm) electrode was scanned at a voltage scan rate of 100 mV s^{-1} from 0 to 1 V vs SCE in a solution containing 20 mM KCl to act as a control experiment. Then the CV was repeated for a bare GC electrode at the same scan rate in a solution containing 1 mM RuCl_3 and 20 mM KCl. Figure 4.1B shows these CV scans with one oxidative peak present in the forward scan. The oxidation

peak is broad and is therefore difficult to determine the onset potential accurately. The peak current is consistent with a one-electron process, indicating that this peak corresponds to the oxidation of Ru(III) to Ru(IV), as RuO_2 .²⁴



Randles-Ševčík Analysis was conducted for the first oxidation peak (figure 4.1 B) as shown below in figure 4.3 using a bare GC working electrode in a solution containing 1 mM RuCl_3 and 20 mM KCl.

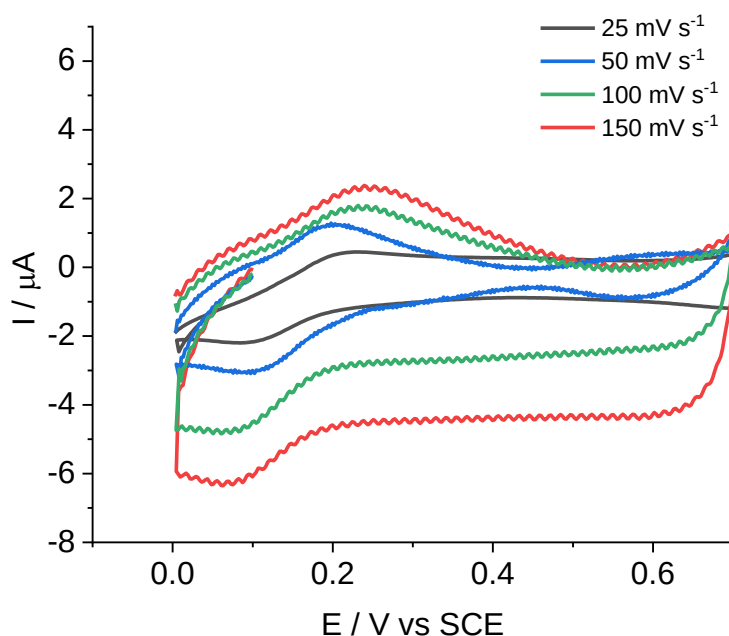


Figure 4.3: Variance of scan rate for CVs conducted using a bare GC electrode in a solution containing 1 mM RuCl_3 and 20 mM KCl.

The gradient of a logarithmic plot of peak current vs scan rate is 0.88, indicating the first peak is neither a purely diffusion-controlled or adsorption-controlled process, as shown in figure 4.4.

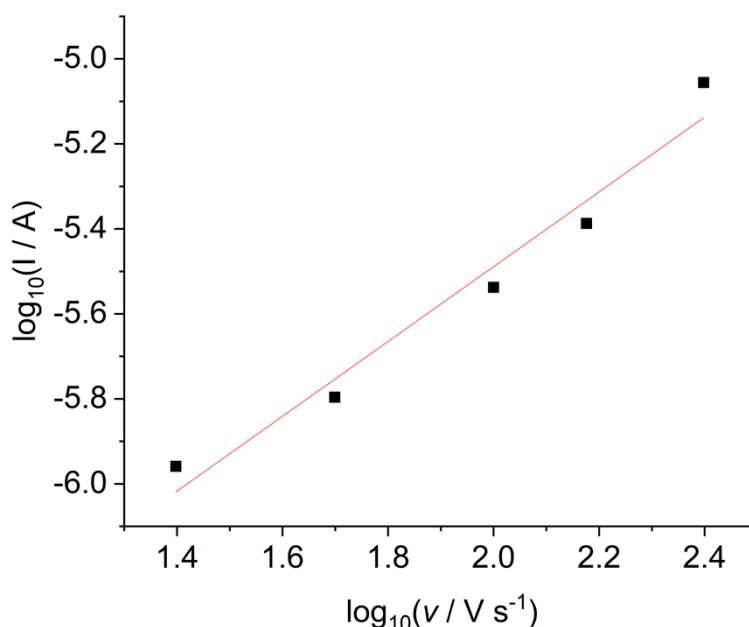


Figure 4.4: Logarithmic plot of peak current vs scan rate for oxidation peak where $\log_{10}(I) = 0.88\log_{10}(v) - 7.30$ and $R^2 = 0.96$.

4.4.1 Nano-Impact Experiment

To determine whether impacts could be detected due to the ruthenium reduction process, chronoamperometry experiments were conducted with and without the addition of 25 pM CB suspension using 9 μm CF microelectrodes in a solution containing 1 mM RuCl_3 , 10 mM KCl and 10 mM HCl across a potential window ranging from -0.40 to -0.55 V vs SCE, previously established from solution voltammetry. Impacts were only observed in the presence of CB NPs, and were recorded to have an onset potential at -0.50 V vs SCE, in excellent agreement with figure 4.1A. A representative chronoamperogram recorded at -0.50 V vs SCE using a 9 μm CF electrode is given in figure 4.5A. The current transients observed were typically single, sharp features indicating elastic-type collisions between the particle and electrode.

A plot of the charge passed per impact (Q / fC) is given in figure 4.5C with impacts ranging from (-23.90 ± 28.20) fC to (-26.0 ± 47.5) fC. An approximate coverage relative a monolayer was calculated using previously described equations 3.12-3.17. This shown in figure 4.5D with coverages ranging between $67.2 \pm 99.5\%$ to $190 \pm 153\%$. The large overlapping error bars can be attributed to the differing the size of impacting carbon black nanoparticles which may include some aggregates.

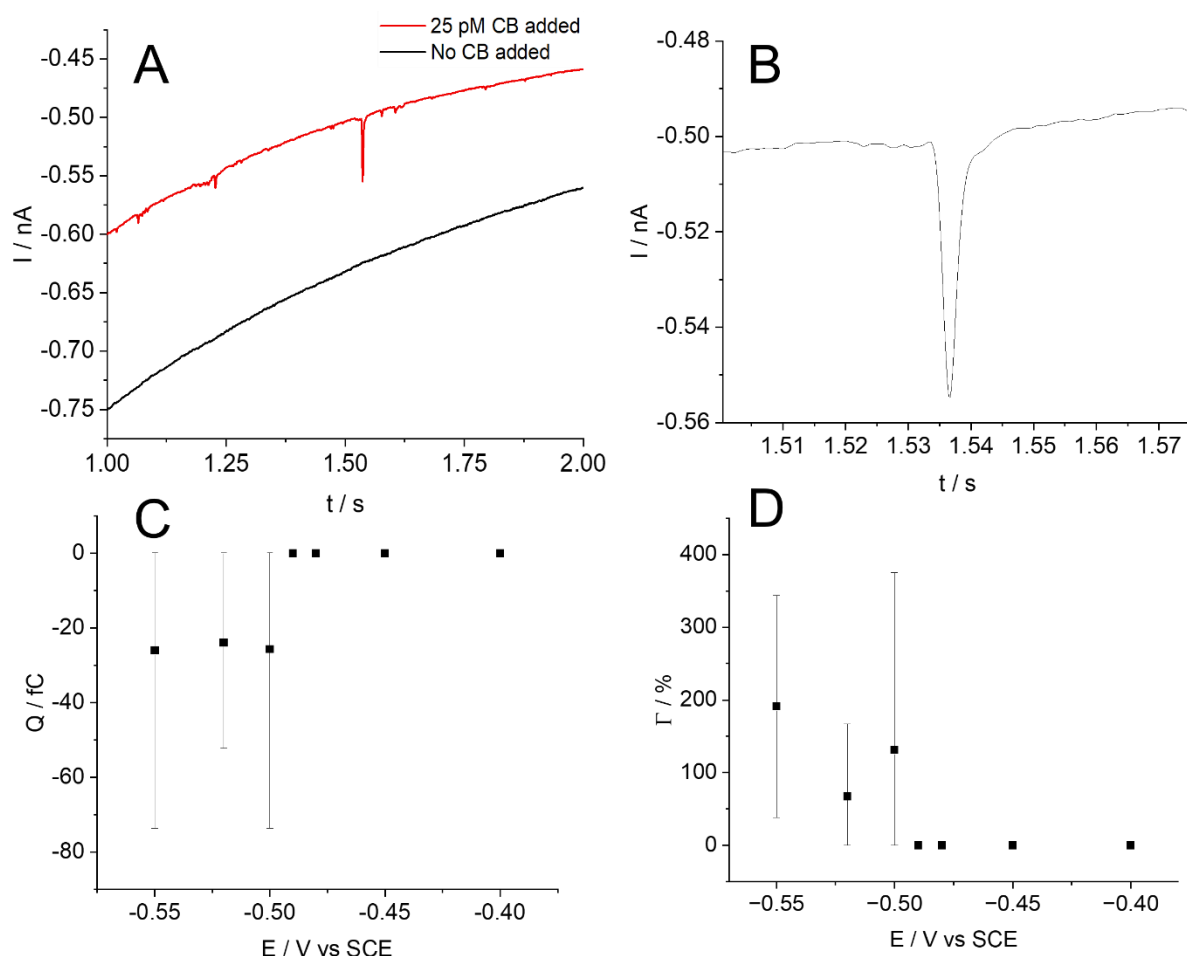


Figure 4.5 (A) shows a representative chronoamperogram performed by holding a 9 μm CF microelectrode at -0.5 V vs SCE in a solution containing 1 mM RuCl_3 , 10 mM KCl and 10 mM HCl with and without the presence of 25 pM CB NPs. (B) shows an enlarged impact event at 1.535 s. (C) is a plot of the average charge passed per impact event (Q / fC), and (D) is a plot of the corresponding coverage of ruthenium on carbon black equivalent to a monolayer. Error bars represent the standard deviation of replicate measurements at each applied potential.

The sphere on a plane equation (equation 4.5)⁴⁰ was used to calculate the peak height during impact chronoamperometry, to provide an estimation of maximum currents. However, it should be noted that the data has been treated with a digital filter (250 Hz) to improve the signal-to-noise ratio and facilitate analysis, which is known to cause distortion of impacts and underestimating the true peak current. As such, comparison of these peak heights to the different-electron processes should be treated with caution and are calculated here for comparison and estimation only.⁴¹ The following parameters in table 4.5 were used to give the calculated values in table 4.6.

$$I_{lim} = 4\pi \ln(2) nFD r_p [A]_{bulk} \quad (4.5)$$

Table 4.5: Parameters used in the sphere on a plane equation.

Parameter	Value
D	$8.69 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
R_p	$5 \times 10^{-6} \text{ cm}$
$[A]_{bulk}$	$1 \times 10^{-6} \text{ mol cm}^{-3}$

Table 4.6: Expected peak heights of impact spike for different electron-reduction processes.

n	I_{lim} / pA
1	36.5
2	73.0
3	109.5

Analogous experiments were conducted to see whether impacts could be detected due to a ruthenium oxidation process. Chronoamperometry experiments were conducted with and without the addition of 25 pM CB suspension using 9 μm CF microelectrodes in a solution containing 1 mM RuCl_3 and 20 mM KCl across a potential window ranging from 0.30 to 0.50 V vs SCE, previously established from solution voltammetry. Impacts were observed with an onset potential at 0.37 V vs SCE. A representative chronoamperogram recorded at 0.5 V vs SCE using a 9 μm CF electrode is given in figure 4.6 A. A variety of peak shapes were observed attributed to different particle-electrode interactions.² A plot of the charge passed per impact (Q / pC) is given in figure 4.6B with impacts ranging from (98.6 ± 99.2) fC to (0.89 ± 1.12) pC.

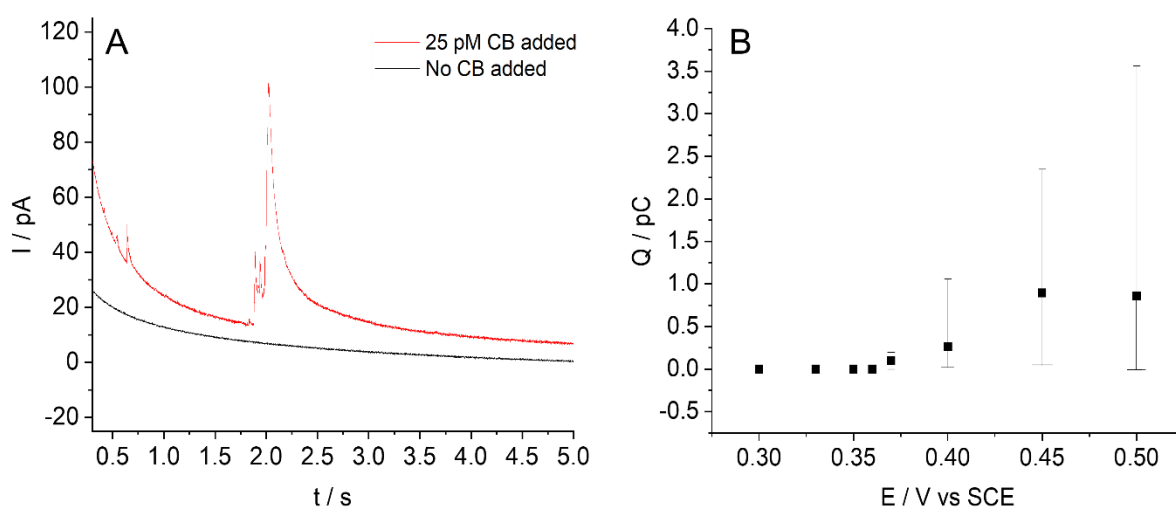


Figure 4.6. (A) shows a representative chronoamperogram performed by holding a 9 μm CF microelectrode at 0.5 V vs SCE in a solution containing 1 mM RuCl_3 and 20 mM KCl with and without the presence of 25 pM CB. (B) shows a plot of charge passed for impact (Q / pC) vs potential. Error bars represent the standard deviation of replicate measurements at each applied potential.

To obtain direct evidence of ruthenium deposition on carbon black, the system was scaled up to 500 mL and a 5 hr chronoamperogram was performed at -0.50 V vs SCE.

A three-electrode cell was used consisting of a saturated SCE reference electrode in a separate glass fritted compartment, a large graphite plate working electrode (area: 6.25 cm²) and a graphite rod as the counter electrode. The solution was continuously agitated with pre-saturated nitrogen gas to lessen the agglomeration of carbon black nanoparticles and increase the rate of impact events. The post-chronoamperometric solution was filtered to yield the Ru-modified CB particles which were washed several times and then dried at 40 °C. The dried particles were first analysed using SEM/EDX revealing large shard-like particles with the presence of a RuO_x species, as shown below in figure 4.7, which is reported to be common in the electrodeposition of ruthenium where changes in the local pH at the electrode can precipitate ruthenium hydroxide/oxide species.⁴² It is postulated that the shard-like structure of these particles could be a consequence of hydrogen embrittlement which can induce fractures and cracks in ruthenium deposits.^{43,44} EDX mapping also revealed the presence of potassium and chlorine, presumably due to residual electrolyte as well as the presence of aluminium which can be attributed to the working electrode preparation.

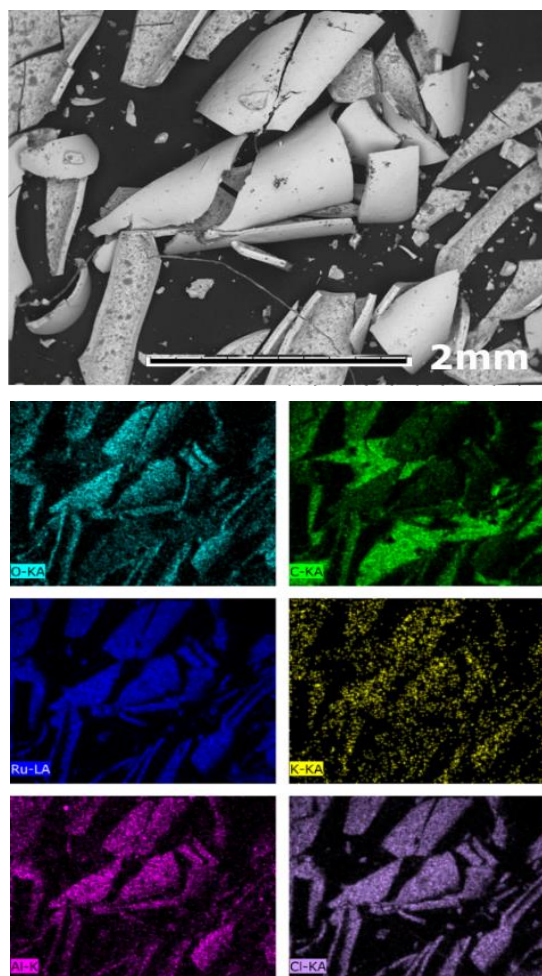


Figure 4.7: SEM/EDX Analysis of Ru-modified CB NP (-0.5 V vs SCE).

Further TGA analysis was conducted which gave a Ru weight loading of ca. 14.1 %. A TGA thermogram is shown in figure 4.8 below. There are three distinct regions of weight loss: from 50 to 200 °C the weight loss of structural water ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$)⁴⁵ from 250 to 350 °C the weight loss attributed to the dehydroxylation of the amorphous material⁴⁵ and finally from 350 to 500 °C the removal of carbon black. From this, a 14.1% ruthenium coverage was determined based on a mass change from 8.6 mg (at 350 °C) to 6.9 mg upon reaching 900 °C. Table 4.7 shows the SEM/EDX average weight percent ratio and compared to unmodified CB NP which contain no ruthenium.

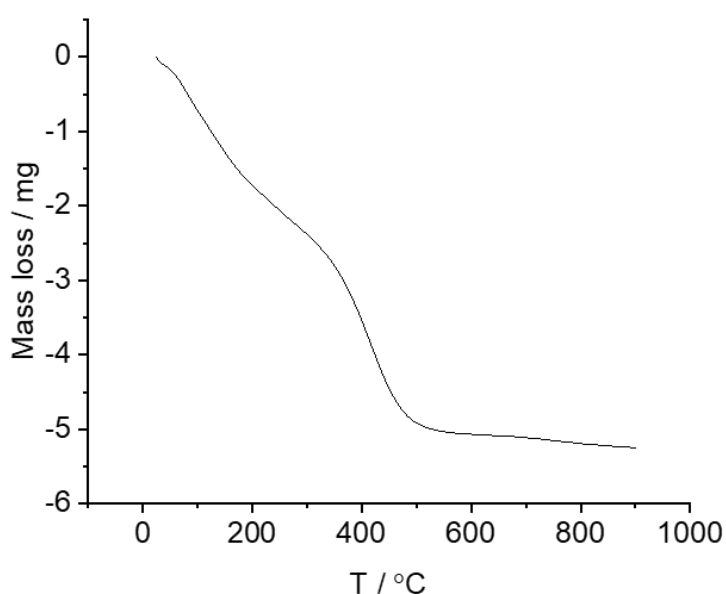
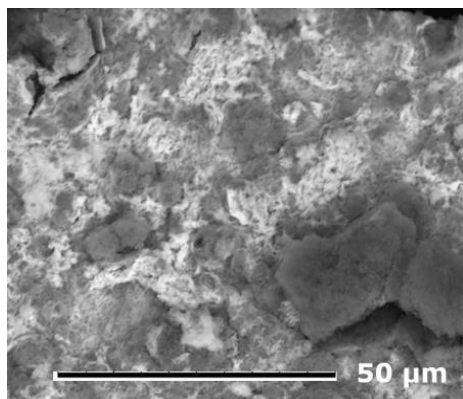


Figure 4.8: TGA thermogram of the 5 hr Ru-modified carbon nanoparticles.

Table 4.7: SEM Image of agglomerated CBNP obtained from chronoamperogram performed at -0.5 V vs SCE in a solution containing 500 pM CB NP, 1 mM RuCl₃, 10 mM KCl and 10 mM HCl to the left. The table displays the ruthenium content determined by SEM/EDX and TGA analysis for the unmodified CB NP and sample held at -0.5 V vs SCE.



Sample	SEM/EDX average weight percent ratio Ru: CB	TGA weight loading of RuO ₂ / %
Unmodified	0	-
-0.5 V vs SCE	0.98 ± 0.11	14.1

XPS analysis was used to further characterise the deposited RuOx species. Here, the 3p core level as shown in figure 4.9A was used due to overlap between the Ru3d with the C1s level (see wide scan in figure 4.9B); a commonly known issue when conducting XPS analysis of carbon supported ruthenium materials.^{46,47} The expected core-level splitting is observed showing the Ru 3p_{3/2} peak which is approximately twice the intensity of Ru 3p_{1/2} peak. A sharp Ru 3p_{3/2} peak is centred at 463.8 eV which corresponds to that of RuO₂ in the literature⁴⁷ and is also confirmed with the presence of oxygen in the wide scan spectra. Furthermore, this is consistent with SEM/EDX analysis which revealed the presence of oxygen. Some chloride is present in the wide scan spectra however, this is likely to be residual electrolyte (KCl) and not unreacted

RuCl_3 due to the fact a lower binding energy (461 eV) is expected for RuCl_3 than the peak observed in the experimental XPS spectrum.

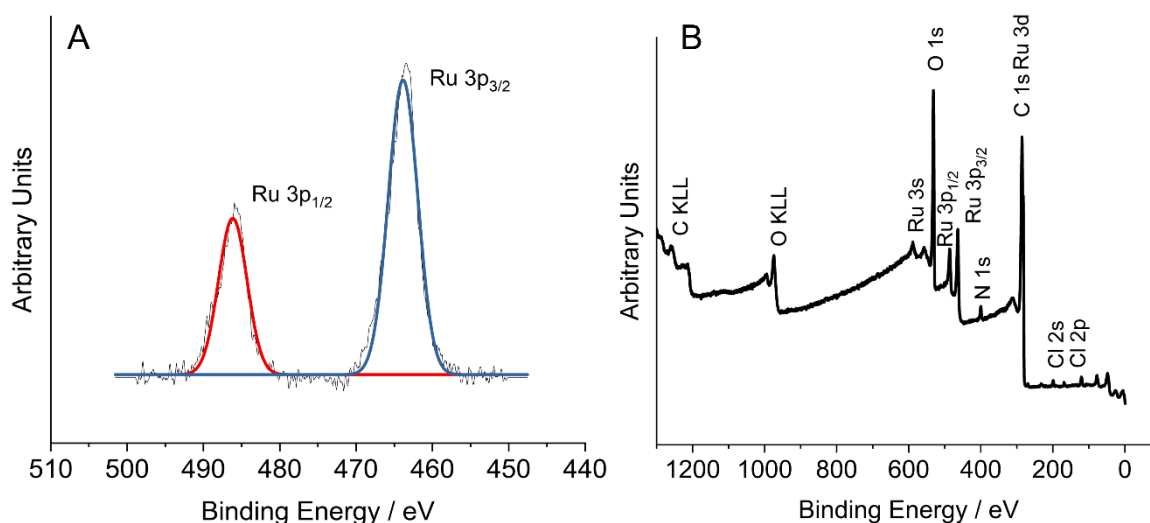


Figure 4.9. (A) High resolution Ru3p XPS spectra of -0.5 V vs SCE modified CB particles showing the core level fitting for RuO_2 in blue and red lines. (B) Wide XPS scan of Ru-modified CB nanoparticles.

4.4.2 Ruthenium Recovery from Low Concentration of RuCl_3

Finally, the use of the nano-impact method as a method to recover ruthenium from low concentration RuCl_3 solution was investigated. This method has been previously demonstrated with aqueous palladium(II) chloride revealing the presence of carbon black nanoparticles increased the recovery rate of Pd by a factor of 1.7 compared to the experiment conducted without the particles under unoptimised conditions.² For this reason, the rate of recovery of ruthenium was monitored by performing a chronoamperogram at -0.5 V vs SCE for 8 hours in the presence of carbon black particles only. A 500 mL solution containing 0.01 M HCl, 0.01 M potassium chloride and 1 mM ruthenium(III) chloride was used with varying concentrations of carbon black (2.5, 5 and 10 nM) and varying volumetric flow rates of nitrogen agitation (1 L min⁻¹, 2 L min⁻¹, 3 L min⁻¹) in an attempt to optimise the experimental conditions. A 5 mL aliquot was taken at regular time intervals and filtered with a 0.22 μm syringe filter for UV/Vis

analysis. UV/Vis analysis was selected due to the speed and ease of this technique whilst still maintaining a relatively high degree of accuracy.

The calibration curve used for UV/Vis analysis along with the spectra is shown below in figure 4.10 and was used to calculate the percentage of Ru(III) recovered from the solution. The calibration curve was obtained by recording the absorbance at 320 nm for RuCl_3 standards ranging from 1 – 37.5 ppm as this gave the best R^2 value. A further calibration curve at 195 nm was attempted, however a large y-intercept was observed. A representative example of the UV/Vis spectrum is shown in figure 4.10B which could indicate the presence of $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$, $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ and/or $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ due to some overlapping peaks at 320 nm. UV/Vis spectra of the possible Ru aqua chloro-complexes redrawn from Cady and Connick⁴⁸ and Fine⁴⁹ are included for reference.

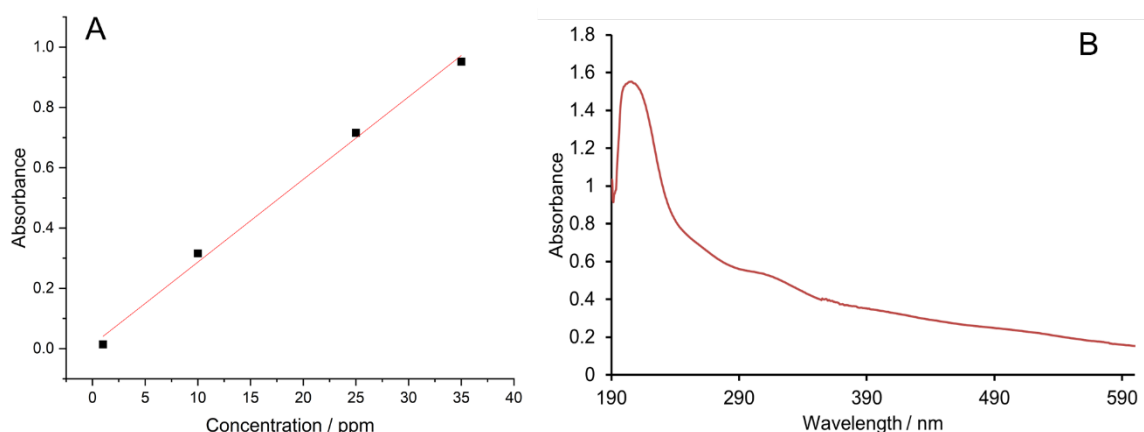


Figure 4.10. (A) Calibration curve at 320 nm where $A = 0.0276C$ and $R^2 = 0.996$. **(B)** Representative UV/Vis spectrum for $\text{RuCl}_3(\text{aq})$ solution.

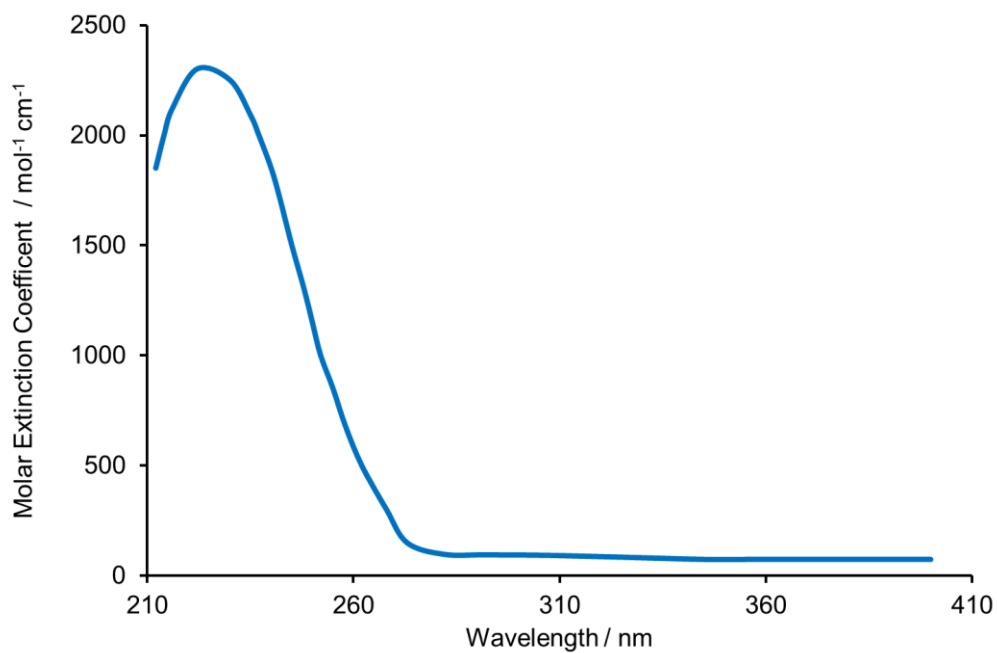


Figure 4.11: UV/Vis spectrum of $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ redrawn from Cady and Connick.⁴⁸

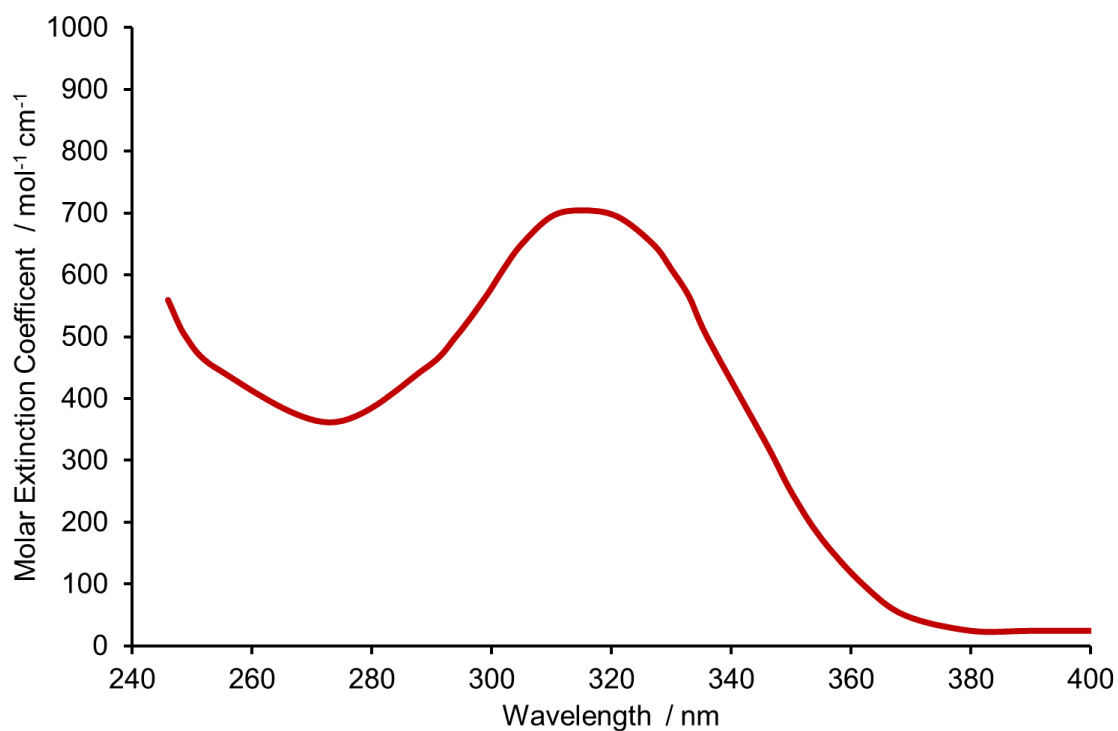


Figure 4.12: UV/Vis spectrum of $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ redrawn from Cady and Connick.⁴⁸

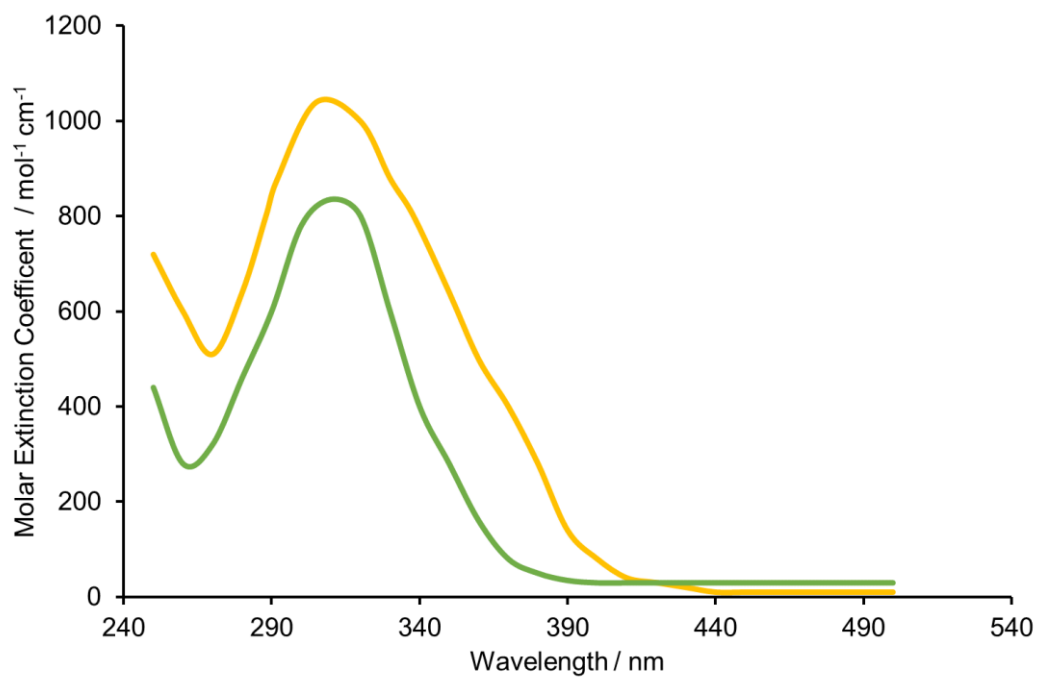


Figure 4.13: UV/Vis spectrum of $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ redrawn from Fine⁴⁹ showing the cis-isomer (yellow) and trans-isomer (green).

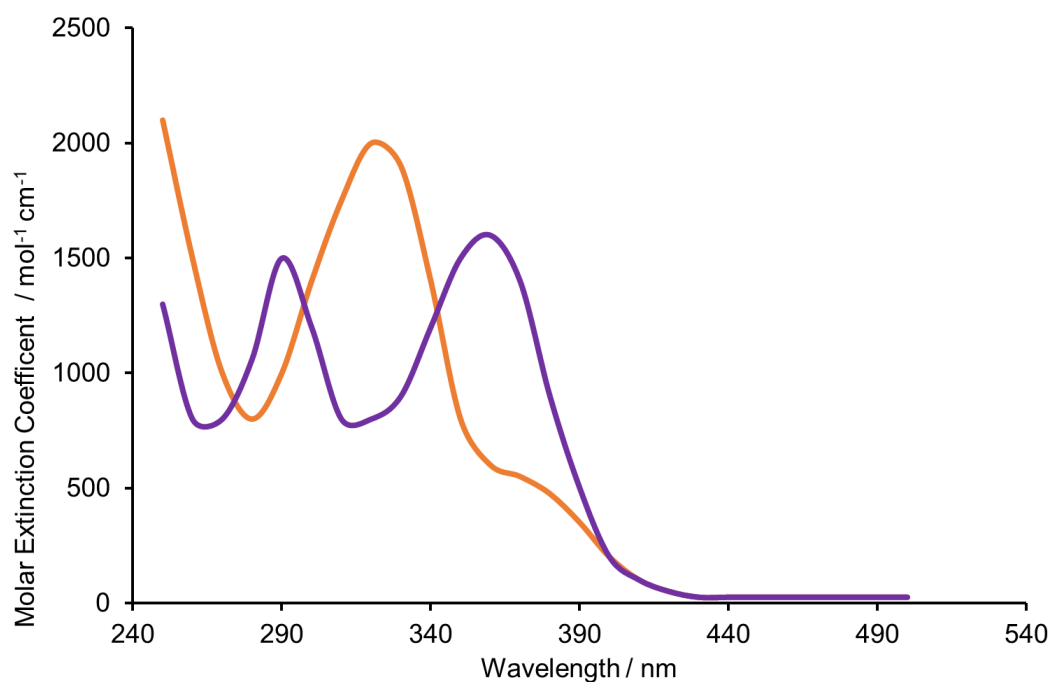


Figure 4.14: UV/Vis spectrum of $[\text{RuCl}_3(\text{H}_2\text{O})_3]$ redrawn from Fine⁴⁹ showing the mer-isomer (orange) and fac-isomer (purple).

The percentage of Ru recovered is shown below in figure 4.15. After 8 hours, the Ru recovery varied from $(87.6 \pm 3.8) \%$ to $(94.7 \pm 8.9) \%$ with no statistically significant differences between the percentage Ru recovered for the different nitrogen flow rates, therefore revealing little dependence of the parameters studied within the ranges selected.

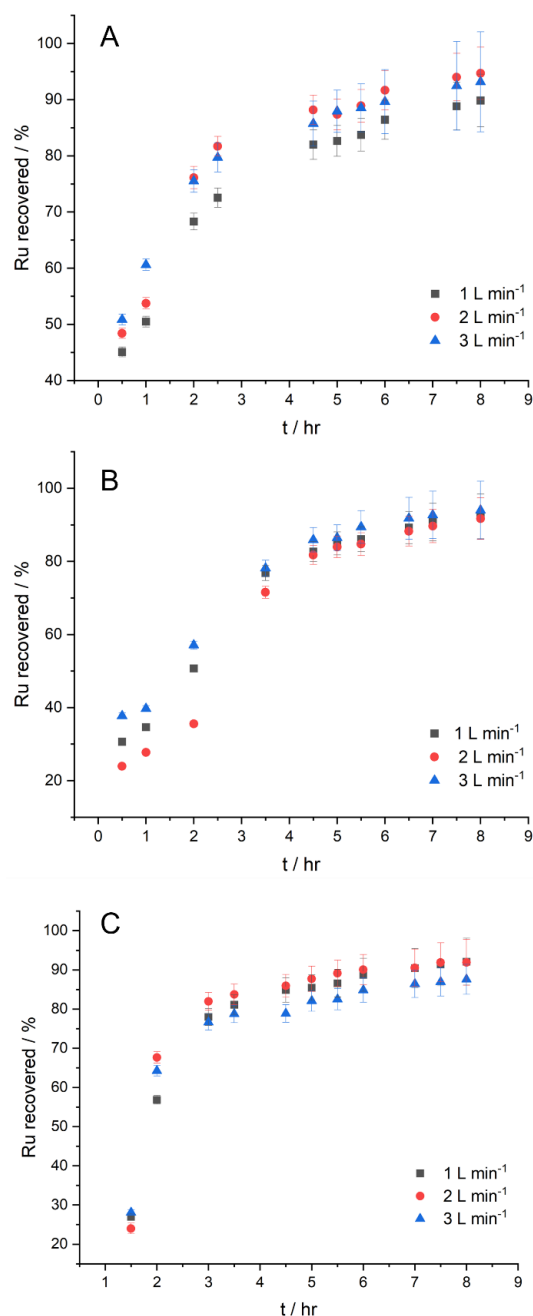


Figure 4.15: Percentage of Ru recovered (%) from solution using **(A)** 2.5 nM, **(B)** 5 nM and **(C)** 10 nM carbon black nanoparticles for 1, 2 and 3 L min⁻¹ nitrogen flow rates. Error bars represent the percentage uncertainty due to the y-intercept of the calibration curve.

4.5 Conclusions

The electrodeposition of ruthenium from Ru(III) on GC and CB-modified GC was observed at onset potentials of -0.55 V vs SCE and -0.5 V vs SCE respectively; analysis indicating a three-electron reduction process. This was further confirmed with the nano-impact experiment in which impacts were observed in the presence of 25 pM CB with a switch on potential in agreement with solution voltammetry. The system was upscaled to generate ca. 14.1 wt% Ru-modified carbon black particles with the SEM/EDX and XPS characterisation revealing a RuO₂ deposit; a commonly observed species associated with the aqueous electrodeposition of Ru(III). Under partially-optimised conditions, >90% of the ruthenium from solution was recovered in ca 8 hours determined by UV/Vis spectroscopy of the electrolyte solution. The electrooxidation of Ru(III) on GC was also observed, however the feature was too broad to accurately define the onset potential. Impact events were also recorded corresponding to this oxidation process.

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5. ELECTROREDUCTION OF NICKEL ON CARBON BLACK VIA NANO-IMPACT ELECTROCHEMISTRY IN AMMONIUM SULFATE AND CHLORIDE ELECTROLYTES

5.1 Abstract

Nano-impact electrochemistry has recently emerged as a promising alternative for the recovery of commercially important metals.¹⁻³ In this study, the reduction of aqueous Ni (II) ions from two electrolytes: nickel sulfate and nickel chloride were observed on carbon black nanoparticles during nano-impacts, with the onset potential of the reduction process in good agreement with solution voltammetry. Coverages of between 0.45 – 2.8 monolayer equivalents were obtained from the reductive impacts and the low levels of nickel deposit were confirmed via SEM/EDX and ICP-MS analysis.

5.2 Introduction

The recovery of industrially valuable metals such as nickel from waste and/or recycling streams is paramount to their continued sustainable use, as well as reducing the harmful effects of disposal on the environment and human health. The primary uses of nickel lie in steelmaking, batteries and catalysts, and current recovery methods are heavily reliant on hydrometallurgical techniques⁴ such as chemical precipitation,⁵ ion flotation⁶ and membrane filtration⁷ which consume large volumes of expensive, and sometimes toxic, solvents. A range of electrochemical techniques have also been employed in nickel recovery from electrodeposition⁸ and electrowinning to electrodialysis⁹ electrocoagulation^{10,11} and electroflotation.^{12,13} However, all of these methods rely on a high aqueous nickel ion concentration which is not always the case

in wastewater and therefore may require costly pre-concentration/ pre-treatment steps.

Nano-impact electrochemistry has recently emerged as a promising alternative to recover low concentration metal species from solution due to advantages such as high rates of mass transport, reduced risk fouling of a single electrode by providing high numbers of particles onto which the target metal can be electroreduced and the particles themselves can be easily separated from solution.¹⁻³ So far, this technique has been demonstrated for metal deposition on metallic particles¹⁴⁻¹⁶ with more recent efforts focused on non-metallic nanoparticles, as a potential means of recovering metal from solution.¹⁻³

The electrodeposition of nickel on carbon substrates has been widely studied in both sulfate¹⁷⁻²¹ and chloride solutions²²⁻²⁵ but it is commonly known that nickel electrodeposition is a highly inhibited process involving various factors such as solution composition, pH, temperature, and electrode.^{26,27} In particular, the coordination chemistry and resulting speciation between nickel and the electrolyte can play a significant factor in the deposition mechanism and the resulting properties of the deposited metal.^{28,29} The use of ammonium sulfate and chloride salts has attracted recent attention due to the inherent advantages associated with these electrolytes such as their high buffering rate and, below pH 8, the avoidance of intermediate adsorbed hydroxide species known to inhibit deposition through passivation.^{18,25,28}

The nano-impact electrochemistry of nickel and nickel oxide nanoparticles have been studied.³⁰⁻³² However, to our knowledge there are no reports of nickel in the context of electrodeposition or metal recovery using this technique. In order to determine whether the nano-impact method may be a candidate for recovery of aqueous Ni(II), this study

investigates the deposition of nickel from both nickel (II) sulfate/ammonium sulfate system and nickel (II) chloride/ammonium chloride at pH 5 on carbon substrates. A pH of 5 was specifically chosen to prevent excessive hydrogen evolution at the working electrode, which can lead to hydrogen embrittlement, and to avoid the precipitation of nickel hydroxide species, which occurs at higher pH levels (≥ 6) and can negatively affect the uniformity and quality of the nickel deposits.

5.3 Experimental

The following chemicals were purchased and used without further purification: nickel (II) sulfate hexahydrate (99%, Sigma Aldrich), nickel (II) chloride (99%, Sigma Aldrich), ammonium sulfate (99%, Sigma Aldrich), ammonium chloride (99%, Sigma-Aldrich), 50 nm carbon black-Vulcan XC-72R nanoparticles (Fuel Cell Store), sulfuric acid (95-98%, Sigma Aldrich), and hydrochloric acid (37%, Honeywell). All solutions were made using ultrapure water (with a resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$). Solutions were thoroughly degassed using nitrogen (oxygen-free, BOC Gases plc) and a nitrogen atmosphere was maintained throughout experiments.

A three-electrode cell arrangement was used for all electrochemical experiments consisting of a standard calomel electrode (SCE, saturated with KCl) reference electrode, a graphite rod (5mm, Goodfellow Cambridge Ltd) as the counter electrode, and either a carbon fibre microelectrode (diameters: 9 μm and 7 μm confirmed by electrochemical calibration) or a glassy carbon (diameter: 3 mm) macroelectrode as the working electrode. The 9 μm CF electrodes were made in-house using pitch-derived carbon fibre (Goodfellow Cambridge Ltd) whilst the 7 μm carbon fibre electrodes were commercial (IJ Cambria Ltd). All working electrodes were prepared by polishing on micro-cloth pads with alumina suspensions of 1, 0.3, 0.05 μm sequentially (all from Buehler Inc, USA). All standard electrochemical experiments

were conducted using an Autolab 128N potentiostat (Metrohm-Autolab BV, Netherlands) controlled by a PC via Nova 2.1 software.

For impact experiments, a bulk solution of CB nanoparticles was prepared and sonicated for 1 hr before use and an aliquot (20 μ L) was taken to achieve the desired nanoparticle (NP) concentration of 20 pM in a solution containing 0.5 mM nickel electrolyte and 20 mM of the corresponding ammonium electrolyte. Chronoamperograms (duration of 30 s) were conducted using the same three-electrode cell as described previously in a bespoke low-noise potentiostat controlled by a PC with PyFemto software.³³

Long-term impact experiments (5 hr) were performed in the solution stated above with the addition of a higher concentration CB NPs (number concentration of 500 pM). The three-electrode cell used consisted of a saturated SCE reference electrode in a separate fritted compartment, graphite plate electrode (diameter: 2.5 cm), and graphite rod (Alfa Aesar) as the counter electrode. The post-chronoamperometric solution was washed and filtered under vacuum using Anodisc™ 47 filter paper with a pore size of 0.02 μ m and the resulting filter cake was dried at 40 °C. For SEM/EDX analysis, the resulting powder was attached to carbon tape, and examined using a Hitachi TM3030 Plus electron microscope. For the ICP-MS analysis, two samples were dissolved in aqua regia for 120 hours, then diluted using ultrapure water to 5% aqua regia and filtered with 0.45 μ m syringe filters (Fisher Scientific). The samples were then analysed using ICP-MS with a PerkinElmer Nexion 300X instrument with a limit of detection of 100 ppt. A calibration curve was generated ranging from 1 ppb to 10 ppb using diluted solutions of a nickel 1000 ppm standard purchased from Sigma Aldrich in 2% nitric acid solution. The nickel content was calculated from the calibration curve.

All other data was processed using a combination of Microsoft Excel and Origin Pro 2021.

5.4 Results and Discussion

Initial experiments into the electrodeposition of nickel from nickel (II) sulfate and nickel (II) chloride on carbon used voltammetry at a glassy carbon (GC) working electrode to observe the reduction wave and find the onset potential. Although controversial due to the multiple ways in which it can be defined,³⁴ a current of $-0.10\ \mu\text{A}$ has been used here to define the onset potential, based on the observed faradaic current in the cathodic process (see figure 5.1). First, a CV was recorded at a scan rate of $100\ \text{mV s}^{-1}$ scanning cathodically from $0\ \text{V}$ vs SCE in degassed solution containing $20\ \text{mM}$ ammonium sulfate to act a control (see fig 5.1A). Then a CV was repeated in a solution containing $20\ \text{mM}$ ammonium sulfate and $0.5\ \text{mM}$ nickel sulfate and the reduction of Ni(II) was observed (equation 5.1) with an onset potential of $-0.50\ \text{V}$ vs SCE (see figure 5.1) and peak potential at $-0.85\ \text{V}$ vs SCE.

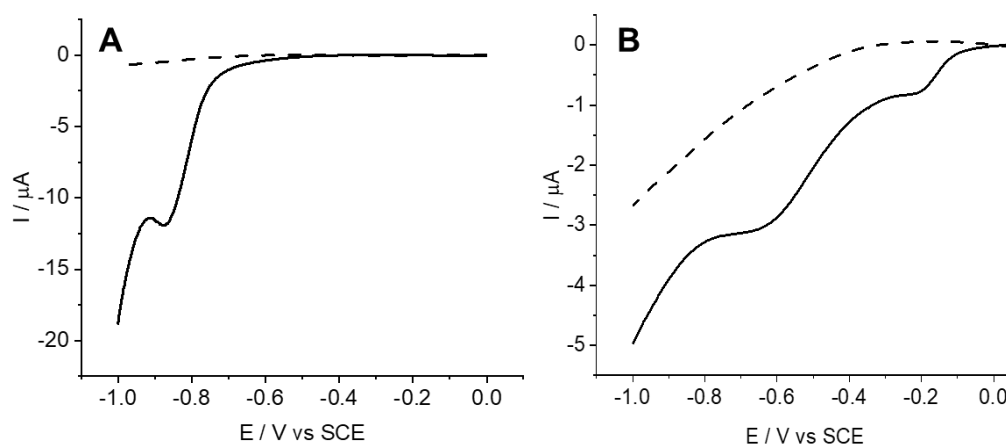
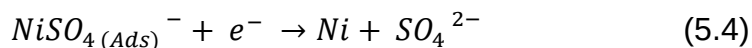
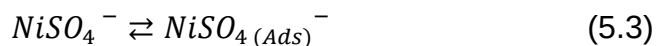
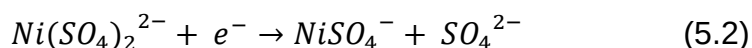


Figure 5.1: Reductive segments of cyclic voltammograms performed using a 3 mm diameter unmodified GC electrode in (---) $20\ \text{mM}\ (\text{NH}_4)_2\text{SO}_4$ and (—) with the addition of $0.5\ \text{mM}\ \text{NiSO}_4$ solution at a voltage scan rate of $100\ \text{mV s}^{-1}$. Figure 1B: Reductive segments of cyclic voltammograms performed using a 3 mm diameter unmodified GC electrode in (---) $20\ \text{mM}\ \text{NH}_4\text{Cl}$ and (—) with the addition of $0.5\ \text{mM}\ \text{NiCl}_2$ solution at a voltage scan rate of $100\ \text{mV s}^{-1}$

The electrodeposition of nickel in ammonium sulfate solutions has been reported to occur via three steps: two electrochemical and one adsorption step (equations 5.1-5.4).¹⁸ At pH 5, the predominantly stable Ni species is reported to be the soluble, negatively charged disulfate, $Ni(SO_4)_2^{2-}$, which undergoes a 1 electron reduction to yield the nickelous sulfate ion (equation 5.2).¹⁸ In the next step (equation 5.3) the nickelous sulfate ion is adsorbed on the electrode surface which is reported to be fast and reversible for low concentration Ni solutions (≤ 5 mM).¹⁸ Finally, the rate determining step is the reduction of Ni^+ to Ni (0) (equation 5.4).¹⁸ Despite this proposed mechanism, only one peak was observed in the CV which is consistent with literature.¹⁸



For the Ni(II) sulfate reduction process, an electrochemically irreversible process was observed (see Figure 5.2A), therefore the irreversible form of the Randles–Ševčík equation (4.3) was used to provide an approximate estimate of the expected peak current. The parameters used are listed in Table 5.1. The calculated peak currents are listed in Table 5.2. Note the transfer coefficient for the rate limiting step is unknown so it is assumed to be 0.5. The number of electrons transferred before the rate limiting step is 1.¹⁹ The experimental peak current was ca. 11 μ A which can therefore be attributed to the electrochemically irreversible two-electron reduction of nickel(II) to nickel metal.

Table 5.1: Parameters used to calculate the peak current for NiSO_4 and NiCl_2 reduction processes.

Parameter	Value for NiSO_4 Reduction Process	Value for NiCl_2 Reduction Process
A	0.07 cm^2	0.07 cm^2
C	$5 \times 10^{-7} \text{ mol cm}^{-3}$	$5 \times 10^{-7} \text{ mol cm}^{-3}$
$\alpha_{n'+1}$	0.5	N/A
ν	0.1 V s^{-1}	0.1 V s^{-1}
D	$5.81 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ³⁵	$9.79 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ³⁶
T	298 K	298 K

Table 5.2: Parameters used to calculate the peak current for NiSO_4 and NiCl_2 reduction processes.

Number of electrons	Peak Current for NiSO_4 Reduction Process / μA	Peak Current for NiCl_2 Reduction Process/ μA
1	17.6	10.4
2	N/A	29.3

The variance of scan rate with peak current for the nickel sulfate reduction process was also investigated and the CV scans along with a logarithmic plot of scan rate vs peak current are shown in Figure 6.2. The gradient of the line 0.746 which indicates a process which is neither purely diffusion- or adsorption-controlled, which is consistent with the proposed deposition mechanism.

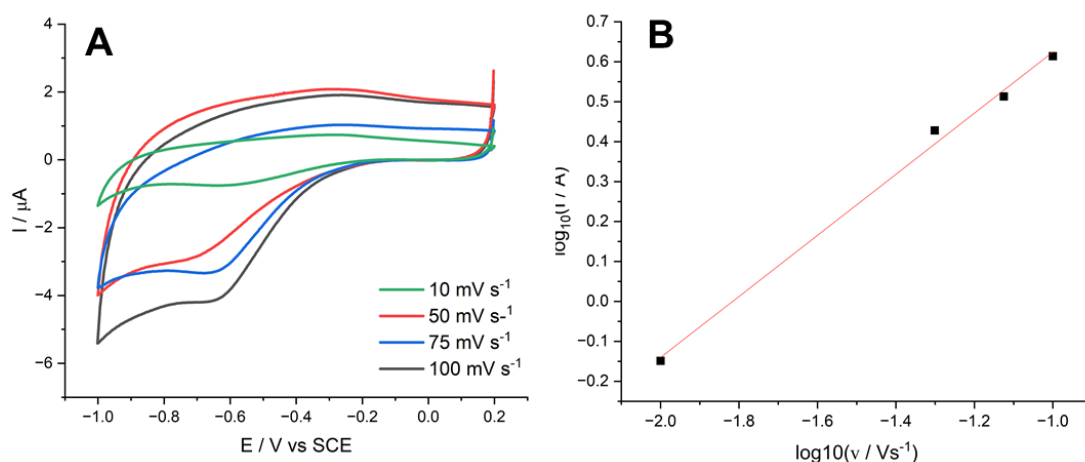


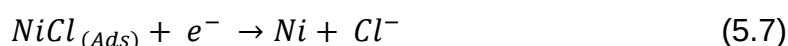
Figure 5.2 A) Variance of scan rate vs peak current conducted in a solution containing 0.5 mM NiSO_4 and 20 mM $(\text{NH}_4)_2\text{SO}_4$. B) Logarithmic plot of peak current vs scan rate where the equation of the line is $\log_{10}(I) = 0.76\log_{10}(v) + 1.39$ and $R^2 = 0.99$.

After thoroughly polishing the working electrode, a CV was recorded at a scan rate of 100 mV s^{-1} scanning cathodically from 0 V vs SCE in degassed solution containing 20 mM ammonium chloride to act a control (see fig 5.1B). Then a CV was repeated in a solution containing 20 mM ammonium chloride and 0.5 mM nickel chloride. At acidic pH ($\text{pH} < 6$), literature reports the predominantly stable species is $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ for high chloride electrolyte concentration.²⁵ However, accounting for the low chloride experimental condition the predominant species is NiCl^+ , as detailed in Table 5.3.

Table 5.3: Calculated equilibria concentrations for 0.5 mM NiCl₂ and 20 mM NH₄Cl solution

Equilibria	K	Species	Calculated Equilibrium Concentration/ mol dm ⁻³	Species in Solution / %
$Ni^{2+} + Cl^{-} \rightleftharpoons NiCl^{+}$	2.1265 ³⁷	$NiCl^{+}$	2.127×10^{-5}	94.7
$Ni^{2+} + Cl^{-} \rightleftharpoons NiCl_{2(aq)}$	5.9237 ³⁷	$NiCl_{2(aq)}$	1.190×10^{-6}	5.3

As shown in figure 5.1B, two cathodic peaks can be observed. The first peak is likely to be the reduction of the NiCl⁺ intermediate to NiCl_(Ads) (equation 5.5) [38]. Therefore, the second peak is ascribed to the one-electron reduction of NiCl_(Ads) to Ni metal (equation 5.6) [38]. An approximate peak current (10.4 μA) was calculated for a one-electron reduction process using the reversible form of the Randles-Sevcik equation. Note that the peak current is significantly lower than the expected peak current which we postulate could be due to equation 5.6 being a kinetically slow rate-determining step, which has been suggested in literature for the mechanism of Ni deposition from other nickel chloride solutions.³⁸



The variance of scan rate with peak current for the nickel chloride reduction process was also investigated and the CV scans along with a logarithmic plot of scan rate vs

peak current for the two respective peaks is shown in Figure 5.3. The gradient of the line for the first reduction peak (figure 5.3B) is 0.741 which indicates a process which isn't purely diffusion- or adsorption-controlled, which is consistent with the proposed deposition mechanism. The gradient of the line for the second reduction peak (figure 5.3C) is 0.896 which indicates a process which isn't purely diffusion- or adsorption-controlled, which is consistent with the proposed deposition mechanism.

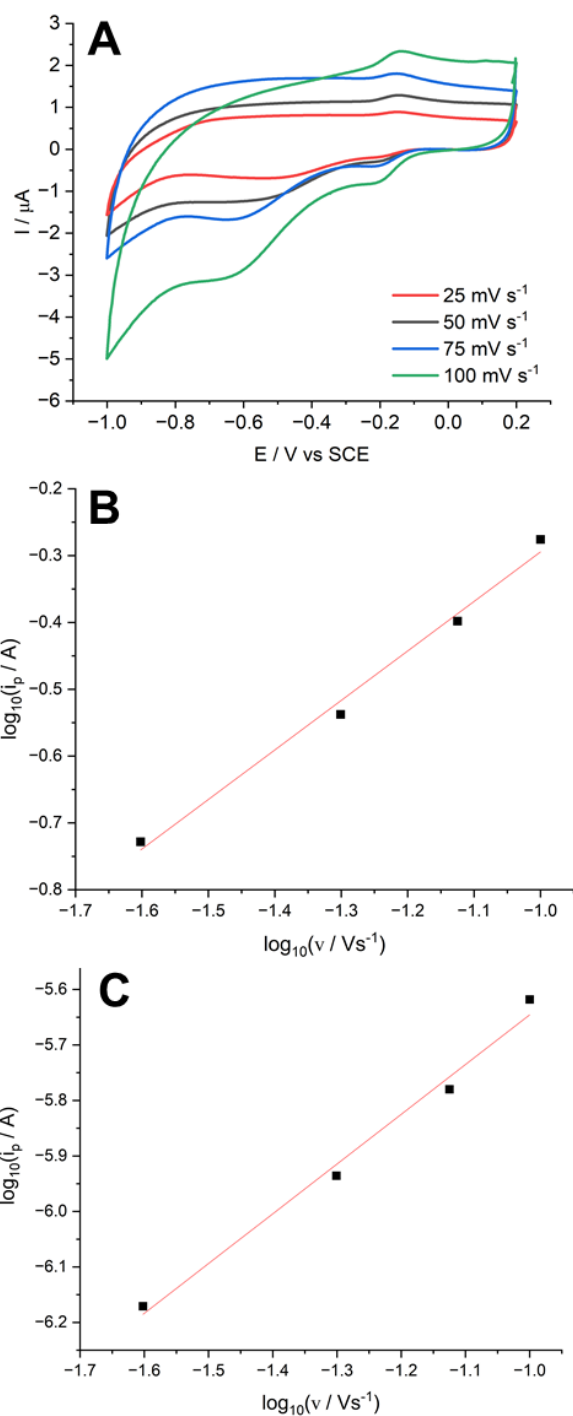


Figure 5.3 A) Variance of scan rate vs peak current conducted in a solution containing 0.5 mM NiCl₂ and 20 mM NH₄Cl. B) Logarithmic plot of peak current for first reductive peak vs scan rate where the equation of the line is $\log_{10}(I) = 0.74\log_{10}(v) + 0.45$ and $R^2 = 0.99$ C) Logarithmic plot of peak current for first reductive peak vs scan rate where the equation of the line is $\log_{10}(I) = 0.8694\log_{10}(v) - 4.7492$ and $R^2 = 0.988$.

5.4 Nano-Impact Experiments

To determine whether impacts could be detected due to nickel deposition, chronoamperometry was conducted with and without the addition of carbon black nanoparticles (20 pM) in solutions containing either 0.5 mM nickel sulfate or chloride and 20 mM of the corresponding ammonium electrolyte at a series of potentials from -0.3 to -0.8 V vs SCE. Impacts in the sulfate electrolyte were observed with an onset potential of -0.49 V vs SCE in excellent agreement with figure 5.1A. A plot of the charge passed (Q / fC) along with a typical chronoamperogram is given in figure 5.4. The charge ranges from $(-2.36 \times 10^{-14} \pm 1.1 \times 10^{-14})$ C to $(-5.00 \times 10^{-14} \pm 7.6 \times 10^{-14})$ C. The large error at -0.7 V vs SCE arises from the variety of impact spikes present from sharp single features to “step-on, step-off” features.

The corresponding coverage is given in fig 5.4C calculated via the following equations (5-8). It can be noted that across all potentials the coverage is less than 1 monolayer: ranging from (62 ± 31) % to (91 ± 62) % relative to a monolayer. Therefore, it is expected that the upscaled recovery experiment might show a relatively low deposit of nickel; owing to the apparent slow kinetics associated with the deposition of the sulfate salt.

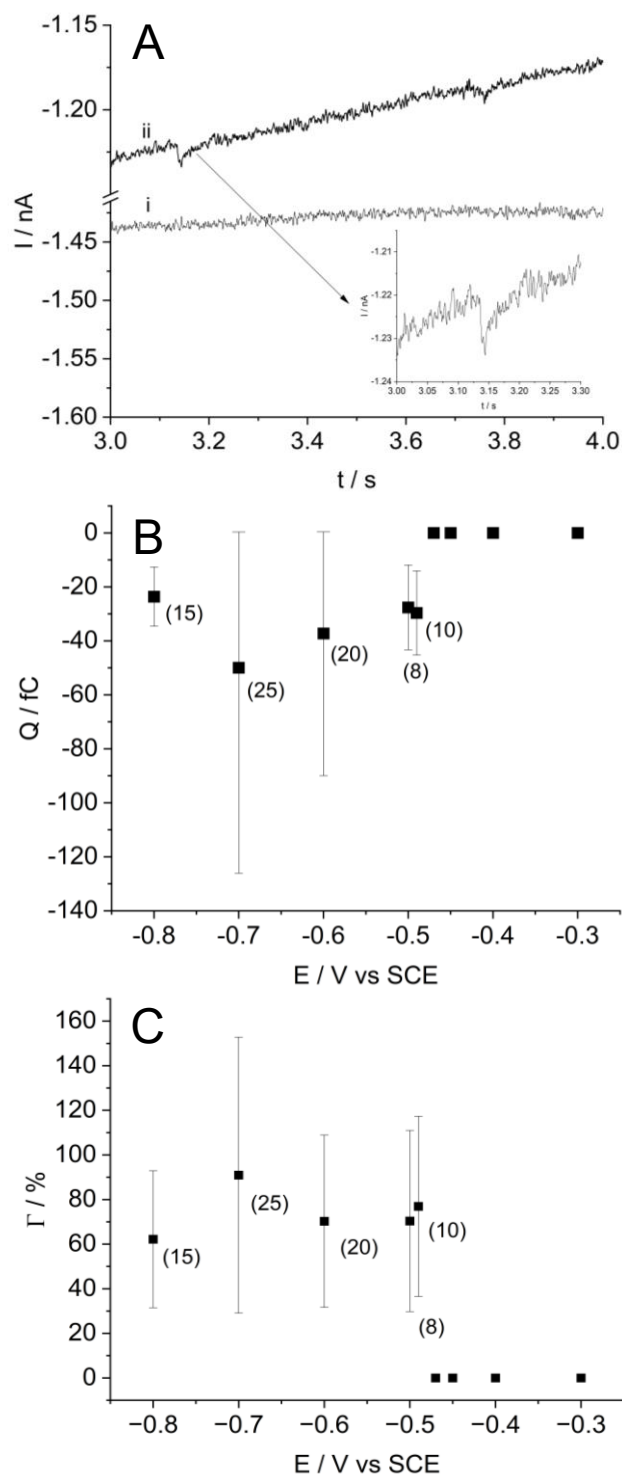


Figure 5.4 A) Representative chronoamperogram by holding a $9\ \mu\text{m}$ CF microelectrode at $-0.7\ \text{V}$ vs SCE in a solution containing $0.5\ \text{mM}$ NiSO_4 and $20\ \text{mM}$ $(\text{NH}_4)_2\text{SO}_4$ with i) and without ii) the addition of carbon black ($20\ \text{pM}$) with an inset of a zoomed in impact. B) Charge passed (Q / fC) for impacts events with the number of peaks analysed indicated in brackets. C) The corresponding coverage of Ni on CB relative to a monolayer.

Analogous scans were conducted in 0.5 mM NiCl₂ and 20 mM NH₄Cl solution to see if impacts could be detected for deposition of Ni from the chloride salt. Impacts in the chloride electrolyte were observed with an onset potential of -0.41 V vs SCE in good agreement with Figure 5.1 B. A plot of the charge passed (Q/ fC) along with a typical chronoamperogram is given in figure 5.5. The charge ranges from $(-1.76 \times 10^{-14} \pm 1.43 \times 10^{-14})$ C to $(-1.76 \times 10^{-13} \pm 6.20 \times 10^{-14})$ C. The large error associated with the charge passed arises from the variety of impact spikes present from sharp single features to “step-on, step-off” features.

The corresponding coverage is given in fig 5.5 C ranging from (45.7 ± 37.0) % to (285 ± 160.7) % relative to a monolayer. Due to the sluggish rate determining step of the chloride mechanism, it is anticipated that relatively low-level deposits of nickel might be observed.

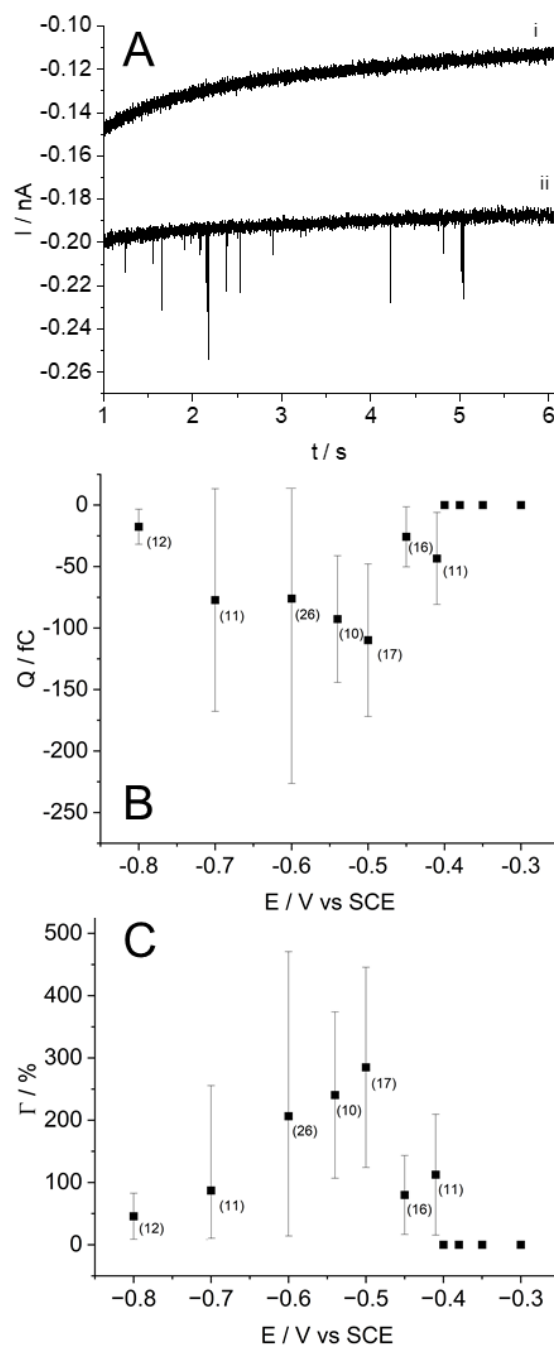


Figure 5.5 A) Representative chronoamperogram by holding a 9 μm CF microelectrode at -0.5 V vs SCE in a solution containing 0.5 mM NiCl_2 and 20 mM NH_4Cl with i) and without ii) the addition of carbon black (20 pM) with an inset of a zoomed in impact. B) Charge passed (Q / fC) vs potential, with the number of peaks analysed indicated in brackets. C) Corresponding coverage of Ni on CB relative to a monolayer calculated from charge passed per impact (Q / fC).

5.4.1 Long-Term Impact Experiment

The previously described impact experiment was upscaled to a 500 mL cell containing either 0.5 mM nickel sulfate or 0.5 mM nickel chloride, the corresponding ammonium electrolyte (20 mM) and 500 pM carbon black suspension. A 5-hour chronoamperogram was conducted using a standard three electrode system consisting of a fritted saturated SCE reference electrode, a graphite plate electrode (diameter 2.5 cm) held at -0.9 V vs SCE and a graphite rod as the counter electrode; this potential was chosen as a significant overpotential to observe higher levels of deposition whilst minimising the hydrogen evolution reaction. The solution was filtered, and the resulting filter cake was dried at 40 °C to yield the modified carbon black particles. The particles were initially analysed using SEM/EDX to give an average weight percent ratio (Ni:CB) of 0.007 ± 0.004 (table 1) and 0.030 ± 0.050 for the sulfate and chloride electrolytes respectively shown in Table 5.4.

According to literature, low Ni sulfate concentrations will result in a low coverage of adsorbed Ni atoms on carbon substrates and consequently a sparse nuclei population [180]. This is because the adsorption rate of NiSO_4^- (equation 5.3) on metallic nickel is slow due to inhibition by adsorbed species ($\text{H}_{(\text{ads})}$ and $\text{SO}_4^{2-}{}_{(\text{ads})}$)^{39,40} hence adsorption and discharge of NiSO_4 on carbon becomes preferable. Therefore, this may result in a large number of very small (potentially nanoscale) nickel clusters deposited across the carbon black nanoparticles which may be difficult to detect via SEM/EDX therefore resulting in a relatively low Ni:C ratio. We expect the same to be the case for nickel chloride solutions in which the deposition mechanism features a similar adsorption step for the corresponding chloride species (equation 5.6).

Typical SEM images of impacted CB NPs from chloride and sulfate electrolytes are shown in figure 5.6. EDX mapping for further examples of Ni-modified CB NP are

shown in figure 5.7, revealing the presence of relatively small nickel deposits on the carbon particles.

Table 5.4: SEM/EDX and ICP-MS characterisation of unmodified and impact modified CB NP.

CBNP Sample	SEM/EDX Average Weight % Ratio Ni/C	ICP-MS- Ni Conc. (ppm)
Unmodified	0	0.10 ± 0.01
-0.9 V vs SCE (NiSO ₄)	0.007 ± 0.004	0.67 ± 0.06
-0.9 vs SCE (NiCl ₂)	0.030 ± 0.050	0.80 ± 0.04

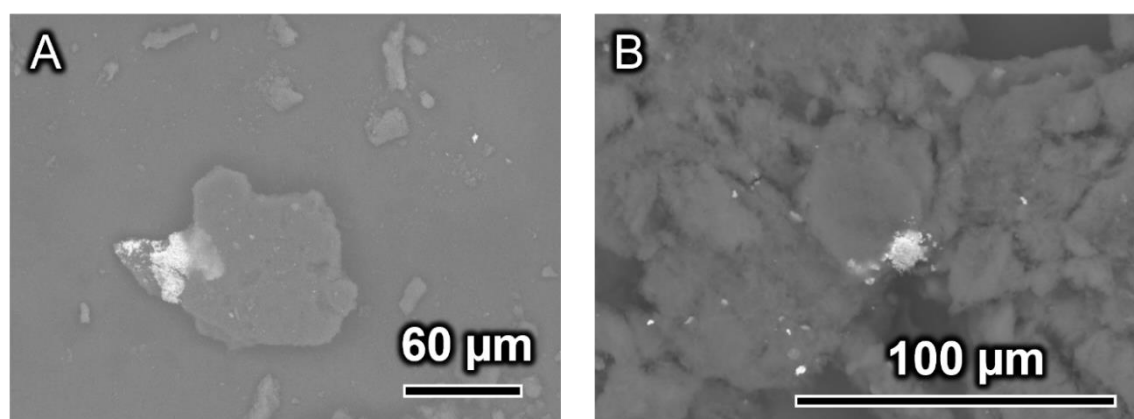


Figure 5.6: SEM images of A) Impacted CB NPs from NiSO₄ at -0.9 V vs SCE and B) Impacted CB NPs from NiCl₂ at -0.9 V vs SCE.

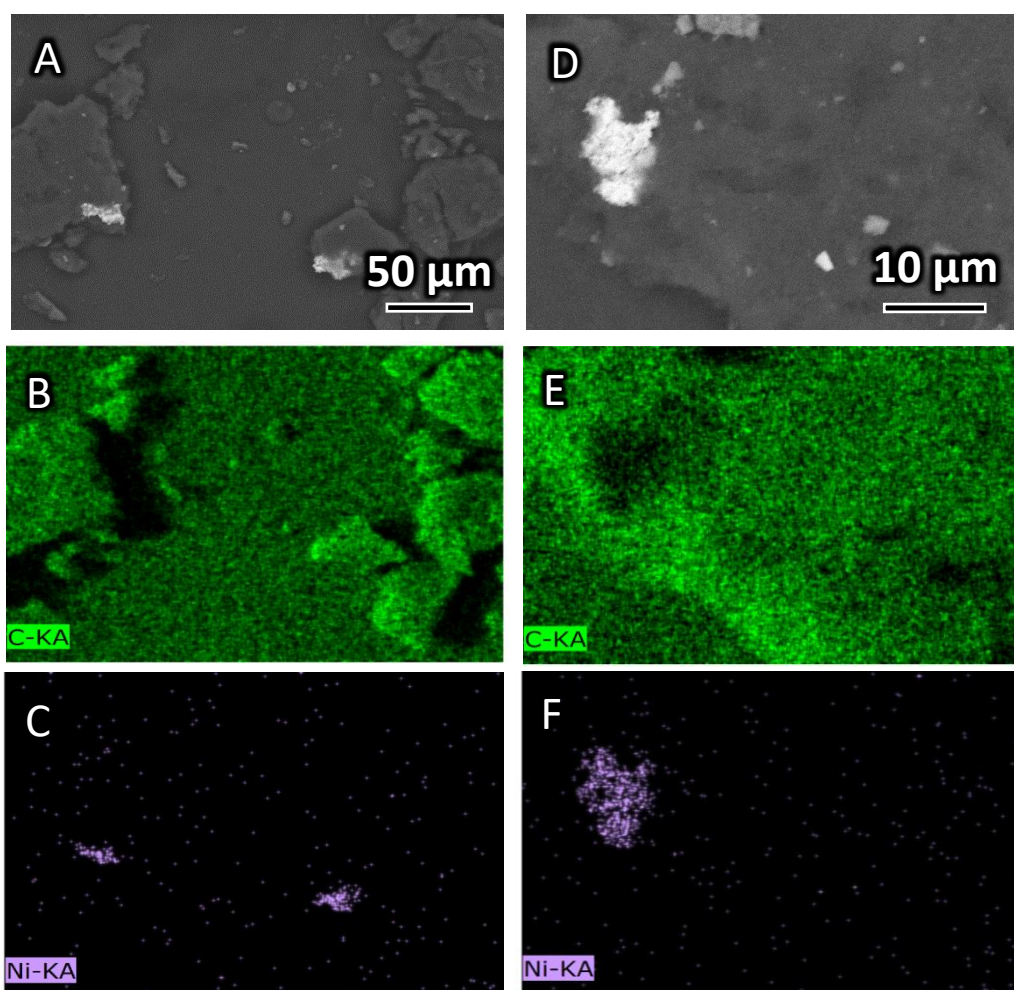


Figure 5.7: A) SEM image of impacted CB NPs from NiSO_4 at -0.9 V vs SCE, B) and C) Carbon and nickel EDX mapping of the particles, respectively. D) SEM image of impacted CB NPs from NiCl_2 at -0.9 V vs SCE, E) and F) Carbon and nickel EDX mapping of the particles, respectively.

In order to accurately quantify the concentration of nickel deposited, the modified particles were analysed and compared to unmodified CB NPs using ICP-MS (table 5.4). A residual nickel content of $0.1 \pm 0.01 \text{ ppm}$ was detected in the unmodified carbon black (corrected for residual nickel found in the aqua regia control sample). Carbon black itself is also known to contain many metal impurities; one of which is nickel.⁴¹ However, a significantly higher nickel content of $0.67 \pm 0.06 \text{ ppm}$ and $0.80 \pm 0.04 \text{ ppm}$ for the Ni-modified CB NP deposited from sulfate and chloride electrolytes respectively

after 120 hours aqua regia digestion was detected, confirming that nickel deposition had occurred under impact.

Due to the relatively low levels of nickel detected from SEM/EDX and ICP-MS analysis, the graphite electrodes from the 5 hr experiments were also examined, as shown in Figure 5.8. A Ni:C weight % ratio of 0.776 and 0.633 was found for the chloride and sulfate electrodes respectively, which is significantly higher than that detected on the particles. Deposition on the substrate electrode can be a significant challenge when using nanoparticles and substrate electrode of the same material, as difference in onset potential can be much less than 100 mV.³

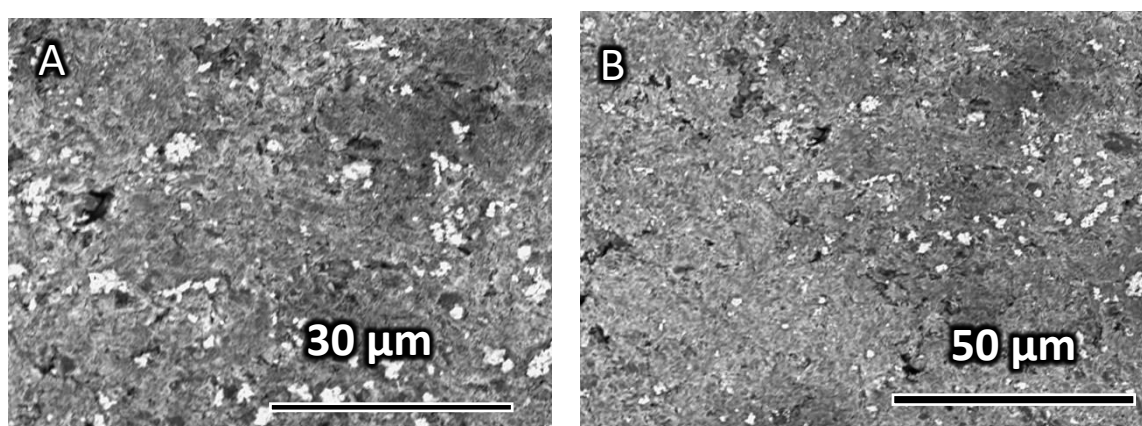


Figure 5.8: A) Graphite plate electrode held at -0.9 V vs SCE in a solution containing NiSO_4 and $(\text{NH}_4)_2\text{SO}_4$. B) Graphite plate electrode held at -0.9 V vs SCE in a solution containing NiCl_2 and NH_4Cl .

5.5 Conclusions

In conclusion, the electrodeposition of nickel from dilute chloride and sulfate solutions in ammonium electrolytes has been studied on glassy carbon via cyclic voltammetry. Reductive nano-impacts were observed for both chloride and sulfate electrolytes with onset potentials of -0.50 V vs SCE and -0.41 V vs SCE respectively, in good agreement with solution voltammetry. The system was upscaled to yield sufficient

material for characterisation revealing low levels of nickel via SEM/EDX and ICP-MS analysis for both electrolytes. We postulate this is due to the slow nucleation kinetics on carbon substrates for low concentration nickel solutions. The graphite electrode was also examined revealing a significant Ni deposit which is a common challenge when the nanoparticles and substrate electrode are made from the same material.

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6. CONCLUSIONS

In summary, this thesis has explored the use of nano-impact electrochemistry as a potential recovery method for three different metals: manganese, ruthenium and nickel. Chapter 1 outlines the challenges associated with the primary extraction of metals due to their varying abundance and finite nature, as well as the negative environmental and social impacts of mining practices. Therefore, the recovery of metals from secondary sources such as e-waste presents a more sustainable alternative and is currently an active area of research. However, current recovery techniques are hindered by issues such as poor selectivity, the production of pollutants and the generation of large volumes of toxic waste.

Electrochemical methods are more attractive due to their higher selectivity and purity of recovered metals as well as their scalability and energy-efficiency. In particular, nano-impact electrochemistry has emerged as a promising recovery method for metals from low concentration solutions due to the higher rate of mass transport to the nanoparticles and therefore increased deposition rate.

The results section contains three chapters in which the use of nano-impact electrochemistry was applied to the recovery of manganese, ruthenium and nickel from low concentration solutions. In chapter 3, the electroreduction and electrooxidation of Mn(II) was investigated using microelectrode studies and macroelectrode studies to establish a potential window for impact experiments. The onset potentials for Mn(II) reduction and oxidation agreed well with literature. Nano-impacts in the presence of 5 pM carbon black were observed corresponding to Mn(II) reduction and oxidation onto carbon black nanoparticles, where the switch on potential aligned with previously observed onset potentials (-1.44 V vs SCE and +0.5 V vs SCE), respectively. The nano-impact experiment was upscaled which gave direct evidence

for Mn deposition on carbon black shown by SEM/ EDX analysis. Lower than expected amounts of MnO_2 were found on the CB NPs, in addition to some intermediate species, which we postulate was due to the complex mechanism of oxidation of Mn(II) .

In chapter 4, the electroreduction of Ru(III) on GC and CB-modified GC was observed at onset potentials of -0.55 V vs SCE and -0.5 V vs SCE respectively; analysis indicating a three-electron reduction process. The electrooxidation of Ru(III) was also investigated, however the feature was too broad to accurately define the onset potential. Nano-impact experiments were performed and reductive impacts were observed in the presence of 25 pM in good agreement with the onset potential established solution voltammetry. Oxidative impacts were also observed corresponding to the electrooxidation process of Ru(III) . The reductive nano-impact experiment was upscaled to generate ca. $14.1 \text{ wt\%}$ Ru-modified carbon black particles with the SEM/EDX and XPS characterisation revealing a RuO_2 deposit; a commonly observed species associated with the aqueous electrodeposition of Ru(III) . Under partially-optimised conditions, $>90\%$ of the ruthenium from solution was recovered in ca. 8 hours.

In Chapter 5, the study focused on the electrodeposition of nickel from dilute chloride and sulfate solutions in ammonium electrolytes on a glassy carbon electrode, using cyclic voltammetry. Reductive nano-impacts were observed for both electrolyte types, with onset potentials of -0.50 V vs. SCE for chloride and -0.41 V vs. SCE for sulfate, consistent with solution voltammetry. The system was then scaled up to generate sufficient material for further analysis, which indicated low levels of nickel deposition, as confirmed by SEM/EDX and ICP-MS. This low deposition levels can be attributed to slow nucleation kinetics on carbon substrates in low-concentration nickel solutions.

The graphite electrode was also examined and showed substantially higher levels nickel deposits than the carbon nanoparticles, a known challenge when both the nanoparticles and the substrate are composed of the same material.

6.1 Future Work

For all metals studied, a significant level of background deposition was observed on the substrate electrode due to both the substrate electrode and nanoparticle core being made of carbon. This similarity in material results in little to no difference in onset potentials for electrodeposition on the electrode and nanoparticles. To improve the selectivity of electrodeposition occurring exclusively on the nanoparticles, using a different substrate electrode with a higher overpotential for the electrodeposition is recommended. Materials such as could boron-doped diamond could prove as a viable alternative, offering additional advantages such as a relatively wide potential window and low capacitive current.

Given the substantial database of individual metals established in this work - Mn, Ru, and Ni, along with Cu, Pd, and Pt in other studies- future work should focus on the recovery of metals from mixed waste solutions that more accurately represent industrial waste streams.

Finally, to use of an impinging jet is recommended to accurately control the level of electrodeposition on the nanoparticles. It would also allow the possibility to manufacture a range of nanoparticle architectures including bimetallic particles for electrocatalysis applications.