



The effect of iron-spiked alkaline electrolyte on Ni-based electrocatalysts towards the oxygen evolution reaction

MM Heath



orcid.org/0000-0003-0094-8128

Dissertation accepted in partial fulfilment of the requirements
for the degree *Master of Science in Chemistry* at the
North-West University

Supervisor: Prof RJ Kriek

Co-supervisor: Prof F Seland

Co-supervisor: Prof S Sunde

Graduation May 2022

27227316

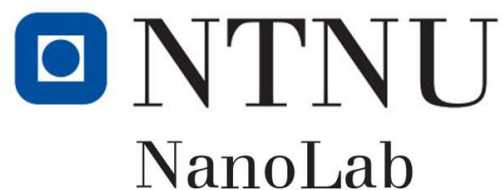
ACKNOWLEDGEMENTS

I am grateful for each person who has had an impact on my life in the past two years. I would like to sincerely thank the following people:

- Prof RJ Kriek, who introduced me to the world of electrochemistry, believed in me and presented me with wonderful opportunities that enriched my life forever. Thank you for teaching me about this amazing field of research.
- Prof S Sunde and Prof F Seland who welcomed me at NTNU with open arms. Thank you for your guidance and everything that I could learn from you.
- Dr F Poureshghi for all the help and guidance in the lab.
- Dr M Potgieter for teaching me new things and always being willing to help when I need it.
- My husband, Nico-Paul Bester. Thank you for your love and support during the past two years, especially during the times I spent on the other side of the world from you.
- My parents, Mark and Ann Heath, for always supporting me in every way you can, believing in my dreams and motivating me to pursue them.

I would like to sincerely thank the following institutions:





This work is based on the research supported wholly / in part by the National Research Foundation of South Africa (Grant Numbers: 123025, 118753)



The Grantholder acknowledges that opinions, findings and conclusions or recommendations expressed in any publication generated by the NRF supported research is that of the author(s) alone, and that the NRF accepts no liability whatsoever in this regard.

PREFACE

The research presented in this dissertation was carried out as a part of the SANOCEAN programme (South Africa/Norway joint research programme on ocean research including blue economy, climate change, the environment and sustainable energy). The focus of this study was on sustainable energy, specifically, water electrolysis. This is a fundamental study, focused on investigating NiFe electrocatalysts for the oxygen evolution reaction (OER), which is the rate-limiting reaction in water electrolysis. NiFe exhibits excellent activity toward the OER, and it is of interest to determine why its activity is so much higher than that of its constituents (Ni and Fe). In this study, Ni and NiO electrocatalysts were studied in both pure KOH and Fe-containing KOH to investigate the effect of Fe on their OER activities and structures. The research presented here was conducted at both NWU (The North-West University, Potchefstroom campus) and NTNU (The Norwegian University of Science and Technology). The transmission electron microscopy (TEM) measurements in this study were conducted by Bjørn G. Solheim, senior engineer at NTNU's TEM Gemini Centre. The scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) analyses were conducted by Innocent Shuro, materials characterisation specialist at the NWU. Furthermore, the X-ray photoelectron spectroscopy (XPS) measurements in this study were performed by Martin F. Sunding at SINTEF materials physics in Oslo. Cyclic voltammetry (CV), in-situ Raman spectroscopy and XPS results were of primary interest. The research approach entailed electrochemical cycling of Ni electrocatalysts with different morphologies and oxidation states in pure KOH, and KOH containing 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe. After 30 CV cycles, the Ni electrocatalysts were subjected to in-situ Raman spectroscopy as well as XPS analyses, to observe the impact of electrolytic Fe on the structural and electronic properties of Ni.

The dissertation is written in South African English.

ABSTRACT

An efficient means to store renewable energy is the electrolytic production of hydrogen. However, the anodic half-cell reaction in water electrolysis is sluggish and requires a good, cost-effective electrocatalyst, such as Ni. Nevertheless, the reason for the high electrocatalytic activity of Ni was proven to be trace amounts of Fe in the alkaline electrolyte. In recent years, numerous efforts have been made to elucidate how Fe enhances the OER activity of Ni. Controversy in the literature exists as to whether Ni or Fe is the active site, and recent literature indicates that it is surface Fe as opposed to Fe in the bulk structure that enhances the OER activity of Ni electrocatalysts. Therefore, this study aims to determine the effect of electrolytic Fe on both the OER activity and the structure of Ni electrocatalysts through electrochemical and physical characterisation. Eight electrocatalysts were investigated in iron-spiked 0.1 M KOH, i.e., colloidal nanoparticles as Ni and NiO, nanosheets as Ni, NiO and NiNiO and magnetron sputtered Ni, NiO and NiNiO. The nanoparticles were prepared with two different synthesis methods (a tailored method and chemical reduction) to produce two unique morphologies and annealing was employed to produce different oxidation states. Cyclic voltammetry (CV) was used to precondition the Ni electrocatalysts, evaluate the OER activity and to give insight into the redox features. Furthermore, in-situ Raman spectroscopy provided insight into the OER active sites. X-ray photoelectron spectroscopy (XPS) was used to analyse the oxidation states of Ni as well as the amount of Fe on the surface of the electrocatalysts before and after cycling. Similar overpotentials were achieved for nanoparticles cycled in pure KOH regardless of the preparation method or as-prepared oxidation state (390 – 415 mV). Lower overpotentials were achieved for sputtered thin films (350 mV). Increasing the electrolytic Fe concentration from 0.007 ppm to 1 mM resulted in increased OER activity with unique behaviour for electrocatalysts with different morphologies. For colloidal nanoparticles, enhanced activity was observed only at 1 mM Fe and overpotentials of 360 mV were achieved. For nanoparticles prepared by reduction (nanosheets), an electrolytic Fe concentration of 0.3 ppm already enhanced the activity. For sputtered electrocatalysts, the minimum overpotential is achieved after the addition of 0.9 ppm Fe to the electrolyte. Raman spectroscopy of nanoparticles confirmed that α -FeOOH appears on the surface of all electrocatalysts at the electrolytic Fe concentrations where enhanced activity is observed, confirmed by the presence of three new peaks (apart from the NiOOH peaks at 480 and 560 cm^{-1}), corresponding to FeOOH. The absence of peaks corresponding to NiFe LDH confirms that the Fe species responsible for enhanced OER activity is indeed surface-bound and not bulk Fe. Furthermore, SEM-EDX and XPS results confirmed that Fe is present on the surface and is not homogeneously distributed. This investigation was successful in preparing and comparing Ni electrocatalysts of different morphologies and identifying FeOOH on the surfaces corresponding

to enhanced activities of all electrocatalysts regardless of morphology. The knowledge obtained in this study can be employed to develop more efficient OER electrocatalysts in the future.

Key terms: Nickel/iron electrocatalysts, Nickel thin films, Nickel oxide nanoparticles, Iron-spiked media, Electrocatalysis, Oxygen evolution reaction (OER), Physical vapor deposition (PVD), In-situ Raman spectroscopy, Cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS)

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
PREFACE	III
ABSTRACT	IV
LIST OF ABBREVIATIONS	XXV
CONFERENCE CONTRIBUTIONS AND PUBLICATIONS.....	XXVII
1. INTRODUCTION	1
1.1 Background	1
1.2 Research aims, objectives and questions	2
1.3 The significance of this study	4
1.4 Limitations	4
1.5 Structural outline	5
2. LITERATURE STUDY	6
2.1 Background	6
2.2 The oxygen evolution reaction (OER) mechanism and kinetics in alkaline solution	8
2.3 Ni-based OER electrocatalysts	11
2.4 The effect of Fe on Ni-based electrocatalysts (for the OER)	15
2.5 NiFe co-synthesised electrocatalysts	17
2.6 Active sites and electrocatalysis.....	18
2.7 The active site debate	20

2.7.1	Ni as active site in NiFe electrocatalysts	20
2.7.2	Fe as active site in NiFe electrocatalysts	21
2.7.3	Synergy between Ni and Fe.....	22
2.7.4	Surface Fe is responsible for the enhanced activity of NiFe electrocatalysts	22
2.8	Nanoparticles versus sputtered thin films as OER electrocatalysts.....	23
2.9	Characterisation techniques.....	24
2.9.1	Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) with Energy Dispersive X-Ray (EDX) Analysis	25
2.9.2	In-situ Raman spectroscopy	26
2.9.3	X-ray photoelectron spectroscopy (XPS)	30
2.9.4	X-ray diffraction (XRD).....	37
2.9.5	Electrochemistry	38
2.9.5.1	Voltammetry	40
2.9.5.1.1	Cyclic voltammetry (CV)	42
2.9.5.1.2	Linear sweep voltammetry (LSV).....	43
2.9.5.1.3	Tafel plots.....	43
2.9.5.2	Electrochemical double-layer (EDL) capacitance.....	49
2.9.5.3	Electrochemical impedance spectroscopy (EIS)	51
3. METHODOLOGY		52
3.1	Research questions.....	52
3.1.1	How is Fe incorporated by Ni electrocatalysts when Fe is present in the electrolyte?	52
3.1.2	How does the morphology of Ni-based electrocatalysts influence electrolytic Fe uptake and OER activity?	54

3.1.2.1	An overview of the synthesis methods employed in this study	54
3.1.3	Is the Ni oxidation state and the electrolytic Fe content interrelated?	55
3.2	Aim	56
3.3	Experimental outline	56
4.	NI-BASED NANOPARTICLES.....	61
4.1	Experimental methods	61
4.1.1	Synthesis of Ni and NiO nanoparticles.....	61
4.1.1.1	The synthesis of colloidal Ni and NiO nanoparticles with a tailored method	61
4.1.1.2	Synthesising Ni, NiO and NiNiO nanosheets with the chemical reduction method	62
4.1.2	Physical characterisation	63
4.1.2.1	TEM.....	63
4.1.2.2	XRD.....	63
4.1.2.3	XPS	63
4.1.3	Electrochemistry	64
4.1.3.1	Electrode preparation	64
4.1.3.2	Ink formulation	64
4.1.3.3	Preparation of electrolyte.....	65
4.1.3.4	Voltammetry techniques	65
4.1.3.5	Chronoamperometry (CA) for Tafel analysis.....	67
4.1.3.6	Evaluation of the electrochemical double layer capacitance	68
4.1.4	In-situ Raman spectroscopy	68
4.2	Results	70

4.2.1	Transmission electron microscopy (TEM) images of Ni-based nanoparticles....	70
4.2.2	X-ray diffraction (XRD) results of Ni-based nanoparticles	72
4.2.3	X-ray photoelectron spectroscopy results of Ni-based nanoparticles after electrochemical cycling in pure and Fe-doped KOH.....	76
4.2.4	Cyclic voltammetry for preconditioning and electrocatalytic activity measurements before and after the addition of electrolytic Fe	85
4.2.4.1	CVs for colloidal Ni prepared by a tailored synthesis	85
4.2.4.2	CVs for colloidal NiO prepared by a tailored synthesis.....	88
4.2.4.3	CVs for Ni prepared by the chemical reduction synthesis method.....	91
4.2.4.4	CVs for NiO prepared by the chemical reduction synthesis method.....	93
4.2.4.5	CVs for NiNiO prepared by the chemical reduction synthesis method	96
4.2.5	Linear sweep voltammetry and Tafel analysis of Ni-based nanoparticles.....	99
4.2.6	Determination of the electrochemical double layer capacitance of Ni-based nanoparticles through cyclic voltammetry	104
4.2.7	In-situ Raman spectroscopy in pure and Fe-doped electrolyte before and after electrochemical cycling.....	106
4.2.7.1	In-situ Raman spectra of colloidal Ni before and after cycling	107
4.2.7.2	In-situ Raman spectra of colloidal NiO before and after cycling	110
4.2.7.3	In-situ Raman spectra of Ni prepared by reduction before and after potential cycling	112
4.2.7.4	In-situ Raman spectra of NiO prepared by reduction before and after potential cycling	113
4.2.7.5	In-situ Raman spectra of NiNiO prepared by reduction before and after potential cycling	115
4.2.7.6	Tables summarising the in-situ Raman results.....	117

5. SPUTTERED THIN FILMS.....	126
5.1 Experimental.....	126
5.1.1 Sputtering Ni, NiO and NiNiO thin films.....	126
5.1.2 SEM and EDX	127
5.1.3 XPS	127
5.1.4 Electrochemical analyses	127
5.1.5 In-situ Raman spectroscopy	127
5.2 Results	128
5.2.1 SEM-EDX results of sputtered Ni-based thin films	128
5.2.2 XPS of sputtered Ni-based samples	132
5.2.3 Electrochemical analysis of sputtered Ni-based samples.....	144
5.2.3.1 CVs of sputtered Ni-based samples.....	144
5.2.3.2 LSVs and Tafel analysis of sputtered Ni-based samples	149
5.2.3.3 LSVs after re-cycling activated samples in pure KOH	153
5.2.3.4 EDL capacitance of sputtered Ni-based samples.....	156
5.2.3.5 Electrochemical impedance spectroscopy toward the determination of charge transfer resistance of sputtered Ni-based thin films.....	159
6. DISCUSSION.....	166
7. CONCLUSION	177
7.1 Summary	177
7.2 Answering the research questions	177
7.3 Contributions	178
7.4 Limitations and recommendations.....	179

BIBLIOGRAPHY	180
APPENDIX A	194
APPENDIX B	207

LIST OF TABLES

Table 2-1: A summary of some of the proposed OER mechanisms found in literature.	9
Table 2-2: Ni and Fe species and their corresponding Raman shifts reported for in-situ experiments in KOH.	28
Table 2-3: Ni and Fe species and their corresponding Raman shifts reported for ex-situ experiments.	30
Table 2-4: A summary of the oxidation states and corresponding binding energies present in the 2p XPS spectra of Ni and Fe containing electrocatalysts.	34
Table 2-5: A summary of Tafel slope values reported in literature for Ni and NiFe OER electrocatalysts.	48
Table 3-1: An outline of the electrocatalysts studied	56
Table 3-2: The experimental techniques that will be used to analyse the electrochemical activity and structure of Ni-based nanoparticles.	58
Table 3-3: The experimental techniques that will be used to analyse the electrochemical activity and structure of sputtered Ni-based thin films.....	59
Table 4-1: Binding energies of the peaks in the Ni 2p XPS spectra of the Ni electrocatalysts cycled in pure and Fe containing KOH.	83
Table 4-2: Relative percentages of Fe in the electrocatalyst samples as determined from XPS spectra of Ni 3p and Fe 3p regions.	84
Table 4-3: Peak positions and peak height ratios obtained from the in-situ Raman spectra of as-prepared samples.	118
Table 4-4: Peak positions and peak height ratios obtained from the in-situ Raman spectra of cycled samples.....	121
Table 5-1: The percentage of Fe relative to the percentage of Ni in each of the as-prepared sputtered samples, as well as after cycling in each electrolyte. ...	131

Table 5-2: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered Ni in KOH containing different concentrations of Fe.....	161
Table 5-3: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered NiO in KOH containing different concentrations of Fe.....	163
Table 5-4: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered NiNiO in KOH containing different concentrations of Fe.....	165
Table B-1: Binding energies of the peaks in the Ni 2p XPS spectra of the Ni electrocatalysts cycled in pure and Fe containing KOH.	212

LIST OF FIGURES

Figure 2-1: A schematic representation of the hydrogen economy (redrawn from Wei <i>et al.</i> ²³).	7
Figure 2-2: The bifunctional OER mechanism (redrawn from Bai <i>et al.</i> ¹¹).	11
Figure 2-3: The Bode Scheme indicating the different phases of Ni.....	13
Figure 2-4: A representation of the Sabatier principle (redrawn from Medford <i>et al.</i> ⁷⁷).	19
Figure 2-5: A schematic representation of the PVD sputtering process (redrawn from Baptista <i>et al.</i> ⁹⁰).	24
Figure 2-6: A schematic representation of the components of an XPS instrument (redrawn from ¹¹²).	31
Figure 2-7: An illustration of Bragg's equation adapted from Atkins and Overton ¹²⁸	37
Figure 2-8: The electrochemical double layer that arises due to potential applied to the working electrode ¹³²	50
Figure 2-9: A depiction of a standard Randle's circuit.	51
Figure 3-1: Synthesis of colloidal Ni nanoparticles from nickel(II) acetylacetonate, oleylamine and tri-n-octylphosphine (redrawn from ⁴⁴).	54
Figure 4-1: The standard three-electrode cell used for electrochemical analyses.	65
Figure 4-2: The setup used for all in-situ Raman spectroscopic measurements.	69
Figure 4-3: TEM images of as-synthesised colloidal (a) Ni and (b) NiO nanoparticles at different magnifications for visualisation of single particles.....	71
Figure 4-4: TEM images of NiNiO nanoparticles prepared by the chemical reduction method.....	72
Figure 4-5: Powder XRD patterns of NiO (blue) and Ni (red) prepared by the tailored synthesis.....	73
Figure 4-6: Powder XRD patterns of NiO (green), Ni (orange) and NiNiO (purple) prepared by the chemical reduction synthesis.....	74

Figure 4-7: X-ray diffraction patterns of GC substrate, colloidal Ni as well as NiO prepared by reduction deposited on the GC substrate.....	75
Figure 4-8: Grazing incidence diffraction patterns of (a) carbon paper and (b) gold substrates.	75
Figure 4-9: XPS survey spectrum for colloidal NiO cycled in pure KOH.....	77
Figure 4-10: Ni 2p XPS spectra of colloidal Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	78
Figure 4-11: Ni 2p XPS spectra of colloidal NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	79
Figure 4-12: Ni 2p XPS spectra of Ni prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	80
Figure 4-13: Ni 2p XPS spectra of NiO prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM KOH.....	81
Figure 4-14: Ni 2p XPS spectra of NiNiO prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	82
Figure 4-15: 30 CV cycles of colloidal Ni performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	85
Figure 4-16: Redox features of colloidal Ni performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	86
Figure 4-17: 30 th CV cycle of colloidal Ni catalyst in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).	87
Figure 4-18: 30 CV cycles of colloidal NiO performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	88
Figure 4-19: The redox features of colloidal NiO in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	89

Figure 4-20: 30 th CV cycle of colloidal NiO catalyst in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).	90
Figure 4-21: 30 CV cycles of Ni prepared by reduction performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	91
Figure 4-22: The redox features of Ni prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	92
Figure 4-23: 30 th CV cycle of the Ni catalyst prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).	93
Figure 4-24: 30 CV cycles of NiO prepared by reduction performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	94
Figure 4-25: The redox features of NiO prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	95
Figure 4-26: 30 th CV cycle of NiO prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).	96
Figure 4-27: 30 CV cycles of NiNiO prepared by reduction performed at 20 mV s ⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	97
Figure 4-28: The redox features of NiNiO prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.....	98
Figure 4-29: 30 th CV cycle of NiNiO prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).	99
Figure 4-30: LSV performed at 1 mV s ⁻¹ of (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction.	100
Figure 4-31: A bar chart indicating the overpotentials of each Ni-based electrocatalyst cycled in pure KOH (purple), 0.3 ppm Fe (red) and 1 mM Fe (green).....	101

Figure 4-32: Tafel plots for (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction after cycling.	102
Figure 4-33: A bar chart illustrating the Tafel slope values of Ni-based nanoparticle electrocatalysts after 30 CV cycles in pure KOH and KOH containing different concentrations of Fe.	103
Figure 4-34: CVs of colloidal Ni in pure KOH performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	104
Figure 4-35: A plot of scan rate against the current response at 0.05 V vs Hg/HgO for (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction.	105
Figure 4-36: A bar chart of the electrochemical double layer capacitance values of Ni-based nanoparticles cycled in pure KOH, and KOH containing 0.3 ppm and 1 mM Fe.	106
Figure 4-37: The current response observed for the potentials applied to the colloidal Ni working electrode in different electrolyte compositions in parallel with in-situ Raman spectroscopy (a) before and (b) after 30 CV cycles.	107
Figure 4-38: Raman spectra of as-prepared colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	108
Figure 4-39: Raman spectra of colloidal Ni after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	109
Figure 4-40: Raman spectra of as-prepared colloidal NiO in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	110
Figure 4-41: Raman spectra of colloidal NiO after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	111
Figure 4-42: Raman spectra of as-prepared Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	112

Figure 4-43: Raman spectra of Ni prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	113
Figure 4-44: Raman spectra of as-prepared NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	114
Figure 4-45: Raman spectra of NiO prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	115
Figure 4-46: Raman spectra of as-prepared NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.	116
Figure 4-47: Raman spectra of NiNiO prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe.	117
Figure 4-48: The 480/560 cm ⁻¹ peak height ratio of each of the electrocatalysts at 0.6 V vs Hg/HgO.	125
Figure 5-1: SEM images of sputtered Ni at (a) 3 mm and (b) 3 μm magnification.	128
Figure 5-2: The percentage oxygen relative to the percentage Ni in each of the as-prepared sputtered samples, as well as after cycling in each electrolyte. ...	129
Figure 5-3: SEM-EDX mapping analysis of the entire surface of a sputtered Ni thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.	132
Figure 5-4: XPS survey spectrum for sputtered Ni after cycling in KOH containing 1 mM Fe.	133
Figure 5-5: Ni 2p XPS spectra of as-prepared sputtered Ni and sputtered Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	134
Figure 5-6: Ni 2p XPS spectra of as-prepared sputtered NiO and sputtered NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.....	135

Figure 5-7: Ni 2p XPS spectra of as-prepared sputtered NiNiO and sputtered NiNiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.....	137
Figure 5-8: O 1s XPS spectra of as-prepared sputtered Ni and sputtered Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.	138
Figure 5-9: O 1s XPS spectra of as-prepared sputtered NiO and sputtered NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.....	139
Figure 5-10: O 1s XPS spectra of as-prepared sputtered NiNiO and sputtered NiNiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.....	140
Figure 5-11: Ni 3p and Fe 3p XPS peaks of sputtered Ni as-prepared and cycled in KOH containing different concentrations of Fe.....	141
Figure 5-12: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered Ni electrocatalysts cycled in KOH containing different concentrations of Fe.....	142
Figure 5-13: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered NiO electrocatalysts cycled in KOH containing different concentrations of Fe.....	143
Figure 5-14: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered NiNiO electrocatalysts cycled in KOH containing different concentrations of Fe.....	144
Figure 5-15: 30 th CV cycle at 20 mV s ⁻¹ of sputtered Ni in pure KOH (purple) and KOH containing six different concentrations of Fe.....	145
Figure 5-16: Redox features of the 30 th CV cycles at 20 mV s ⁻¹ of sputtered Ni in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink) and 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange) 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).	146

Figure 5-17: 30 th CV cycle at 20 mV s ⁻¹ of sputtered NiO in pure KOH (purple) and KOH containing six different concentrations of Fe.....	147
Figure 5-18: Redox features of the 30 th CV cycles at 20 mV s ⁻¹ of sputtered NiO in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink) and 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange), 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).	148
Figure 5-19: 30 th CV cycle at 20 mV s ⁻¹ of sputtered NiNiO in pure KOH (purple) and KOH containing six different concentrations of Fe.....	148
Figure 5-20: Redox features of the 30 th CV cycles at 20 mV s ⁻¹ of sputtered NiNiO in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink), 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange) 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).	149
Figure 5-21: LSVs at 1 mV s ⁻¹ of sputtered (a) Ni (b) NiO and (c) NiNiO after 30 CVs in pure KOH (purple), and KOH containing six different concentrations of Fe.	150
Figure 5-22: A bar chart summarising the overpotential values of sputtered Ni, NiO and NiNiO after 30 CV cycles in KOH containing different concentrations of Fe.	151
Figure 5-23: Tafel plots for sputtered Ni after cycling in pure KOH and KOH containing six different Fe concentrations.....	152
Figure 5-24: Tafel plots for sputtered NiO after cycling in pure KOH and KOH containing six different Fe concentrations.....	152
Figure 5-25: Tafel plots for sputtered NiNiO after cycling in pure KOH and KOH containing six different Fe concentrations.....	153
Figure 5-26: LSVs of sputtered Ni after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).....	154
Figure 5-27: LSVs of sputtered NiO after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).....	155

Figure 5-28: LSVs of sputtered NiNiO after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).....	155
Figure 5-29: CVs of sputtered Ni in KOH containing 0.003 ppm Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.....	156
Figure 5-30: A plot of scan rate against the current response at 0.05 V vs Hg/HgO for sputtered (a) Ni, (b) NiO and (c) NiNiO in different Fe concentrations.	157
Figure 5-31: A bar chart summarising the electrochemical double layer capacitance values of sputtered Ni, NiO and NiNiO after 30 CVs in KOH containing different concentrations of Fe.....	158
Figure 5-32: Nyquist plots obtained from the EIS measurements of sputtered Ni performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.	160
Figure 5-33: Nyquist plots obtained from the EIS measurements of sputtered NiO performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.....	162
Figure 5-34: Nyquist plots obtained from the EIS measurements of sputtered NiNiO performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.....	164
Figure 5-35: A bar chart of the charge transfer resistance at 0.63 V for sputtered Ni,NiO and NiNiO in KOH containing different concentrations of Fe.	165
Figure 6-1: A bar chart summarizing the OER overpotentials of each of the Ni-based electrocatalysts after 30 CV cycles in pure KOH, 0.3 ppm Fe and 1 mM Fe.	167
Figure 6-2: A bar chart summarizing the OER overpotentials of each of the Ni-based electrocatalysts after 30 CV cycles in pure KOH, 0.3 ppm Fe and 1 mM Fe.	169

Figure 6-3: Fe concentrations in the bulk (EDX) and on the surface (XPS) of sputtered Ni electrocatalysts after cycling in KOH containing Fe.	172
Figure A-1: CVs of colloidal Ni in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	194
Figure A-2: CVs of colloidal NiO in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	195
Figure A-3: CVs of NiO prepared by reduction in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	196
Figure A-4: CVs of NiNiO prepared by reduction in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	197
Figure A-5: In-situ Raman spectra of Colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.	198
Figure A-6: In-situ Raman spectra of Colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.	199
Figure A-7: In-situ Raman spectra of Colloidal NiO in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.	200
Figure A-8: In-situ Raman spectra of Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.	201
Figure A-9: In-situ Raman spectra of Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.	202

Figure A-10: In-situ Raman spectra of NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.	203
Figure A-11: In-situ Raman spectra of NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.	204
Figure A-12: In-situ Raman spectra of NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.	205
Figure A-13: In-situ Raman spectra of NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.	206
Figure B-1: SEM-EDX mapping analysis of the entire surface of a sputtered Ni thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.	207
Figure B-2: SEM-EDX mapping analysis of the entire surface of a sputtered NiO thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.	208
Figure B-3: SEM-EDX mapping analysis of the entire surface of a sputtered NiO thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.	209
Figure B-4: SEM-EDX mapping analysis of the entire surface of a sputtered NiNiO thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.	210
Figure B-5: SEM-EDX mapping analysis of the entire surface of a sputtered NiNiO thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.	211
Figure B-6: CVs of sputtered Ni in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	213
Figure B-7: CVs of sputtered NiO in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.	214

Figure B-8: CVs of sputtered NiNiO in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO. 215

LIST OF ABBREVIATIONS

η	Overpotential
μ	micro
$^{\circ}\text{C}$	Degrees Celsius
A	Ampere
C_{DL}	Double Layer Capacitance
CA	Cronoamperometry
CE	Counter Electrode
CV	Cyclic Voltammetry
DFT	Density Functional Theory
E^0	Standard Electrode Potential
E_{eq}	Equilibrium Potential
ECSA	Electrochemical Surface Area
EDL	Electrochemical Double Layer
EDX	Energy Dispersive X-ray Spectrometry
F	Faraday constant
Fe	Iron
FeOOH	Iron oxyhydroxide
GC	Glassy Carbon
H_2	Hydrogen
H_2O	Water
HER	Hydrogen Evolution Reaction
Hg/HgO	Mercury/Mercury Oxide
i	Current
j	Current density
KOH	Potassium Hydroxide
LDH	Layered Double Hydroxide
LSV	Linear Sweep Voltammetry
M	Molar
Ni	Nickel
NiOOH	Nickel Oxyhydroxide
$\text{Ni}(\text{OH})_2$	Nickel hydroxide
O_2	Oxygen
OER	Oxygen Evolution Reaction
PVD	Physical Vapor Deposition

R	Gas constant
R	Resistance (as used for iR correction)
RE	Reference Electrode
RDE	Rotating Disk Electrode
RHE	Reversible Hydrogen Electrode
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
V	Volt
WE	Working Electrode

CONFERENCE CONTRIBUTIONS AND PUBLICATIONS

Conference

M.M. Heath, R.J. Kriek, M. Potgieter, F. Seland and S. Sunde. An in-situ Raman spectroscopic study of nickel-based electrocatalysts in iron-spiked media towards the oxygen evolution reaction. Oral presentation at: The 31st Catalysis Society of South Africa (CATSA) international conference. 7-10 November 2021. Via virtual platform.

Articles

Two papers will be submitted to peer reviewed journals, with the following provisional titles:

1. An in-situ Raman spectroscopic study of the effect of electrolytic Fe on Ni electrocatalysts towards the oxygen evolution reaction (OER)
2. The effect of iron-spiked alkaline electrolyte on the electrocatalytic activity of magnetron sputtered Ni electrocatalysts

1. INTRODUCTION

Nickel/Iron (NiFe)-based electrocatalysts are of the most efficient non-noble metal oxygen evolution reaction (OER) electrocatalysts to date¹. In addition, trace amounts of Fe in alkaline electrolyte have been reported to enhance the OER activity of Ni². However, conflicting views exist as to whether Ni or Fe is the active site in these electrocatalysts and how Fe enhances the activity of Ni. This research aims to investigate the effect of electrolytic Fe on the structure and OER activity of Ni electrocatalysts. This section serves as an introduction to this study by outlining the background, discussing the research problem, the research aims and objectives, the significance of the research and lastly the limitations.

1.1 Background

Due to the increasing demand for renewable energy worldwide, efficient energy storage technologies are needed, as most renewable energy sources are intermittent³. Splitting water to form hydrogen and oxygen in a process called water electrolysis, is a promising solution to store energy in the form of hydrogen. Water electrolysis involves two half-cell reactions, of which the anodic oxygen evolution reaction (OER) is rate-limiting because of its slow kinetics. Therefore, an efficient and cheap electrocatalyst is required to overcome the high overpotential of the OER. Although noble metals such as platinum are excellent OER electrocatalysts in terms of activity, they are very expensive and therefore not a practical solution to large scale water splitting. Several transition metals have proven to be promising alternatives as OER electrocatalysts⁴. In particular, Ni has been investigated as an OER electrocatalyst for decades and numerous studies have proven Ni to be an excellent electrocatalyst. Fe has also been studied but did not receive much attention for being a good OER electrocatalyst. However, Fe is renowned for increasing the activity of Ni electrocatalysts, or even being the reason for the excellent performance of Ni, by unintentionally incorporating into the structure of Ni from alkaline electrolytes^{2,5,6}. Although Ni and Fe have been known as OER electrocatalysts for the last century, their popularity has increased dramatically in recent years⁷. Currently, it is well known that Fe enhances the electrocatalytic activity of Ni and NiO towards the OER in alkaline solutions. However, controversy in the literature exists regarding whether Ni or Fe is the active site for OER and how exactly the addition of Fe enhances the OER activity of Ni electrocatalysts. Although the research is contradictory, the common point is that Fe alters the active phase. In addition, recent literature indicate that Fe on the surface of NiFe electrocatalysts is responsible for the enhanced OER activity thereof and not Fe in the bulk structure^{8,9,10,11}.

It is important to understand why and how Fe enhances the OER activity of Ni electrocatalysts as this will aid in developing more efficient electrocatalysts. To understand how the structures of Ni electrocatalysts are modified by the presence of Fe will aid in OER electrocatalyst design. It is also important for electrochemists to accurately report the OER activities of electrocatalysts, which cannot be done if the activity of an electrocatalyst is unintentionally altered by the presence of another species.

In order to effectively solve the debate regarding the active site of NiFe electrocatalyst and to determine how Fe enhances the OER activity of Ni, many research efforts have been conducted. The research usually combines an array of electrochemical techniques as well as physical characterisation techniques. A key point is that in-situ techniques are critical towards answering these questions, as information is required about the electrocatalyst structure during the OER. In-situ Raman spectroscopy is a powerful tool that can be used to monitor the structural changes of Ni (oxides and oxyhydroxides) as a function of applied potential. Numerous studies have used in-situ Raman spectroscopy to gather information on the effects of aging⁶, Fe-content^{12,13,14}, temperature, isotope exchange¹⁵ and other parameters¹⁶ on the structure of Ni catalysts. In addition to Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) is also a powerful tool to evaluate how the structure and composition of Ni electrocatalysts are influenced by electrochemistry in Fe-containing electrolytes. This technique can also analyse the Fe content in the surface of electrocatalyst films after Fe has been adsorbed/incorporated.

1.2 Research aims, objectives and questions

Given the unanswered questions in literature regarding the activity enhancing effect of Fe on Ni electrocatalysts, this study will aim to identify and evaluate the impact of electrolytic Fe on the OER activity and structure of Ni electrocatalysts. Various electrochemical analysis methods and physical characterisation techniques will be employed to gain insight into the effect of Fe originating from the electrolyte on Ni electrocatalysts. Physical characterisation will be done before, during and after electrochemical analyses in KOH doped with different concentrations of Fe. This will be done to determine how Fe structurally alters Ni, where the Fe incorporates into the structure and whether Ni or Fe is the active site in NiFe-based electrocatalysts. Instead of investigating only one type of Ni electrocatalyst, investigating various types of morphologies and oxidation states further aids in understanding the relationship between Ni electrocatalysts and electrolytic Fe. Therefore, two different morphologies of nanoparticles as well as sputtered samples will be prepared and investigated in this study to ascertain how morphology influences Fe uptake. This has not been studied before and could provide insight into the link between Fe incorporation and Ni electrocatalyst morphology. Additionally, these electrocatalysts will be prepared as Ni, NiO and NiNiO to evaluate how the as-prepared oxidation state influences Fe

incorporation and therefore OER activity. The OER activity of each electrocatalyst cycled in KOH containing different Fe concentrations, determined with electrochemical techniques, will be correlated with structural and electronic changes observed with physical analysis techniques.

Ultimately, the aim of this study is to evaluate the effect of different concentrations of electrolytic Fe on the structure and OER activity of Ni-based electrocatalysts of different morphologies. The research questions arising from the aim are as follows:

- i. How is Fe incorporated by Ni electrocatalysts when Fe is present in the electrolyte?

Is Fe replacing some of the lattice Ni in the structure, or is it only present on the surface of Ni? In addition, different electrolytic Fe concentrations will be investigated. This will determine the effect of the concentration of Fe in the electrolyte on the nature of its inclusion into the structure of Ni electrocatalysts.

- ii. How does the morphology of Ni-based electrocatalysts influence electrolytic Fe uptake and OER activity?

Does the different electrocatalyst morphologies result in different saturation points for Fe uptake? How does this influence the OER activity?

- iii. Is the electrolytic Fe content and the Ni oxidation state interrelated?

Does the as-prepared oxidation state of Ni electrocatalysts influence Fe uptake and OER activity? In addition, what is the effect of the electrolytic Fe concentration on the oxidation state of Ni and does this have an influence on the OER activity?

This study aims to answer these questions by combining electrochemistry with in-situ Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDX). Electrochemical analyses will show how the OER activity of different Ni electrocatalysts is influenced by added Fe in the electrolyte. In-situ Raman spectroscopy will be used to obtain information on the electrocatalyst structure under working conditions, which will shed light on the active structure. Furthermore, XPS will be used to examine the electronic structure and composition before and after electrochemical testing in KOH electrolyte containing sub ppm as well as concentrated amounts of iron. Lastly, EDX and EDX mapping semi quantitatively indicates the composition and the homogeneity of the electrocatalysts. Comparing EDX and XPS results could yield information about the bulk composition versus surface composition, respectively.

1.3 The significance of this study

The knowledge obtained from this study will contribute to filling the gap in the literature regarding how Fe enhances the OER activity of Ni electrocatalysts and ultimately to determine the OER active site in NiFe electrocatalysts. The study will help electrochemists gain a thorough understanding of how different concentrations of electrolytic Fe influences Ni electrocatalysts. If a better understanding is obtained about the way in which Fe enhances OER activity of Ni-based electrocatalysts, it will aid the development of more efficient and cost-effective electrocatalysts for the OER. By studying both nanoparticles and sputtered thin films along with different electrolytic Fe concentrations, insight will be obtained regarding the optimum morphology for Fe uptake and the optimum Fe concentration. This research can then be used to further enhance the OER activity of NiFe-based electrocatalysts.

Fundamental research is crucial toward the development of better OER electrocatalysts. This is why this study uses an array of different physical characterisation methods to support the electrochemical data obtained. This allows us to gain insight into structural, compositional and electronic changes of Ni electrocatalysts that follow electrochemical testing in Fe containing electrolyte.

1.4 Limitations

This study is one of a fundamental nature and the scope is limited to laboratory-based benchtop electrochemical experiments. This implies that the electrocatalysts are not tested large-scale or in real-world practical systems such as alkaline electrolyzers. Furthermore, the study is limited to a single in-situ technique, which is in-situ Raman spectroscopy. Ideally, more in situ techniques should be performed to obtain a better insight into the active structures. Post-mortem analyses often yield inadequate results pertaining to OER active structures, because the electrocatalyst under investigation is not at operational potential or pH, which can lead to ambiguous argumentation regarding the active site. To truly understand the working mechanism of electrocatalysts and get a clear idea of what the active site is, the electrocatalysts need to be studied under reaction conditions. In-situ X-ray absorption spectroscopy (XAS)¹⁷ and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)¹⁸ are techniques that have recently been employed to study electrocatalysts in-situ and would be ideal towards answering the research questions in this study. Unfortunately, the researcher did not have access to these techniques during the study.

1.5 Structural outline

In section one, the framework of the study has been introduced. The research aims, objectives and questions have been outlined and the significance of the study has been explained. This section has also shed light on the limitations of the study. Section two will review the existing literature on Ni, Fe and NiFe-based electrocatalysts as well as how related studies have employed the characterisation techniques that will be used in this study. Section three will explain the methodology used in pursuit of answering the research questions. Sections four and five will outline the experimental methods as well as the results obtained from them for nanoparticles and sputtered electrocatalysts, respectively. Section six will discuss these results and sections seven and eight will conclude this study by summarizing the final conclusions and giving recommendations for future studies.

2. LITERATURE STUDY

This section provides a thorough review of the literature currently available on Ni and NiFe OER electrocatalysts as well as different methods that are commonly used to study these electrocatalysts. First, a background is given to the current energy crisis and water electrolysis towards the production of hydrogen. In section 2.1, it is pointed out that the OER is the rate-limiting reaction in water electrolysis and therefore requires an efficient electrocatalyst. Noble metals are efficient electrocatalysts but are expensive and therefore transition metals are researched as OER electrocatalysts. Before looking at these transition metals, the reader is introduced to the OER mechanism in section 2.2. Thereafter, previous research on Ni electrocatalysts for the OER is discussed (section 2.3). Here, it is discovered that unintentional Fe incorporation from alkaline electrolytes have provided misleading results regarding the OER activity of Ni, which leads to the next section (2.4), describing the effect of Fe on Ni electrocatalysts. After the Fe enhancing effect has been discovered, researchers started to intentionally synthesise NiFe electrocatalysts, discussed in the following section. After this, we start looking into active sites and the active site debate (sections 2.6 and 2.7); is Ni or Fe the active site in NiFe electrocatalysts and how does Fe enhance the activity of Ni electrocatalysts? This is the main research question in this study. Therefore, the subsequent sections (2.8 and 2.9) will focus on the types of electrocatalysts and different characterisation techniques that have predominantly been used in previous studies to investigate similar questions. This is also the techniques that will be used in this study to answer the research questions posed in the previous section.

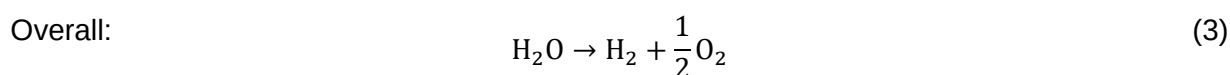
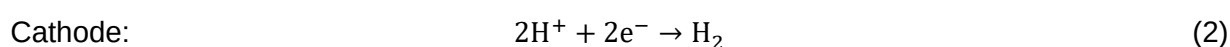
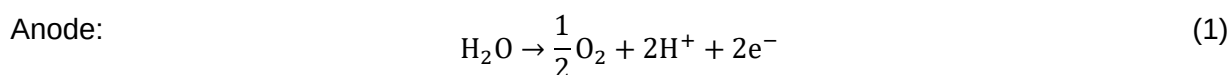
2.1 Background

85% of the energy produced globally stem from fossil fuels such as crude oil, coal and natural gas, which all consist of hydrocarbons¹⁹. During combustion, these hydrocarbons produce carbon dioxide (CO₂) and water when enough oxygen is present¹⁹. CO₂ is a greenhouse gas that contributes to global warming and climate change. Furthermore, the natural carbon cycle on earth is disrupted by the excessive production of CO₂ through fossil fuel combustion¹⁹. All of this is exacerbated by an increasing demand for energy; the global energy demand is predicted to be double in 2032 of what it was in 2017⁴. In addition, fossil fuel is a non-renewable energy source that cannot provide long term global energy security. Therefore, a clean, renewable, and sustainable energy alternative is of utmost importance.

This need for renewable energy led to the development of renewable energy technologies in recent decades. However, most renewable energies are intermittent such as solar and wind.

Hydrogen can effectively be used to store this energy by means of water electrolysis driven by renewable energy. For over twelve decades, water electrolysis has been utilized to produce hydrogen²⁰. Only in recent years, hydrogen became renowned as one of the most important energy storage solutions of this century³. Hydrogen can be used in systems such as fuel cells, which efficiently react hydrogen and oxygen to release the stored energy, with zero emissions.

During water electrolysis, water is the reactant that yields oxygen and hydrogen when a direct current is applied²¹. The reactions involved are as follows^{21,22}:



At the positive anode, water is oxidized, and oxygen is evolved, resulting in this reaction being termed the oxygen evolution reaction (OER), depicted in equation (1). Hydrogen gas is evolved during the cathodic reduction reaction of hydrogen ions, identifying equation (2) as the hydrogen evolution reaction (HER). When these reactions are reversed, hydrogen can be used as fuel to generate electrical power in fuel cells. The anodic reaction is then termed the hydrogen oxidation reaction (HOR) and the cathodic reaction the oxygen reduction reaction (ORR)²³. A summary of the four reactions involved in the hydrogen economy can be seen in the following scheme ²³:

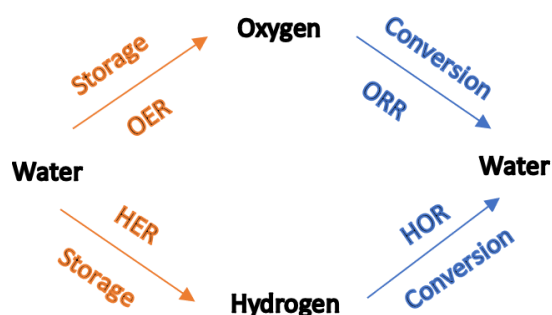


Figure 2-1: A schematic representation of the hydrogen economy (redrawn from Wei *et al.*²³).

The sluggish kinetics of the OER and ORR²³ cause the storage and conversion of hydrogen to be less efficient and, as a result, to be more expensive. Catalysts such as platinum (Pt), iridium (Ir), Ruthenium (Ru) and their oxides are excellent electrocatalysts for these reactions. RuO₂ and

IrO₂, which are considered as the benchmarks for OER electrocatalysts, require (for current density of 10 mA cm⁻²) an overpotential of 200 mV in acid and 300 mV in base²⁴. However, these noble metals are extremely expensive and rare, rendering them impractical for commercial use.

In practice, water electrolysis is commonly performed in alkaline medium^{21,22,25}. The OER reaction in alkaline medium involves the oxidation of hydroxyl groups to produce H₂O and O₂ by losing a total of four electrons⁷. Multiple electron transfer involves multiple reaction steps with one electron transfer per step²⁶. A build-up of energy at each step results in the slow kinetics of this reaction^{7,4}. Consequently, a suitable OER electrocatalyst is needed. An ideal electrocatalyst for the OER should be abundant, durable, inexpensive, scalable and have a high OER activity⁷. Therefore, transition metal electrocatalysts have been widely studied over the past few decades^{23,4,25}. Transition metals have multivalent oxidation states (M^{+2/+3/+4}), which makes them appropriate candidates for OER electrocatalysis as these states are proved to be the active sites for OER⁴. Before taking a deeper look into the transition metal electrocatalysts, the OER mechanism should first be considered.

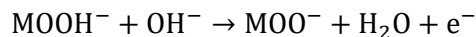
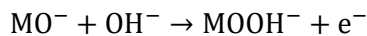
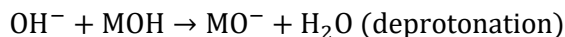
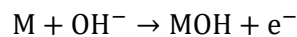
2.2 The oxygen evolution reaction (OER) mechanism and kinetics in alkaline solution

The mechanism of the OER is much more complex than the mechanism of its cathodic counterpart^{25,23}. In addition, controversy exists in literature regarding the exact mechanism^{20,27,28,29,30,31}. This is in part due to the fact that every instance of OER on a specific electrode surface is unique³². A summary of some of the proposed mechanisms can be seen in Table 2-1. In all the reaction mechanisms, M denotes a surface- or metal site on the electrocatalyst where the OER occurs (the catalytically active site). All the reaction mechanisms start with the initial adsorption of hydroxide ions to the active site.

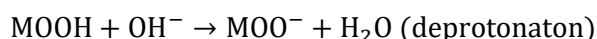
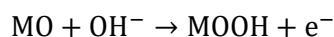
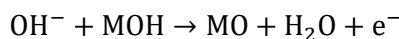
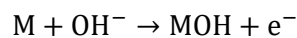
Table 2-1: A summary of some of the proposed OER mechanisms found in literature.

Mechanism	Description	Source
$\text{OH}^- + \text{M} \rightarrow \text{MOH} + \text{e}^-$ $2\text{MOH} \rightarrow \text{MO} + \text{M} + \text{H}_2\text{O}$ $2\text{MO} \rightarrow 2\text{M} + \text{O}_2$	The oxide path	1956, Bockris ³³
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MO} + \text{H}_2\text{O} + \text{e}^-$ $2\text{MO} \rightarrow 2\text{M} + \text{O}_2$	The electrochemical oxide path	1956, Bockris ³³
$2\text{OH}^- + 2\text{M} \rightarrow 2\text{MOH} + 2\text{e}^-$ $2\text{OH}^- + 2\text{MOH} \rightarrow 2\text{MO} + 2\text{H}_2\text{O} + 2\text{e}^-$ $\text{MO} + \text{MO} \rightarrow \text{O}_2 + 2\text{M}$	Nickel anodes	1982, LeRoy ²⁰
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MH}_2\text{O}_2 + \text{e}^-$ $\text{MH}_2\text{O}_2 + \text{OH}^- \rightarrow \text{MO}_2\text{H}^- + \text{H}_2\text{O}$ $\text{MH}_2\text{O}_2 + \text{MO}_2\text{H}^- \rightarrow 2\text{M} + \text{OH}^- + \text{O}_2$	Bockris path	1984, Bockris and Otagawa ^{34,35}
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MO}^- + \text{H}_2\text{O}$ $\text{MO}^- \rightarrow \text{MO} + \text{e}^-$ $2\text{MO} \rightarrow 2\text{M} + \text{O}_2$	Krasil'shchikov Nickel oxides	1997, Miller and Rocheleau ²⁷
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MO} + \text{H}_2\text{O} + \text{e}^-$ $\text{MO} + 2\text{OH}^- \rightarrow \text{MOO}^- + \text{H}_2\text{O} + \text{e}^-$ $\text{MOO}^- \rightarrow \text{M} + \text{O}_2 + \text{e}^-$	Suitable for 3d transition metals	2020, Anantharaj ³¹
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MO} + \text{H}_2\text{O} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MOOH} + \text{e}^-$ $\text{MOOH} + \text{OH}^- \rightarrow \text{MOO}^- + \text{H}_2\text{O}$ $\text{MOO}^- \rightarrow \text{M} + \text{O}_2 + \text{e}^-$		2015, Shinagawa ²⁹
$\text{M} + \text{OH}^- \rightarrow \text{MOH} + \text{e}^-$ $\text{MOH} + \text{OH}^- \rightarrow \text{MO} + \text{H}_2\text{O} + \text{e}^-$ $\text{MO} + \text{OH}^- \rightarrow \text{MOOH} + \text{e}^-$ $\text{MOOH} + \text{OH}^- \rightarrow \text{M} + \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$	The "classical" OER mechanism ³⁶	2020, Zhou ²⁵ 2016, Diaz-Morales ³⁶

Diaz-Morales *et al.* used spectro-electrochemical methods to prove the pH dependence of Ni catalysts in purified alkaline electrolyte and proposed a OER mechanism based on these findings³⁶. They used surface enhanced Raman spectroscopy (SERS) and ¹⁸O isotope labelling and ascribed peaks in the region 800-1350 cm⁻¹ to a superoxo (O-O) vibration³⁶. The superoxo (NiOO⁻) species is said to be obtained when NiOOH is deprotonated, which is in accordance with the pH-dependance of the activity and Raman bands³⁶. Based on these findings, they propose two possible OER mechanisms which differ from the "classical" concerted mechanism in that charged surface species are involved³⁶. The first mechanism they propose involves the deprotonation of adsorbed OH to yield a negatively charged surface oxide³⁶:



In the second mechanism they propose the deprotonation of adsorbed OOH resulting in negatively charged superoxide³⁶:



In both mechanisms the formation of O_2 occurs through the decomposition of the superoxide³⁶. This second mechanism is the same as the mechanism proposed by Shinagawa *et al.*²⁹. Since there exists experimental evidence that a superoxo species is present when the OER is catalyzed by transition metals^{36,37}, a mechanism involving this species is likely in this case. Since the pH dependence of the OER indicates that deprotonation likely occurs within the mechanism, the mechanism proposed by Shinagawa *et al.*²⁹, which is the same as the second mechanism proposed by Diaz-Morales *et al.*³⁶, is a viable OER mechanism for transition metals in alkaline media.

However, when more than one transition metal is present in an electrocatalyst, the mechanism can become more complicated. Indeed, it has been proven with spectroscopic techniques that $NiOO^-$ (superoxo species) is a precursor for dioxygen in the OER mechanism of Ni electrocatalysts but not NiFe electrocatalysts¹⁵. Therefore, NiFe electrocatalysts have a different OER mechanism than Ni electrocatalysts. A bifunctional mechanism (Figure 2-2) has recently been proposed, where one metal site is the MO site and the other is a hydrogen acceptor (A)^{11,38}. This mechanism has been identified as the OER mechanism for FeOOH-NiOOH (NiOOH with clusters of FeOOH covalently bonded to its surface), where Fe is the FeO entity and Ni acts as hydrogen acceptor¹¹.

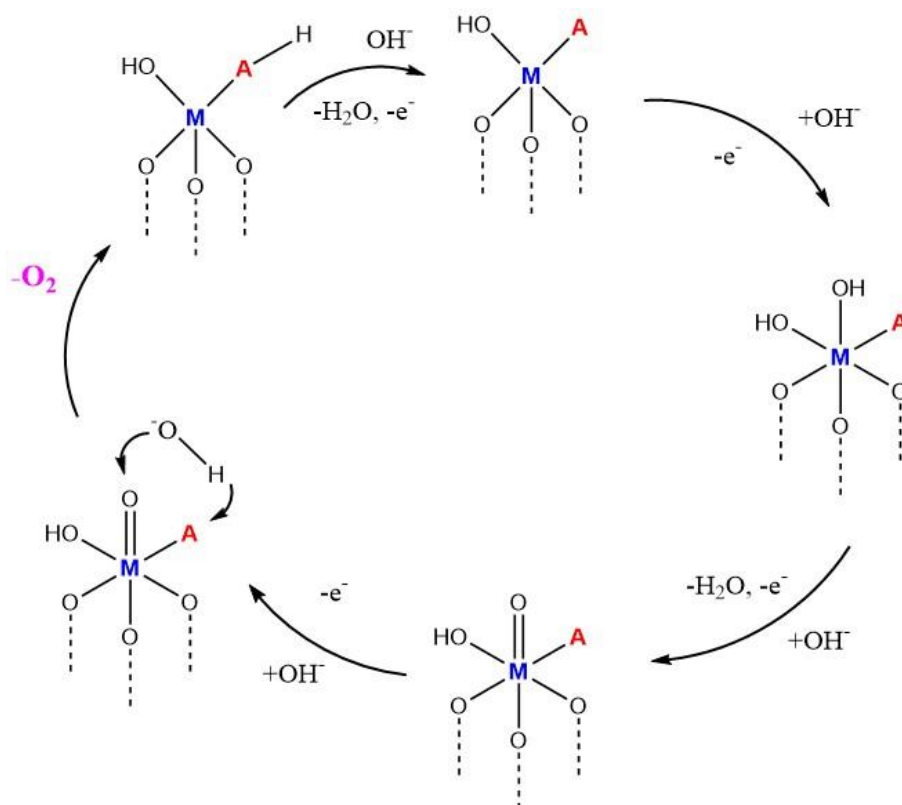


Figure 2-2: The bifunctional OER mechanism (redrawn from Bai *et al.*¹¹).

Now that an understanding of the OER mechanism is obtained, Ni OER electrocatalysts can be explored in more detail.

2.3 Ni-based OER electrocatalysts

Ni has been extensively studied as an OER electrocatalyst for the past few decades. This is because Ni electrodes are affordable, widely available and stable in alkaline media²⁶. Ni has been synthesised and studied in various forms and phases. This includes metallic/polycrystalline polished Ni^{39,26,40,32}, direct current (DC) sputtered Ni⁴¹, radio frequency (RF) sputtered Ni⁴² and various morphologies of Ni nanoparticles^{43,44,45,46,47,48}. These electrocatalysts often include various phases of Ni including oxides and hydroxides. The oxidation states of Ni electrocatalysts are well known to have an impact on their OER performance⁴. The structure of a heterogeneous catalyst can also influence the rate of the electrochemical reaction(s) taking place. In 1969 Boudart *et al.* classified catalytic reactions as structure-sensitive or structure-insensitive⁴⁹. This means that not only the type of transition metal, but also structural factors, such as its morphology and crystal structure, can have an influence on its electrocatalytic activity. Different morphologies and types of Ni OER electrocatalysts are often reported to exhibit different OER activities^{8,50}. Therefore, the OER with Ni as electrocatalyst can be classified as a structure-sensitive reaction

and it can be expected that different morphologies or oxidation states of Ni will exhibit different activities and electrocatalytic properties.

A recent example is a study comparing 1D hollow NiO nanofibers with 3D NiO nanoparticles and found that the former had an overpotential that was 133 mV vs RHE (at 10 mA cm⁻²) lower than that of the latter⁵¹. Although the 3D nanoparticles had smaller particle size, which is said to lead to better OER activities, it was outperformed by the 1D nanofibers⁵¹. This indicates that the morphology of nanomaterials dictates their OER activity rather than their size. The nanofibers had a larger electrochemically active surface area (ECSA) and thus more active sites where the OER could take place, since active sites were available on both external and internal surfaces of the fibers⁵¹. The nanofibers also had a rough surface which promoted the detachment of bubbles⁵¹. Another study compared mesoporous NiO electrocatalysts consisting of nanoplates, nanorods and nanoparticles⁵². They found that the sample with the highest pore volume, consisting of mainly nanoplates, exhibited the best OER activity⁵². These studies are demonstrations of the close relationship that exists between OER activity and the morphology of Ni electrocatalysts.

In addition to different morphologies, different oxidation states of Ni are often synthesised. This is because the higher oxidation states of Ni, such as Ni²⁺ or Ni³⁺, are said to be more active for OER^{4,53,54}. NiO is often synthesised as electrocatalyst material and is generally believed to exhibit better OER activity than Ni^{4,24,55}. Ni(OH)₂ is also commonly prepared as one of two phases, which will be discussed subsequently^{56,57}.

Although different oxidation states of Ni can be synthesised, it is well known that a thin layer of oxide is formed immediately when a Ni electrode comes in contact with air²⁶. Furthermore, when immersed in an alkaline solution, a film of Ni(OH)₂ is spontaneously formed on the surface of the electrocatalyst^{48,55}. A study that performed XPS on a black nickel coating found that the main component on the surface was Ni(OH)₂³². After a part of the surface layer was removed with argon etching, the prevailing surface compound was NiO³². This indicates that layers with different oxidation states can form on the same Ni electrode.

Ni(OH)₂ exists as an alpha (α) and a beta (β) phase and it is said that it is the alpha phase that forms spontaneously^{26,56}. α-Ni(OH)₂ and β-Ni(OH)₂ have different crystal structures with the main difference being the stacking of planes along the c-axis. The planes in α-Ni(OH)₂ are disordered and have larger interplane spacing than in β-Ni(OH)₂²⁶. In addition, electrochemical ageing is claimed to irreversibly convert α-Ni(OH)₂ to β-Ni(OH)₂^{56,26,40,16,58}.

When an anodic potential is applied, $\text{Ni}(\text{OH})_2$ is oxidized to NiOOH , which can also exist in one of two phases; alpha (α) and gamma (γ). $\alpha\text{-Ni}(\text{OH})_2$ is oxidized to $\gamma\text{-NiOOH}$ and $\beta\text{-Ni}(\text{OH})_2$ to $\beta\text{-NiOOH}$ and the latter is said to occur at higher potentials than the former²⁶. The famous Bode scheme, as first published by Bode *et al.* in 1966, illustrates these phases and transitions and can be seen in Figure 2-3⁵⁹.

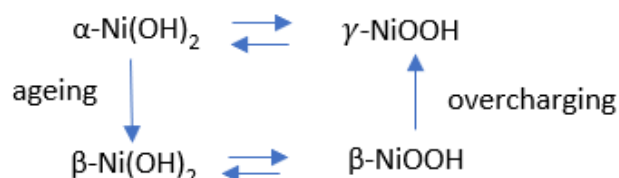


Figure 2-3: The Bode Scheme indicating the different phases of Ni.

The structures of metal oxides and hydroxides such as $\text{Ni}(\text{OH})_2$ and NiOOH are said to be edge-sharing layers of octahedral NiO_6 ^{14,5, 60,61}. These structures are layered with water and anions intercalating between the layers^{60,5,61}. The high activity of these materials are often ascribed to the large surface area and electrolyte accessibility. However, a single layer of this material has been analysed and the activity was found to be superior to the layered structure due to an increased number of active edge sites and better conductivity⁶¹.

As a metal is studied in a certain pH-range, while known electrode potentials are applied to this metal, a Pourbaix diagram is an important tool that should be used. Beverskog and Puigdomenech published Pourbaix diagrams for Ni at various temperatures, which predict the phases of Ni that will be present under certain applied potentials⁵⁸. They report that the oxidation of $\text{Ni}(\text{OH})_2$ in alkaline media yields solid phase higher oxides with semiconductor properties and write this reaction in the simplified form:



Furthermore, they mention that the preparation method and exact composition of alkaline electrolyte will influence the chemical nature of the higher oxides⁵⁸. At 25°C and basic pH (13), the Pourbaix diagram indicates that $\beta\text{-Ni}(\text{OH})_2$ will be the stable phase of Ni at potentials between -0.5 V and 0.6 V vs SHE⁵⁸. When the potential is increased further, NiOOH phases are stable.

In addition, some studies readily synthesise Ni electrocatalysts in the form of $\alpha\text{-Ni}(\text{OH})_2$ and $\beta\text{-Ni}(\text{OH})_2$. In 1992, Portemer *et al.* synthesised both of these phases with electrochemical impregnation, which is basically the cathodic deposition of $\text{Ni}(\text{OH})_2$ from an electrolyte containing $\text{Ni}(\text{NO}_3)_2$ ⁵⁷. When the temperature of the impregnation bath was below 60°C, an

α -type $\text{Ni}(\text{OH})_2$ was formed and above this temperature a mixture of both phases was obtained⁵⁷. Another early study on the structural changes of Ni in OER environments, found that $\text{Ni}(\text{OH})_2$ electrodeposited onto an electrode surface was a mixture of α - and β - $\text{Ni}(\text{OH})_2$ ⁶². In a later study, β - $\text{Ni}(\text{OH})_2$ was formed by cycling α - $\text{Ni}(\text{OH})_2$ between 0.25 and 0.35 V vs Hg/HgO in 8 M KOH for 15 hours⁵⁶.

It can be very difficult to differentiate between these two phases of $\text{Ni}(\text{OH})_2$, since they are very sensitive to factors in-situ, such as potential. To further complicate matters, it was recently discovered that Fe impurities in electrolyte affects the structure of these electrocatalysts⁵. Most studies that investigated the structural differences between α - $\text{Ni}(\text{OH})_2/\gamma$ - NiOOH and β - $\text{Ni}(\text{OH})_2/\beta$ - NiOOH were conducted in unpurified electrolyte and therefore reported structural changes could have occurred due to unintentional Fe incorporation⁶. Klaus *et al.* performed electrochemical experiments in rigorously Fe-free KOH and used these results along with quartz crystal microbalance (QCM) and physical characterisation techniques to assess the structural changes of $\text{Ni}(\text{OH})_2$ ⁶. They found that β - $\text{Ni}(\text{OH})_2/\beta$ - NiOOH is the predominant phase when as-deposited α - $\text{Ni}(\text{OH})_2$ was aged in purified alkaline electrolyte (1 M KOH)⁶. Their findings in purified KOH were in accordance with the Bode scheme.

An important term that needs to be defined when Ni electrocatalysts are studied is preconditioning or pretreatment. Ni electrodes are often subjected to ageing in alkaline electrolyte, potential holds at a certain potential or electrochemical cycling to “activate” the surface of the electrocatalyst. During preconditioning, $\text{Ni}(\text{OH})_2$ is gradually oxidised to NiOOH , so that the concentration of NiOOH increases relative to that of $\text{Ni}(\text{OH})_2$ ⁶³. It is reported that a colour change can be observed from colourless $\text{Ni}(\text{OH})_2$ to grey NiOOH ⁶³. Preconditioning is also said to stabilise the surface and provide reproducible results⁶⁴. A lot of different preconditioning regimes are reported by researchers. For example, the electrodes are held at an anodic potential of 0.75 V vs NHE for 3 hours⁶⁵ or 30 CV cycles between 0.3 and 0.75 V vs Hg/HgO are performed in 1 M KOH⁶¹. An older study tried cathodically polarizing a polished Ni electrode at different potentials for different time periods, but found that cycling the electrode between -0.8 V and 1.2 V vs RHE for 8-10 cycles provided to best reproducibility⁶⁴. Some studies use a series of steps to precondition Ni electrocatalysts. Nardi *et al.* first soaked a Ni catalysts in KOH for 5 minutes, whereafter it was cycled twice between 1.1 and 1.8 V vs RHE and then held at 0.85 V vs RHE for 30 minutes⁸. Another recent study used linear sweep voltammetry (LSV) to activate Ni electrocatalysts, by performing five consecutive LSVs⁶³.

Until quite recently, Ni was thought to exhibit excellent OER activity with low overpotentials (around 330 mV vs RHE at 10 mA cm⁻¹)^{50,52,55}. Even as recently as 2020, it was reported that NiO nanofibers exhibited an overpotential of merely 322 mV vs RHE at 10 mA cm⁻¹ in unpurified KOH⁵¹. Although the morphology of these particles seemed to be the cause of their superior activity, the incorporation of Fe from KOH cannot be ruled out and could contribute to the high OER activity. In 2014, Trotochaud *et al.* conducted the first study of Ni electrocatalysts towards the OER in rigorously Fe-free conditions and proved that Ni is not a highly active OER electrocatalyst⁵. The focus has since shifted from pure Ni electrocatalysts to NiFe electrocatalysts or the effect of Fe impurities on Ni electrocatalysts.

2.4 The effect of Fe on Ni-based electrocatalysts (for the OER)

Fe is a transition metal that does not receive much attention as OER electrocatalyst in and of itself. This is because this transition metal has slow OER kinetics and is a bad conductor⁶⁶. What has drawn attention to Fe in OER applications over the last few decades, however, has been the notable effect it has on the OER activity of Ni. Three decades ago, Corrigan reported that reagent grade KOH contains trace amounts of Fe, which has a significant impact on the OER activity of Ni electrodes². He states in his work that Fe is deposited into the Ni film during potential cycling, which increases the OER activity of the Ni dramatically². Subsequent to this study, the topic of the effect of Fe on Ni OER electrocatalyst did not receive much attention in literature until quite recently, in 2014⁵. Before this recent study, a lot of claims were made to the excellent activity of Ni towards the OER (even though unpurified electrolytes were used).

In 2012, Yeo and Bell studied α -Ni(OH)₂ and β -Ni(OH)₂ employing voltammetric techniques and in-situ Raman spectroscopy⁵⁶. They aged Ni in concentrated reagent grade KOH to obtain β -Ni(OH)₂. Therefore the increased OER activity and changes in Raman features observed and ascribed to β -Ni(OH)₂/ β -NiOOH in their study is likely due to unintentional Fe incorporation from the electrolyte. There are many more examples of studies that report excellent activity for Ni electrodes when unpurified KOH was used, with the high activity resulting from unintentional electrolytic Fe incorporation. One example is Stern and Hu who found that Ni(OH)₂ nanoparticles exhibited excellent OER activity with an overpotential at 10 mA cm⁻¹ of only 299 mV⁶⁷. They repeated the experiment for the Ni(OH)₂ nanoparticles in purified KOH and found a drastic decline in OER activity. They therefore concluded that Fe impurities that incorporate into NiOOH to form Ni_xFe_{1-x}OOH as active phase is critical for achieving excellent OER activities⁶⁷.

Klaus *et al.* conducted a study of Ni in both purified and reagent grade KOH to evaluate this effect of unintentional Fe incorporation on the associated structure (in-situ Raman spectroscopy) and

OER activity (cyclic voltammetry)⁶. This study reported a dramatic decrease in Tafel slope as well as overpotential when the Ni electrodes were aged in unpurified KOH for 6 days, which was comparable to values of Ni-Fe catalysts. In addition, the Raman features also showed notable changes, which they ascribe to the formation of a NiFe-LDH structure due to Fe incorporation from the electrolyte⁶.

In order to eliminate Fe from experiments, all components must be soaked in 1 M H₂SO₄ and glassware must be eliminated^{6,7,6,5}. Semiconductor (SC) grade KOH (99.99%) can be purchased and used or KOH can be purified. Trotochaud *et al.* used 1 M TraceSelect KOH containing <36 ppb Fe and still found significant (5%) Fe incorporation into Ni(OH)₂ after just 5 CV cycles and 2% Fe after leaving the Ni(OH)₂ film in the KOH for 12 minutes⁵. They subsequently developed a method to rigorously purify KOH by using ultrapure Ni(NO₃)₂·6H₂O to absorb the Fe in the electrolyte. By using this purified KOH, they found no evidence of Fe incorporation into the Ni film even after 300 CV cycles⁵.

Aside from incidental incorporation of Fe from unpurified KOH, some studies spike the electrolyte with known concentrations of Fe to observe the effect thereof on OER activity of Ni. During a previous study, changes were observed in OER activity and structure of NiO_x films after electrochemical cycling in reagent grade KOH and KOH saturated with Fe (~0.7 mM Fe)⁸. The films cycled in reagent grade and Fe saturated 0.1 M KOH had overpotentials of 0.54 V and 0.48 V at 10 mA cm⁻², respectively⁸. Interestingly, while the OER activity of the film cycled in saturated KOH was higher, this film had a smaller electrochemically active surface area (ECSA), as suggested by the size of the redox features seen in the CV⁸. Both CV and XPS results in this study indicate that a high Fe concentration limits the amount of oxidation occurring on the NiO_x surface during electrochemical cycling⁸. They also found that Fe incorporation is not dependent on applied potential but is a diffusion-limited process⁸. These effects of Fe incorporation are interesting and important towards OER electrocatalyst development. Therefore, similar studies were subsequently conducted. Burke Stevens *et al.* spiked a pure KOH solution with 1 mM Fe(NO₃)₃ and found an immediate increase in OER activity for a Ni(OH)₂ catalyst cycled in the solution⁹. The overpotential showed a 130-150 mV decrease along with an anodic shift of the oxidation peak (E_{pa}) and a decreased integrated area of this peak⁹. After 100 cycles they performed inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis and found that the film contained 23-25% Fe⁹. This is slightly lower than the 10-15% Fe that the NiO_x film mentioned in the previous study contained after cycling in a similar amount of Fe⁸. However, less cycles were performed, consequently providing less time for Fe incorporation. Another study showed that the OER activity of co-electrodeposited NiFe electrocatalysts is enhanced with increasing Fe concentration, up to 10% Fe, and that the overpotential does not vary much

between 15% and 50% Fe¹². Therefore, it is clear that there exists a saturation point where the activity of Ni electrocatalysts cannot be enhanced further with increasing Fe concentrations. The knowledge obtained from the studies showing that unintentional Fe incorporation increases the OER activity of Ni, led to numerous studies developing co-synthesised NiFe.

2.5 NiFe co-synthesised electrocatalysts

A group of electrocatalysts generally referred to as Ni(Fe)O_xH_y are known as the most active OER electrocatalysts in alkaline media⁶⁸. Since it has become evident that Fe enhances the OER activity of Ni electrocatalysts, researchers have started to synthesise electrocatalysts where Ni and Fe are co-deposited or co-precipitated. In this manner, the ratio of Ni and Fe can be carefully controlled and optimised. One of the earliest studies where Ni and Fe were co-deposited was performed by Miller and Rocheleau where Ni and Fe targets were used to co-sputter different compositions of Ni and Fe²⁷. They found an overpotential as low as 283 mV at 8 mA cm⁻² and a Tafel slope of 34.5 mV/dec for a sample containing 5.2 mole percent Fe. A later study reviewed three different types of NiFe materials including NiFe alloys, NiFe oxides and NiFe LDHs⁷. It is difficult to fine-tune the exact composition of alloys, and with the NiFe oxides a delicate balance exists between crystalline (obtained through annealing) and amorphous structures⁷. Although NiFe LDHs pose some problems regarding conductivity, these materials are excellent OER electrocatalysts as they are accessible to the electrolyte. Numerous researchers have recently studied NiFe-LDH structures as OER electrocatalysts^{1,13,69,70,71}.

Trotochaud *et al.* synthesised Ni_{0.95}Fe_{0.05}(OH)₂ and Ni_{0.75}Fe_{0.25}(OH)₂ by means of electrodeposition where the deposition solution contained Ni and Fe precursors in a certain ratio⁵. CVs of the co-deposited films did not exhibit changes with cycling or ageing, which shows that the OER activity is inherent to the mixed Ni-Fe structure⁵. Louie and Bell also reported that electrodeposited Ni-Fe films were stable with no changes during cycling in unpurified electrolyte¹². Both studies compared co-deposited samples with samples containing Fe incorporated from the electrolyte. The reason that co-deposited NiFe is more stable than Ni incorporating Fe from electrolyte, is that the Fe is distributed more uniformly throughout the film in co-deposited species⁹. While co-deposited NiFe is more stable than Fe incorporated from electrolyte, it does not necessarily have better activity. It was found films containing similar amounts of Fe, both co-deposited and incorporated Fe, had similar OER activity⁹.

After discovering that Fe enhances the OER activity of Ni electrocatalysts, the focus of literature shifted to uncovering how Fe enhances the activity. The main question researchers ask is whether it is Ni or Fe that acts as the OER active site. Before entering into a discussion about the active site debate, a few fundamental principles should first be considered.

2.6 Active sites and electrocatalysis

As the discussion that follows is of a fundamental nature, it is important to first understand the fundamentals of how a catalyst works and what an active site is. A catalyst is a material that increases the rate of a chemical reaction without being consumed itself⁷². Electrocatalysts are materials present on electrode surfaces (or are electrodes themselves) and are designed to improve the kinetics of electrocatalytic reactions⁷³. An electrocatalyst is different from conventional catalysts in the sense that the electrochemical reaction cannot take place without it.

Furthermore, a catalytic process is defined as homogeneous when the catalyst and reacting species are in the same phase and as heterogeneous when the catalyst is in a different phase⁷⁴. The transition metal electrocatalysts in this study are heterogeneous electrocatalysts as they are in the solid phase while the electrolyte is in the liquid phase. A heterogeneous catalyst repeatedly forms active sites with the reacting species during a catalytic reaction⁷². Therefore, to understand heterogeneous catalysts, an understanding of active sites is important. In 1925, Taylor suggested that only a small portion of the total catalyst surface is active, thus introducing the idea of active sites for the first time⁷⁵. These active sites are believed to be atoms or groups of atoms located at surface defects⁷⁴. Engineering structural defects are known to create highly active surface sites, but it is important to note that not all types of defects improve activity⁷⁶. Studying active sites is complex and research is only in the beginning phases of understanding the exact nature of it. It is, however, clear how the active sites enhance catalytic reactions. Reactants adsorb and bind non-permanently to the active site for the catalytic reaction to take place, thereby lowering the activation energy of the reaction⁷⁴. If the reactants bind too strong or too weak to the active site, the catalytic activity will decrease^{74,76}. This phenomenon is well known as the Sabatier principle, which highlights that an optimum bond strength exists, defining the ideal catalyst for a certain reaction⁷⁷. The Sabatier principle is illustrated in Figure 2-4.

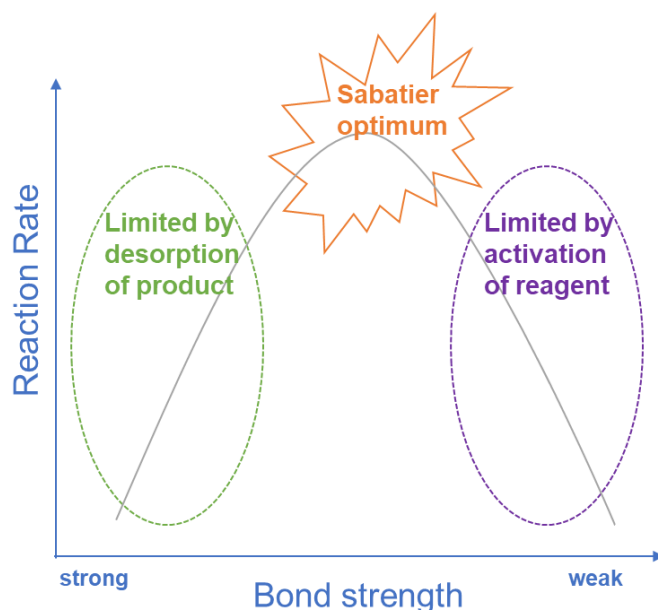


Figure 2-4: A representation of the Sabatier principle (redrawn from Medford *et al.*⁷⁷).

Computational methods, such as density functional theory (DFT), as well as experimental investigations are commonly used in literature to illustrate the volcano-type relation (Figure 2-4) of OER electrocatalysts^{78,77,79}. For transition metal OER electrocatalysts, a surface metal site (M) is considered as the OER active site⁷⁸. The OER intermediates are considered to be M-O, M-OH and M-OOH^{78,80}. A plot of M-O bond strength (oxygen adsorption energy) against OER activity yields a graph that resembles a volcano^{78,79,80}.

There are a lot of factors that have an influence on active sites and contribute to enhancing catalytic reactions. Firstly, alloys are often used instead of their pure metal counterparts in order to enhance the catalytic activity^{74,76}. This activity enhancement in alloys is said to be obtained through the optimisation of the electronic structure and geometry of the active sites^{74,76}. The alteration of the electronic structure of the active sites are referred to as ligand effects⁷⁶. Alloying atoms are not in direct contact with the adsorbates, but affects the adsorption energies of the active sites by altering their electronic structure⁷⁶. Geometric effects refer to the alteration of the spatial arrangement of active sites when interatomic distances are changed or atoms are added or removed⁷⁶. Secondly, the size and shape of particles also has an influence on active sites by altering their binding energies⁷⁶. The shape of a particle determines which crystallographic plane is exposed⁷⁶. Lastly, the electrolyte also has an influence on the active sites⁷⁶. It is clear that multiple factors work together to determine the structural and catalytic properties of active sites and that this is a complex relationship. These properties are often used to fine-tune and enhance catalyst activities. It should be kept in mind that stability and selectivity also change when these properties are varied and the electrocatalyst system as a whole should be studied⁷⁶.

Identifying and studying active sites is of utmost importance for catalyst development⁷⁴. Heterogeneous OER electrocatalysts are said to have dynamic structures exhibiting phase-transitions and changes in electronic structure as potential is varied⁸¹. It is therefore essential to use in-situ methods when studying active sites as they cannot be studied in the absence of the reactants or applied potential⁷².

2.7 The active site debate

It is undeniable that Fe enhances the OER activity of Ni electrocatalysts as this is evident throughout literature on this topic. However, it remains uncertain how and why the OER activity is so much better when Fe is present. The mechanism whereby Fe enhances the activity has not yet been elucidated. The most important question for researchers on this topic is whether it is Ni or Fe that acts as the active site. As stated in the previous section, the active site is the term used to describe the species responsible for catalysing the OER. There are a few main hypotheses in literature regarding the active site in NiFe electrocatalysts. The first one is that Ni is the active site and that the presence of Fe helps to activate Ni in various ways. The second is that Fe itself is the active site. A lot of recent studies indicate that it is Fe present on the surface (at defect- or edge sites) that is responsible for the excellent activity of these electrocatalysts. Each of these hypotheses will be explored in more detail in the following subsections.

2.7.1 Ni as active site in NiFe electrocatalysts

Some studies point toward Ni being the active site^{56,12,5,65}. Louie and Bell hypothesised in one of the earliest fundamental studies of NiFe electrocatalysts that Ni is the active site¹². They based this hypothesis on structural and electrochemical similarities between NiFe and Ni aged in KOH. The Tafel slope of co-deposited NiFe catalysts was the same as for Ni catalyst aged in KOH¹². Furthermore, the Raman features of NiFe films and those of aged Ni were similar¹². However, the KOH used in their study was not purified and thus contained iron. Therefore, the reason aged Ni showed similar behaviour to co-deposited NiFe could be because it incorporated Fe from the electrolyte.

Other studies stating that Ni is the active site provide various mechanisms in which Fe is said to activate the Ni active site. These include Ni-Fe partial-charge transfer⁵ or Fe acting as a Lewis acid to increase the valency of Ni⁶⁵, which both result in a Ni⁴⁺ site. This higher oxidation state is said to enhance the OER activity on the Ni sites. Another factor thought to be the reason for the increased activity, is the enhanced conductivity of Ni electrocatalysts after the addition of Fe. However, it is stated that enhanced conductivity cannot solely account for the OER activity of NiFe electrocatalysts⁵.

CV indicated that the incorporation of Fe suppresses the oxidation of the NiO film, as the oxidation peak decreases in intensity and shifts to higher potentials as the amount of Fe in the electrocatalyst increases¹². This indicates that the incorporation of Fe renders the oxidation of Ni(OH)₂ to NiOOH more difficult. Therefore, researchers claimed that the decrease in the oxidation state of Ni increased the OER activity¹². This is contradictory to other studies claiming that a high oxidation state increases OER activity^{5,65}. Later studies claimed that neither conductivity nor electronic effects (such as decreased oxidation or a Ni⁴⁺ oxidation state) has an influence on the OER activity and therefore cannot explain why Fe enhances the OER activity of Ni.

CVs of Ni films that were cycled in 1 mM Fe as well as co-deposited NiFe films were studied and it was found that the redox features of the films differed dramatically⁹. Even though the redox features (sizes, shapes and positions of oxidation and reduction waves in the CVs) differed, the OER activity was similar. Indeed, the CVs reported by Trotochaud *et al.* also exhibited very different redox features for co-deposited Fe and impurity-based Fe although the OER activity was the same⁵. The conductivities of both samples were also studied and it was found that co-deposited samples exhibited an increase in conductivity with Fe content whereas the film incorporating Fe from the electrolyte showed no increase in conductivity⁹. Again, irrespective of the difference in conductivity, both samples showed similar OER activity. Through the findings in these studies it is clear that neither bulk electronic structure nor conductivity is the reason for the increased OER activity of NiFe electrocatalysts⁹.

2.7.2 Fe as active site in NiFe electrocatalysts

There are quite a number of fairly recent studies that have claimed Fe to be the active site^{9,6,60,78,13,15}. As opposed to those covered in the previous subsection, these studies often explain how Ni enables Fe to be the active site. For example, Ni is said to stabilize Fe active sites and also facilitates the conductivity of the NiFe film⁷⁸. Furthermore, it is proposed that Fe replaces Ni at octahedral Ni sites^{60,14}. X-ray absorption spectroscopy (XAS) and DFT calculations indicated that Fe at these octahedral sites have a short Fe-O bond length that is optimum for adsorption of OER intermediates⁶⁰. Other research suggests that Fe increases disorder in the electrocatalyst structure, which increases the OER activity⁸².

In addition, a few recent studies have employed isotope exchange experiments to indicate that Fe is the active site. Lee *et al.* used oxygen isotopes to differentiate between Ni and Fe active sites as Ni exchanges lattice oxygen with oxygen from OH⁻ in the electrolyte, but Fe does not¹. Furthermore, ⁵⁶Fe and ⁵⁷Fe exchange proved that Fe sites are dynamically active, which means that Fe in the catalyst layer is constantly exchanging with Fe in the electrolyte⁸³.

2.7.3 Synergy between Ni and Fe

Some of the earliest, as well as recent studies, suggest that a synergistic effect between the Ni and Fe is responsible for the enhanced activity^{2,84}. A synergistic effect between NiOOH and FeOOH was recently suggested to be responsible for the high catalytic activity of NiFe catalysts^{84,38}. Both NiOOH and FeOOH are said to be the OER active sites^{84,38}. The structure of a Ni electrocatalyst cycled in Fe containing KOH was found to be γ -NiOOH containing clusters of γ -FeOOH³⁸. DFT computations indicated that this structure could support a bifunctional OER reaction mechanism where both Ni and Fe are active sites³⁸. A later study used in-situ Raman spectroscopy to verify that a bifunctional mechanism (Figure 2-2) indeed holds true for these FeOOH-NiOOH type electrocatalysts¹¹. This means that when Fe is present on the surface of Ni electrocatalysts, a synergistic mechanism leads to increased OER activity due to faster kinetics of the rate-determining step.

2.7.4 Surface Fe is responsible for the enhanced activity of NiFe electrocatalysts

Recent literature focused on surface/edge Fe sites and why these are likely the active sites. Structural defects are often stated to enhance the (electro)catalytic activity of (electro)chemical reactions by introducing particularly active surface sites⁷⁶. This leads to yet another question on this topic: is it surface sites that are active or the bulk material? Bulk Fe is that Fe incorporates into the $\text{Ni}(\text{OH})_2$ structure where Fe^{3+} replaces some of the Ni^{2+} and the excess charge is compensated for by the presence of anions between the sheets¹⁰. This structure is sometimes referred to as NiFe LDH and is usually obtained by codeposition of Ni and Fe. On the other hand, surface Fe is Fe that is initially precipitated/ adsorbed on the electrocatalyst surface at different sites including corner- and edge sites¹⁰. This Fe usually originates from the electrolyte.

Numerous recent studies found that it is surface Fe that increases the OER activity of Ni electrocatalysts and not bulk Fe and in the absence of Fe in the electrolyte, the activity of NiFe electrocatalysts decreases^{83,8,71,10}. When NiFe electrocatalysts are cycled in purified KOH, the OER activity decreases with time¹⁰. However, if even trace amounts of Fe is present the electrolyte, the activity does not decrease. In addition, studies have found that the OER takes place exclusively at the near-surface region of electrocatalysts, further supporting the hypothesis that species at the surface are the active sites^{68,85}.

Furthermore, clear distinctions exist between bulk Fe and surface Fe. When Fe replaces Ni in the bulk structure, it alters the electronic structure and conductivity of the electrocatalyst⁹. This is why it is often observed that oxidation peaks in CVs shift anodically and decrease in size when Fe is incorporated into the structure⁶. As discussed in 2.7.1, these changes in electronic structure and

conductivity have been thought to increase the OER activity of NiFe electrocatalysts. However, these changes are merely the product of Fe incorporating into the structure of Ni electrocatalysts and do not play any role in the enhancement of the OER activity. If these electrochemical changes are observed during cyclic voltammetry, it is proof that Fe has incorporated into the bulk structure. When Fe is only present on the surface of the electrocatalyst, these electronic changes are not observed (the oxidation peak does not shift anodically and does not get smaller), but an increase in OER activity is still apparent⁹. Fe is often present both in the bulk structure and on the surface, but it is the Fe on the surface that is crucial for the enhanced OER activity. Furthermore, there exists an optimum amount of Fe that needs to be present in the electrolyte to increase the OER activity of Ni electrocatalysts⁸. Various factors, such as the method of catalyst deposition or morphology can influence the concentration of Fe in the bulk versus the concentration in defect/edge sites⁹. Therefore, the optimum Fe concentration (and Fe saturation point) may differ for electrocatalysts depending on preparation methods and thus morphologies.

Numerous researchers employ defect engineering to enhance electrocatalytic activity of various electrocatalysts. Some studies generate surface defects to investigate active sites. Peng *et al.* used acid etching to create edge Fe-sites which they proved to be more active for OER than lattice Fe or Ni sites¹³. They used DFT and spectroscopic techniques to support this statement. As there exists a delicate balance between the number of Fe and Ni sites (both edge and lattice) they also state that Fe could enhance OER performance through an interaction with Ni¹³. Li *et al.* investigated oxygen vacancy defects in NiFe-LDH electrocatalysts⁷⁰. This is similar to the aforementioned study where NaCl was added to the precursor solution to produce O vacancies whereas HNO₃ was added to the precursor solution to yield edge Fe-sites. The structures as observed by TEM were also similar as well as the volcano-type correlation between the amount of NaCl or HNO₃ added and the OER activity. Another recent study showed that increased OER activity was achieved by ultrasmall electrocatalyst particle sizes which provided abundant edge- and corner Fe sites⁶⁶.

It is therefore clear that Fe needs to be present at the Ni electrocatalyst surface in order to enhance the OER activity. When there are an abundance of edge sites or defects, the activity is enhanced further as this increases the number of active sites (Fe on the surface).

2.8 Nanoparticles versus sputtered thin films as OER electrocatalysts

To study the effect of Fe on Ni electrocatalysts, Ni electrocatalysts have to be prepared. Both nanoparticles and sputtered thin films have been used in previous studies investigating electrocatalytic properties of Ni. Nanoparticles of different shapes and sizes can be synthesised to serve as OER electrocatalysts. The interest in nanoparticles as electrocatalysts have increased

over the last two decades⁸⁶. They often exhibit excellent electrocatalytic activity due to their small size, resulting in large effective surface areas. In addition, nanoparticles exhibit unique chemical, electronic and magnetic properties that vary from those of the bulk materials⁸⁶.

Numerous studies have used physical vapor deposition (PVD), or more specifically magnetron sputtering, to produce thin film electrocatalysts^{27,42,87,88}. PVD is a deposition method where a target of a desired material is used to deposit a thin layer of material on a substrate. In a high vacuum chamber, collisions of an ionized sputtering gas (Ar) with the surface of the target transforms the target into atomic particles that are directed to the substrate to form a coating⁸⁹.

An illustration of the PVD process can be seen in Figure 2-5. Since a large number of samples can be prepared at once, reproducibility of these samples is increased compared to nanoparticle electrocatalysts, where inks have to be drop-casted one electrode at a time. The physical and chemical properties of transition metal thin films prepared with PVD will more closely resemble bulk materials than nanoparticles. For these reasons, films deposited with PVD might be easier to use in fundamental studies of electrocatalysts than nanoparticle samples.

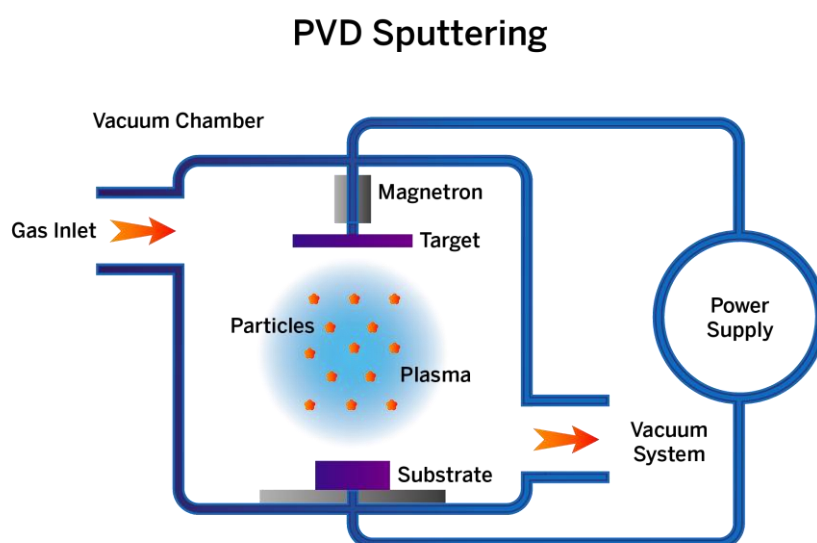


Figure 2-5: A schematic representation of the PVD sputtering process (redrawn from Baptista *et al.*⁹⁰).

2.9 Characterisation techniques

Various characterisation techniques have previously been employed to investigate the effect of Fe on the structure (TEM, SEM, in-situ Raman spectroscopy and XRD) and OER activity (CV, LSV) of Ni electrocatalysts. It is important to have a basic idea of the working principles and/or

the background of each technique. Additionally, it is important to review what has previously been reported in literature regarding these techniques, including previous results pertaining to similar studies. Therefore, a brief introduction, followed by a short discussion of what has previously been done in literature, is presented for each characterisation technique.

2.9.1 Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) with Energy Dispersive X-Ray (EDX) Analysis

SEM and TEM analyses are tools for obtaining visual information on the structure and morphology of synthesised OER electrocatalysts. SEM can also be used to determine the thickness of thin-films deposited on planar electrodes²³. Furthermore, SEM can reveal if there is a uniform distribution of the electrocatalyst on the electrode surface^{84,91}. Elemental mapping can reveal the distribution of various elements within the sample, which can be very useful to observe the distribution of Ni, Fe and oxygen, for example⁸⁴. Numerous studies employ TEM to reveal the average particle size of single particles in nanoparticle catalysts^{43,92}. Roy *et al.* used TEM to determine the size distribution of nanoparticles obtained from a magnetron sputtering nanoparticle source by analysing the TEM images with ImageJ⁶⁸. SEM can also be used to determine particle size⁹³. TEM and SEM are also used to show agglomeration of these nanoparticles and the size of these agglomerates^{68,92}. Nanoparticles often tend to coalesce, especially during electrochemical testing⁶⁸. In some studies it is also important to indicate the absence of agglomeration⁸⁴.

Selected area electron diffraction (SAED) can be carried out with a TEM instrument and is included in some studies to show diffraction rings that can be attributed to planes of crystal structures such as Ni or NiO^{92,84,91}. Furthermore, high resolution TEM (HRTEM) is often included in studies as it reveals crystal plane spacings, which can be attributed to certain crystal planes of relevant species^{84,94,91}. For example, Hu *et al.* studied a FeNiO_xH_y nanofoam structure with HRTEM and found crystal plane spacings of 0.228 and 0.262 nm, which they attributed to the (301) and (012) crystal planes of FeOOH and Ni(OH)₂, respectively⁸⁴. HRTEM also provides us with more detailed information at the atomic level. Roy *et al.* deposited NiFe nanoparticles on graphene-coated Au TEM grids and subjected these grids to electrochemical cycling in KOH⁶⁸. In this manner, information can successfully be obtained of how these particles are altered after electrochemical testing. They found that the particles preserved their shape and polycrystallinity (as indicated by the non-uniform orientation of lattice fringes) after cycling⁶⁸.

Trotochaud *et al.* used SEM to observe Ni and NiFe catalysts that had a platelet-like structure before and after ageing in Fe-free electrolyte⁵. SEM images showed that the size of the platelets increased after ageing and that samples containing Fe had a larger platelet size⁵. Pierozynski *et*

al. also performed post mortem SEM analysis after 100 CV cycles of Ni foam and found a thick oxide layer on the surface⁹¹. Hu *et al.* used TEM to analyse their nanoflake arrays before and after OER and found that the particles had a rougher surface and were less crystalline after OER⁸⁴.

In addition, EDX is usually performed along with SEM and TEM to indicate the elemental composition at the sampling site. EDX is semi-quantitative and can provide an estimate of the amount of each element present in the sample. It can therefore supplement other quantitative analyses. In conclusion, SEM is usually employed to obtain general information about morphology, agglomeration and particle size of samples. TEM provides a more in-depth understanding of particles including average particle size and crystallinity.

2.9.2 In-situ Raman spectroscopy

There are numerous analysis techniques based on the interaction between light and matter, or more specifically, molecules and the bonds within them. One such technique is Raman spectroscopy where a sample is bombarded with monochromatic light and the light scattered from the front surface of the sample is detected and analysed. An incident photon (radiation) can either obtain energy from molecules in the sample or lose energy to molecules in the sample and therefore yield scattered light with increased or decreased frequencies resulting in anti-Stokes and Stokes lines, respectively⁹⁵. When the frequency (energy) of a scattered photon differs from that of the incident photon, we refer to it as inelastic scattering, which is known as the Raman effect⁹⁶. Most of the light is scattered without a change in frequency and doesn't provide useful information about the sample⁹⁶. This is known as Rayleigh scattering^{96,95}. Around 0.0000001% of light is inelastically scattered and depend on the chemical structure of the sample⁹⁷. The incident monochromatic laser beam interacts with molecules in the sample. Bonds between atoms in the molecule start to vibrate because of this interaction and this directly impacts the frequency of light scattered from the sample. A detector converts this scattered light to a Raman spectrum. The energy difference between the laser (incident light) and the light scattered by the sample is referred to as the Raman shift, reported as wavenumbers. The Raman shift represents the energy of molecular vibrations independent of the laser wavelength. Peaks in the Raman spectrum thus appear at Raman shift (cm^{-1}) values. The peaks in the spectrum thus represent the vibrations of molecular bonds and can be used to identify molecules, compounds, and crystal structures. Raman spectroscopy is an excellent non-destructive technique to obtain an exact fingerprint of a sample. Molecules and their chemical states can be accurately identified with this technique.

Raman spectroscopy is a sensitive technique in the low-frequency range where the characteristic vibrations of metal oxides, hydroxides and oxyhydroxides appear⁹⁸. Therefore, Raman is a

suitable technique to use for the in-situ analysis of Ni and Fe OER electrocatalysts and the intermediated and active sites involved. In alkaline solution, Ni(OH)_2 and NiOOH are of utmost importance to monitor as these 'species' are indicative of Ni oxidation taking place when the potential is increased from 0.3 V to 0.4 V and upward.

Peaks at around 480 and 560 cm^{-1} are the most prominent peaks of NiOOH to be analysed in-situ to monitor structural changes of the Ni electrocatalysts. The peak at 560 cm^{-1} arises due to the O-Ni-O stretching (polarized A_{1g}) mode and the peak at 480 cm^{-1} represents the O-Ni-O bending (depolarized E_g) mode of NiOOH ^{1,99}. These peaks might shift, and the relative intensity of these peaks are said to change when Fe is incorporating into the structure⁶. It was also found that NiOOH peaks start to appear at lower potentials when Fe is present in the structure⁶. Also interesting to note is that bonds that become shorter will be blue shifted (higher wavenumbers) and elongated bonds will be red shifted (smaller wavenumbers)¹⁶.

Furthermore, Raman peaks corresponding to Fe can also occur, especially if a separate Fe phase is present at higher concentrations of Fe in the electrolyte. Pourbaix diagrams of Fe show that Fe_2O_3 , FeO_4^{2-} , and other species in the +3 oxidation state (such as FeOOH) can be present at the potential, pH, and temperature conditions of OER experiments¹⁰⁰. A study specifically investigating the decomposition of $\text{Fe(NO}_3)_3$, reports a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ at room temperature¹⁰¹. Therefore, when $\text{Fe(NO}_3)_3$ is used as dopant in electrolyte, Raman features of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ could be expected if these species interact with the electrocatalyst film. Zhang *et al.* studied the in-situ conversion of $\text{Fe}_2\text{O}_3\text{-Ni(OH)}_2$ to $\text{NiFe}_2\text{O}_4\text{-NiOOH}$ with Raman spectroscopy and found that peaks at 475 and 558 cm^{-1} intensified as potential was increased from 0 to 0.6 V vs Hg/HgO, indicating formation of NiOOH ¹⁰². Additionally, a characteristic band at around 700 cm^{-1} emerges at 0.4 V, which they ascribe to the start of NiFe_2O_4 formation¹⁰². A peak at this position could be expected when the electrolyte is doped with Fe. However, Yeo and Bell reported a peak at 735 cm^{-1} arising due to Teflon, so this peak should be analysed with care⁵⁶. In addition, during the backward scan, peaks at 330, 487 and 698 cm^{-1} were ascribed to NiFe_2O_4 and one band at 527 cm^{-1} was ascribed to some residual Ni(OH)_2 ¹⁰².

When the film is submerged in KOH, peaks in the O-H stretching region might be obscured due to the broad maximum between 3000 cm^{-1} and 3700 cm^{-1} observed due to electrolyte present in the electrocatalyst film⁶². It is reported that water and cations intercalate between the layers of Ni(OH)_2 and NiOOH ⁶². Kostecki *et al.* reported that this broad maximum decreased substantially upon oxidation, indicating a difference in intercalated water content for oxidized and reduced phases⁶².

Some studies on NiO materials mention that no Raman peaks were observed for the thin films when they are in the reduced state where OER is not occurring⁹⁹. It is indeed so that the NiOOH peaks at 480 and 560 cm⁻¹ will not be seen in the reduced state. However, peaks for NiO (also referred to as bunsenite) can be observed both inside and outside KOH. It should be noted that differences in peak shifts and intensities will occur based on size, strain and disorder.

In addition, it is important to carefully differentiate between peaks examined and reported ex-situ and in-situ, because even without applied potential, electrolyte interactions and pH will influence the peaks observed. Therefore, two separate tables are constructed to summarise relevant peaks reported in literature. Table 2-2 summarises peaks reported from previous in-situ experiments and Table 2-3 summarises peaks reported from previous ex-situ experiments.

Table 2-2: Ni and Fe species and their corresponding Raman shifts reported for in-situ experiments in KOH.

Species	Raman Shift (cm ⁻¹)	Potential (V vs Hg/HgO)
α -Ni(OH) ₂	460-465 ⁶ , 3625-3670 ¹²	0 to 0.5
β -Ni(OH) ₂	445-449 ⁶ , 3580 ¹²	0 to 0.5
Ni(OH) ₂ (not specified α or β)	460 (small) ¹⁶ , 449, 494 and broad 530 (disordered Ni(OH) ₂) ^{12,102} , 453 and 495 ⁶	0 to 0.4
NiO	490 (blueshift up to 531 observed for samples treated at higher temperatures) ¹⁶	0 to 0.4
γ -NiOOH	479 and 558 ⁵⁶	0.5 to 0.6
β -NiOOH	486 and 561 ⁵⁶	0.5 to 0.6
NiOOH (not specified γ or β)	480 and 560 (Ni ⁱⁱⁱ -O) ^{12,6,56,15} , broad 850-1200 (O-O of NiOO ⁻) ^{15,1} 475-494 and 558-562 (depending on treatment temperature) ¹⁶	0.5 to 0.6

Table continues next page.

Table 2-2 (continued).

Ni(Fe)OOH	480 and 560 (Ni ⁱⁱⁱ -O) with lower 480/560 peak height ratio and broader peaks than NiOOH ^{6,15,12} , 475 and 555 ^{12,103} , shoulder at 494 ¹² , broad 850-1200 (O-O of NiOO ⁻) ¹⁵	0.5 to 0.6
NiFe LDH	Broad 528 ¹⁰³	0 to 0.4
α -FeOOH	92, 205, 300, 401, 554 and 686 ¹⁰⁴	N.A.
α -Fe ₂ O ₃	224 and 498 (A _{1g} modes), 245, 291, 410 and 610 (E _g) ¹⁰⁵	0 to 0.6
Ni(OH) ₂ -Fe ₂ O ₃	475 and 558 ¹⁰²	0.2 to 0.4
NiFe ₂ O ₄ -NiOOH	330, 487 and 698, 475 and 558 (intense/sharp), 700 ¹⁰²	0.4 to 0.6
Teflon (control)	735 ⁵⁶	N.A.
Glassy carbon (control)	1360, 1620, 1580 ¹⁰⁶	N.A.

In many of the in-situ studies performed in literature, where Fe was doped in the electrolyte or co-deposited with Ni, no distinct peaks for Fe was observed. This is likely because of the inherent structure of these species. However, the sensitivity of Raman spectroscopy can be increased if found necessary. Surface enhanced Raman spectroscopy (SERS) intensifies the Raman signal with several orders of magnitude by modifying the surface on which the sample to be analysed is placed⁶. Previous researchers have electrochemically roughened a gold electrode in order to perform SERS¹⁰⁷. Yet another study electrochemically deposited Ag microparticles along with Ni (the electrocatalyst studied) to obtain surface enhancement⁶². Even without surface enhancement, Raman proves to be an effective technique to observe in-situ how the structure of OER electrocatalysts changes with applied potential. This technique can be used in this study towards answering the research questions.

Table 2-3 summarised peak positions of ex-situ Raman spectra of Ni and Fe species found in literature.

Table 2-3: Ni and Fe species and their corresponding Raman shifts reported for ex-situ experiments.

Species	Raman Shift (cm ⁻¹)
NiO (bunsenite)	400-440, 560, 740, 925, 1100, 40, 1500, 2800 ¹⁰⁸ Three major peaks: 496.5, 1093.1, and 1524.8 ¹⁰⁹
Ni(OH) ₂	Small peak centered at 480 (Ni-OH stretch) ¹⁶ , 3681 (O-H stretch) ¹⁶ , 460 and 492 (Ni-O stretching) ¹⁶
β-Ni(OH) ₂	316, 445, 868 ¹¹⁰ , 3587 accompanied by minor peak at 3607 (A _{1g} symmetric stretching of hydroxyl) ¹⁶ 306, 445, 510, 3579 (commercially purchased) ⁶²
α-Ni(OH) ₂	460, 495 ¹¹⁰ , 3600 (broad, low intensity) ¹⁶ 306, 460, 524, 3656 ⁶²
Fe _x Ni _{1-x} O (with x=0 and x=0.2)	Broad band at 500 slightly shifted to higher wavenumbers (and less broad) with increasing Fe content ¹⁴ .
NiFe LDH	536 (Ni-O) and 694 (Fe-OH) ¹³

2.9.3 X-ray photoelectron spectroscopy (XPS)

In X-ray photoelectron spectroscopy, a sample is bombarded with photoelectrons, and a photon of known energy is absorbed, which leads to the ejection of an electron from an orbital of the sample if the energy of the photon is sufficient⁹⁵. The kinetic energy (KE) remaining on the ejected electron is measured¹¹¹. This kinetic energy is directly related to the electron binding energy (BE), which provides unique information the element and its environment¹¹¹. BE is used to construct the XPS spectrum as it is not dependent on the X-ray energy. The equation used to derive BE from KE is as follows¹¹¹:

$$KE = E_{ph} - \phi - BE \quad (5)$$

where E_{ph} is the energy of the incident photon and ϕ is the work function of the instrument. XPS can detect the quantity of any element from Li to U present in the top 5 to 10 nm of a sample's

surface assuming that the element is present in quantities >0.05 atomic %¹¹¹. The working principle of an XPS instrument is illustrated in Figure 2-6.

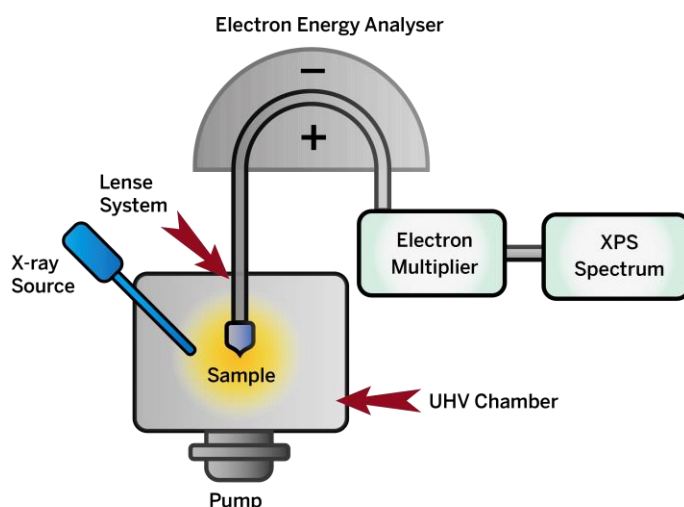


Figure 2-6: A schematic representation of the components of an XPS instrument (redrawn from¹¹²).

XPS can be used to determine the electronic structure and composition of electrocatalysts before and after electrochemical experiments. Trotochaud *et al.* recorded XPS Fe 2p spectra after cycling and aging Ni electrocatalysts in pure and TraceSelect KOH and found that 2% Fe is present in the Ni film after aging without voltage and 5% after 5 CV cycles⁵. They used a Mg K α X-ray source as this avoids the overlapping of Ni Auger features with Fe 2p peaks that occur when an Al source is used⁵. It is stated that a nonmonochromated Mg K α source is vital to detect low concentrations of Fe in samples⁵. Peaks at around 711 and 724 eV in the 2p spectra of Fe were used to quantify the amount of Fe present. Subsequent to this study, more studies followed that employed XPS to evaluate how cycling in Fe-containing electrolytes affects the electronic structure of Ni electrocatalysts and how much Fe is incorporated into the electrocatalysts from the electrolyte.

Nardi *et al.* cycled NiO films in reagent grade KOH and Fe saturated KOH and used XPS to investigate structural and compositional changes in the electrocatalysts after OER⁸. In order to analyse changes, a pristine sample was also analysed that has not been subjected to any electrochemistry or Fe contamination. Several interesting observations resulted from the XPS analysis in their study. Firstly, XPS quantification from the survey scans indicated that the O:Ni ratio for the pristine sample was 1 whereas the ratio was 1.3 and 1.5 for samples cycled in Fe

saturated and reagent grade KOH, respectively⁸. They also performed high-resolution scans of the Ni 2p_{3/2} peak and fits of the peaks at 854 and 856 eV, attributed to Ni²⁺ and Ni³⁺, respectively⁸. The ratio of the Ni²⁺ : Ni³⁺ peaks is an indication of how much NiO or Ni(OH)₂ is present in the film compared to NiOOH. Interestingly, this ratio was 1.5:1 for the pristine sample and 1.6:1 and 2.1:1 for the sample cycled in Fe saturated KOH and reagent grade KOH, respectively⁸. This indicated that increased concentrations of Fe in electrolyte inhibits oxidation in the films. Furthermore, they used the Fe 3p peak at 56 eV to evaluate the amount of Fe in their samples as the use of a Al K α x-ray source prevented them from using the Fe 2p region⁸. Any Fe in the pristine sample and the sample cycled in reagent grade KOH could not be detected by the Fe 3p signal⁸. 10% to 15% of Fe was estimated to be present in the sample cycled in saturated KOH by analysing the ratio of the Ni 3p and Fe 3p peaks⁸. Another study after this, used XPS to evaluate how NiFe films change after electrochemical cycling. Roy *et al.* employed XPS to observe NiFe films before and after cycling⁶⁸. Before cycling, Ni (852.6 eV) and Fe (706.6 eV) were in the metallic state. After electrochemical cycling in 1 M KOH, NiO (853.7 eV), Ni(OH)₂ (855.8 eV), FeOOH (711.6 eV) and Fe₂O₃ (710.8 eV) were found to be present⁶⁸. Interestingly, XPS quantification indicated that the Fe content was 25% before cycling and only 15% after cycling⁶⁸.

In other studies, XPS is usually used to determine the electronic structure of co-synthesised NiFe electrocatalysts. Fu *et al.* studied Ni_xFe_y nanofoams and reported the high resolution XPS spectrum for Ni 2p_{1/2} and 2p_{3/2}, which consisted of peaks at 852.5 and 869.7 eV (metallic Ni), 855.9 and 873.7 eV (oxidized Ni) and two satellite peaks at 861.5 and 880.1 eV⁸². In addition, Fe 2p_{1/2} and Fe2p_{3/2} peaks were reported at around 725 eV and 711 eV, respectively⁸². The Fe 2p_{1/2} peak was very small (almost not visible) compared to the Fe2p_{3/2} peak. These results are similar to a study of Fe-doped NiO nanocrystals, reporting NiO peaks at 855 and 862 eV¹⁴. The peaks in the Fe 2p spectrum are also similar (711 and 724 eV) and are ascribed to Fe₂O₃ (Fe³⁺)¹⁴. The peak for Fe 2p_{1/2} is bigger and more visible in this study. In another study, XPS was used to obtain the composition of NiFe LDH electrocatalysts¹³. They report Ni 2p_{1/2} and 2p_{3/2} peaks at 874.6 eV and 856.8 eV (Ni²⁺) and Fe 2p_{3/2} at 712.2 eV (Fe³⁺), which is said to confirm a NiFe LDH structure¹³. These results are in agreement with a previous study also reporting NiFe LDH¹⁰³. In addition, Fominykh *et al.* characterised Fe_xNi_{1-x}O nanoparticles with XPS and stated that a separate Fe phase is not present for their particles¹⁴. According to them, a separate Fe₂O₃ phase can be identified by the presence of shake-up peaks at 719 and 732 eV in the Fe 2p spectrum¹⁴.

XPS spectra of Fe, especially ternary oxides, is notoriously difficult to analyse because of multiplet splitting effects, shake-up peaks, asymmetric peak shapes, a steeply rising background and uncertain, overlapping binding energies^{113,114,115}. During photoionization, a core electron vacancy

is formed. If an atom has an unpaired electron in the outer shell (unpaired valence electrons), this unpaired core electron can couple with it, creating a number of final states^{115,116}. This phenomenon is known as multiplet splitting. Furthermore, shake-up peaks occur when the kinetic energy of an ejected photoelectron is reduced due a valence electron that transitioned to a different energy level¹¹¹.

It is because of these features of Fe (and also Ni) 2p spectra, that binding energy databases cannot be successfully used to identify the chemical states present¹¹⁵. The available databases do not provide information on crucial parameters for peak fitting of metal oxides such as peak widths and asymmetries¹¹⁵. It is important to be able to make a prediction of what metal species is expected to be present in an XPS spectrum as this will provide a valuable guide to peak fitting¹¹⁷. Therefore, a thorough literature search on the XPS spectra of these transition metals under similar analysis methods as an anticipated study is needed. If $\text{Fe}(\text{NO}_3)_3$ is added to KOH as Fe dopant, the reaction will be:



Literature frequently reports the presence of FeOOH (sometimes referred to as the OER active site in NiFe catalysts) and/or Fe_2O_3 in NiFe catalysts. A variety of ferrous oxidase and hydroxides can form during oxidation in an alkaline solution¹¹⁴. A summary of the possible oxidation states of Ni and Fe reported in literature along with their corresponding binding energies is presented in Table 2-4.

As stated before, Fe exhibits complex multiplet splitting in the 2p region. This occurs for high spin Fe in the +2 or +3 oxidation state which contain unpaired d electrons^{115,116}. McIntyre and Zetaruk performed an advanced analysis of XPS spectra of various Fe compounds¹¹⁴. It can be seen that the mean binding energies of $2p_{3/2}$ peaks are often the same or very similar for +3 Fe compounds and that they can virtually only be distinguished based on the multiplet splitting distribution within each peak¹¹⁴. The main core line (the envelope consisting of fitted multiplet-split peaks) of these +3 Fe oxides is asymmetric to the high-energy side and has a weak satellite peak located 8 eV above it¹¹⁴. Because of multiplet splitting, the full width at half maximum (FWHM) of the 2p peaks are broad (± 3 eV, or larger depending on experimental factors)¹¹⁴. McIntyre and Zetaruk provided a table summarizing the binding energies of the major core lines of different Fe oxides, of which some are included in Table 2-4¹¹⁴.

Table 2-4: A summary of the oxidation states and corresponding binding energies present in the 2p XPS spectra of Ni and Fe containing electrocatalysts.

Metal oxidation state	Type of sample and sample history	Binding energy (eV) of 2p_{3/2} peak	Binding energy (eV) of 2p_{1/2} peak	Binding energy (eV) of satellite peak(s)	Reference
NiOOH (+3)	NiO cycled in KOH	855.7		Broad satellite around 862	2015, Nardi <i>et al.</i> ⁸
Ni (+2)	NiFe LDH	855.7	872.5	860 and 879	2014, Lu <i>et al.</i> ¹⁰³
NiO or Ni(OH) ₂ (+2)	NiO cycled in KOH	853.7		Broad satellite	2015, Nardi <i>et al.</i> ⁸
NiO (+2)	Fe-doped crystalline NiO nanoparticles	855.18 (Gauss FWHM=3.586)	861.52 (Gauss FWHM=5.411)		2015, Fominykh <i>et al.</i> ¹⁴
NiO(+2)	NiNiO nanoparticles	855.5	872.5	860.9 (855.5 satellite), 879.4 (872.5 satellite)	2020, Faid <i>et al.</i> ⁴⁶
NiO(+2)	Annealed NiO	853.9			2020, Steimecke <i>et al.</i> ¹⁶
Ni (+2)	NiFe LDH	855.6	873.2	861.4 and 878.8	2017, Dutta <i>et al.</i> ¹¹⁸
Ni-OH (+2)	NiFe LDH	856.7	874.6		2017, Dutta <i>et al.</i> ¹¹⁸
Ni(OH) ₂ (+2)	NiFe nanoparticles after OER	855.8		861.5	2018, Roy <i>et al.</i> ⁶⁸
NiO (+2)	NiFe nanoparticles	853.7			2018, Roy <i>et al.</i> ⁶⁸
Ni (+2)	NiFe nanofoam	855.9	873.7	861.5 and 880.1	2018, Fu <i>et al.</i> ⁸²
Ni (+2)	NiFe LDH	856.8	874.6	862 and 881	2020, Peng <i>et al.</i> ¹³
Metallic Ni (0)	NiNiO nanoparticles	853.8	871.4		2020, Faid <i>et al.</i> ⁴⁶
Metallic Ni (0)	NiFe nanoparticles	852.6		859	2018, Roy <i>et al.</i> ⁶⁸
Metallic Ni (0)	NiFe nanofoam	852.4	869.7		2018, Fu <i>et al.</i> ⁸²

Table continues next page.

Table 2-4 (continued).

Metallic Ni (0)	NiFe LDH	852.8	870.1		2017, Dutta <i>et al.</i> ¹¹⁸
Fe (+3)	NiFe LDH	713.7	724		2014, Lu <i>et al.</i> ¹⁰³
Fe (+3)	NiFe LDH	712.3			2017, Dutta <i>et al.</i> ¹¹⁸
Fe (+3)	NiFe LDH	709.8 and 712.2	725		2020, Peng <i>et al.</i> ¹³
Fe (+3)	Fe nanocomposite	710.8	724.4	719 and 731	2018, Huang <i>et al.</i> ¹¹⁹
Fe ₂ O ₃ (+3)	Fe-doped crystalline NiO nanoparticles	711.21 (Gauss FWHM=4.979)	723.89 (Gauss FWHM=2.752)	719 and 732 if a separate phase is present	2015, Fominykh <i>et al.</i> ¹⁴
Fe ₂ O ₃ (+3)	NiFe nanoparticles after OER	710.8			2018, Roy <i>et al.</i> ⁶⁸
Fe ₂ O ₃ (+3)		711.0±0.15			1977, McIntyre and Zetaruk ¹¹⁴
Fe ₂ O ₃ (+3)	Fe _x O _y nanoparticles			717.9	2017, Yao <i>et al.</i> ¹²⁰
Fe ₃ O ₄ (+3 or +2)	Fe _x O _y nanoparticles	710.1	724		2017, Yao <i>et al.</i> ¹²⁰
Fe ₃ O ₄ (+3 or +2)	Fe ₃ O ₄ nanoparticles	711	725	718	2015, Pan ¹²¹
Fe ₃ O ₄ (+3)	Fe ₃ O ₄ nanoparticles	711.3	725.8	717	2015, Zhang <i>et al.</i> ¹²²
Fe ₃ O ₄ (+3)	Fe ₃ O ₄ nanoparticles	712.1	725.4	718.9	2015, Meng <i>et al.</i> ¹²³

Table continues next page.

Table 2-4 (continued).

Fe ₃ O ₄ (+2)	Fe ₃ O ₄ nanoparticles	710.3	723.8	2015, Meng <i>et al.</i> ¹²³	
FeOOH (+3)		711.3	725	719.3	2007, Martinez <i>et al.</i> ¹²⁴
α-FeOOH (+3)		711.9±0.2			1977, McIntyre and Zetaruk ¹¹⁴
FeOOH (+3)	NiFe nanoparticles after OER	711.6			2018, Roy <i>et al.</i> ⁶⁸
FeO (+2)	NiFeS nanofoam	710.3		715.4	2016, Ganesan <i>et al.</i> ⁵²
Metallic Fe (0)	NiFe nanoparticles	706.6			2018, Roy <i>et al.</i> ⁶⁸
Metallic Fe (0)		706.9±0.10			1977, McIntyre and Zetaruk ¹¹⁴
Metallic Fe (0)	NiFeS nanofoam	706.7		719.2	2016, Ganesan <i>et al.</i> ⁵²

Biesinger *et al.* also performed a thorough study of the different oxide and hydroxide phases of Fe and provide fitting parameters that can be used to analyse the complicated XPS spectra of these materials¹¹⁵. They provide a table that outlines all of these parameters including the multiplet and satellite structure. The table they provide can be of immense value when fitting XPS spectra.

In addition to the Ni 2p and Fe 2p peaks, the O 1s peak can also provide useful information of Ni electrocatalysts before and after electrochemical analysis (in pure and Fe containing electrolytes). The high-resolution scan of O 1s can indicate if Ni is present as NiO (529 eV⁸, 529.3 eV^{115,125}) or Ni(OH)₂ (531.3 eV¹²⁶, 531 eV⁸, 530.9 eV¹¹⁵). The O 1s peaks of almost all Fe oxide species, including α- and γ-FeOOH, occur at 529.9 eV¹¹⁵. The O1s peak of Fe(OH)₃ occurs at 531.3 eV.

The proximity of the binding energies of Ni and Fe oxide peaks could render them difficult to separate. In addition, there is also a species occurring at higher binding energies of ~532.5 eV, which is mostly ascribed to adsorbed water⁸, but in some cases to NiOOH¹²⁵.

Lastly, it is also possible to perform in-situ XPS. If one has access to such instrumentation it would be invaluable for the study of active sites. Vovk *et al.* studied the redox reaction of perovskite oxide electrodes in an electrochemical cell mounted in an ultrahigh vacuum (UHV) chamber⁶⁸. In addition, near-ambient pressure (NAP) XPS allows the in-situ study of systems without the need of a UHV environment. For example, Arrigo *et al.* used NAP-XPS to study electrolysis on Pt electrodes¹²⁷.

2.9.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) is the most important technique for determining the crystal structure of synthesised particles. XRD is based on the idea that layers of atoms are equivalent to reflecting planes as described by Bragg's equation:

$$2d \sin\theta = n\lambda \quad (7)$$

where d is the separation of atom planes and n is an integer¹²⁸. In this analysis technique, a crystalline sample is subjected to an X-ray beam, which is reflected at a certain angle, θ , corresponding to the separation of planes in the crystal¹²⁸. This process and the basis for the Bragg's equation is illustrated in Figure 2-7.

Two types of X-ray techniques are available: powder XRD and single-crystal XRD. Powdered samples contain numerous crystallites, which are randomly oriented¹²⁸. In mixtures of compounds, each individual crystalline phase can be detected at a level of 5 to 10 mass percentage of the compound in the mixture¹²⁸.

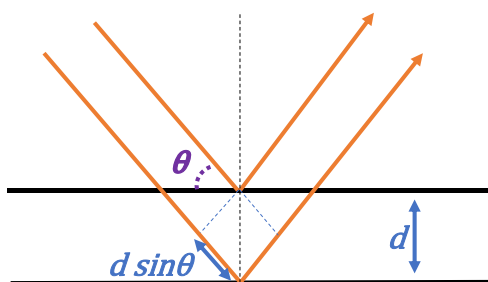


Figure 2-7: An illustration of Bragg's equation adapted from Atkins and Overton¹²⁸.

XRD can be employed to evaluate the crystal structure of different electrocatalyst powders. Additionally, grazing-incidence (GIXRD) can be used to evaluate deposited inks before and after electrochemistry. Trotochaud *et al.* has employed GIXRD to evaluate the crystal structures of $\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2$ films before and after aging in 1 M purified KOH for 24 hours⁵. Increased peak intensities after aging was ascribed to the increased crystallinity of the samples. Nardi *et al.* also used GIXRD to analyse thin (18 nm thick) NiO films deposited by ALD on a Si wafer⁸.

2.9.5 Electrochemistry

Various electrochemical analysis techniques are employed to investigate the electrochemical response of electrocatalysts. These techniques provide insight into the activity and stability of electrocatalysts. Electrochemical reactions take place at an electrode-electrolyte interface, where the electrode is a solid conducting material and the electrolyte is an ionic conducting solution. Electrochemical experiments are conducted in an electrochemical cell. To study the kinetics of certain electrode reactions, a three-electrode cell is required. The cell consists of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). The WE is where the reaction to be studied takes place; in the case of this study, the OER. The material, shape, cleaning and pre-treatment of the working electrode is chosen based on the specific interest of a study. An electrocatalyst itself can be a WE (such as a solid Ni metal WE), or it can be deposited on a WE, which in this case serves as a substrate/support for the electrocatalyst. A WE can impact the OER activity due to its structure, conductivity and wettability⁴. Flat surface and 3D WEs are the two main classes of WE supports which both have advantages and disadvantages⁴. In fundamental studies where the OER activities of electrocatalysts are to be compared, the WE needs to be sufficiently conductive and inert as to not interfere with the kinetics of the electrocatalyst films. The electrode also needs to be thoroughly cleaned and polished to have a smooth surface that does not influence the surface area of the catalyst films. A glassy carbon (GC) disk is commonly used as WE (whereupon the catalyst is drop-casted as a uniform film) in a Teflon-shrouded rotating disk electrode (RDE)^{23,81}. Powdered catalysts (such as nanoparticles) have to be prepared as an ink with solvents and a binder such as Nafion⁸¹. A binder is needed to stabilize catalysts when GC supports are used⁴. Binders are a major drawback of using GC supports as the use of them results in poor wettability and unavoidable agglomeration of catalyst powders⁴. The prepared ink is drop-casted onto the WE to produce an electrocatalyst film. The loading refers to the amount of catalyst drop-casted onto the electrode substrate. Both too high and too low loadings lead to unsatisfactory results. Loadings that are too low result in the electrode not being completely covered with the catalyst and too high loadings lead to agglomeration²³. In addition, Nafion loading should also be limited as high loadings results in extra mass transport resistance²³.

The RE controls or measures the potential applied to the working electrode²³. The RE of choice in alkaline media is Hg/HgO with a Teflon case⁸¹. It is common practice (and also recommended) to report measured or applied potentials with respect to the reversible hydrogen electrode (RHE)^{23,81,129}. Although the standard hydrogen electrode (SHE) is used as a universal RE (assigned a potential of 0.00 V)¹³⁰, it is not ideal for comparing results obtained in different electrolytes. This is because the pH changes the potential range where the reaction occurs on the SHE scale²³. The RHE compensates for pH dependence and can be expressed by the following equation²³:

$$E_{\text{RHE}} = E_{\text{SHE}} + \text{pH} \times \ln 10 \frac{RT}{F} \quad (8)$$

where E_{SHE} is the potential value versus SHE, $-\text{pH}$ is the pH-value of the electrolyte, R denotes the universal gas constant, T the absolute temperature, and F the Faraday constant. Furthermore, it is recommended that the reference electrode used in the experiments (Hg/HgO in this case) should be calibrated against the RHE prior to initial use as well as periodically^{23,81}. An RHE can be made by using a Pt WE and CE and a H_2 saturated electrolyte (identical to the electrolyte used in the experiments)^{23,81,129}. The WE is cycled (± 200 mV) around the expected value for the RHE at a scan rate of 10 mV s^{-1} ^{23,81}. The RHE potential vs the reference electrode in question can be obtained from taking the average of the potentials at zero current for the forward and reverse sweeps^{23,81}. This procedure differs slightly according to different sources. Wei *et al.* recommends the use of a Pt disk electrode rotated at 1600 rpm²³, while others recommend stirring the solution⁸¹ and others mention no convection¹²⁹. Chen *et al.* performed an LSV at a scan-rate of 0.5 mV s^{-1} and obtained the potential value at the intercept at zero current as -0.855 V in 0.1 M KOH ¹²⁹. This value is referred to as the offset potential (E_{offset}) and can be used to convert measured potentials (E_{measured}) to values vs RHE employing the following equation²³:

$$E_{\text{RHE}} = E_{\text{measured}} - E_{\text{offset}} \quad (9)$$

Lastly, the counter electrode allows for current to flow in the electrochemical cell. If an oxidation reaction takes place at the working electrode, then a reduction reaction takes place at the counter electrode. The counter electrode must therefore sufficiently accept electrons when an oxidation reaction takes place at the working electrode without disturbing the reaction at the working electrode²³. Platinum can tolerate large currents to effectively balance the charge and is therefore a common counter electrode material^{23,81}. The surface area of the platinum should be sufficient, which can be obtained by using a coiled wire, for example. Platinum tends to dissolve under anodic potentials and must therefore be placed in a porous container when used as counter electrode for the hydrogen evolution reaction (HER)^{23,81}. However, platinum does not dissolve

under cathodic potentials and can thus be used as counter electrode for the OER without this precaution⁸¹.

In addition, an electrolyte also must be chosen. The electrolyte is the ionic, conductive solution that allows the electrochemical reaction to take place. Different electrolytes greatly influence the electrocatalytic performance of electrocatalysts⁴. OER electrocatalysis is more favourable in alkaline solution⁴. KOH is a common alkaline electrolyte. The choice of cell material and cleaning of the cell is also very important. Glass cells should not be used when alkaline electrolyte is used as it dissolves in alkaline environments and components such as Fe leaches from the glass^{23,81}. Teflon cells and cell components are used instead. Wei *et al.* proposes a thorough cleaning method for Teflon cells that they adapted from Pedersen *et al.*¹³¹. The cell is first precleaned by soaking in NaOH, then the cell is soaked in piranha solution (H₂SO₄ and 30% H₂O₂ in a 3:1 ratio), whereafter it is soaked in 18.2 MΩ cm⁻¹ Millipore water at 85-90 °C for 24 hours with the water being changed 5 times²³.

2.9.5.1 Voltammetry

During voltammetry, a known potential is applied to the working electrode and the corresponding current response is measured. Techniques involving the measurement of current as a function of applied potential is referred to as potentiodynamic or voltammetric techniques¹³². Since an oxidation reaction is examined in this study, a positive potential is applied to the working electrode. This causes the species at the working electrode to be oxidised. The electrode where oxidation takes place is known as the anode¹³². Electrons are transferred from a species in the electrolyte to a vacant electronic state on the solid electrode, which causes an oxidation current. This type of current is known as Faradaic current. This occurs when electrons move across the electrode-solution interface. Faradaic processes yield to Faraday's law, which states that the chemical reaction that occurs at the electrode is proportional to the faradaic current¹³².

During these processes, an electroactive species reacts (through oxidation in this case) at the electrode surface and forms a product. It is necessary that new reactants are transported from the bulk solution to the electrode surface and products are transported away from the electrode. The term used to describe this is mass transport¹³². This is vital for electrochemical change to continuously occur. Mass transport can occur via three mechanisms; diffusion, migration and convection¹³². Convection is used in most electrochemical experiments as this overcomes mass transport limitations. This means that the rate of the electrochemical reaction is not limited by mass-transport. Convection is achieved by either stirring the solution or rotating the electrode. For RDE experiments, a rotation rate of 1600 rpm is mostly used²³. Therefore, the reactions

studied are not limited by mass transport and it will be the kinetics of the electron transfer reaction at the WE that determines the rate of the electrochemical reaction.

A common benchmark often used to compare the activity of different electrocatalysts is the value of the overpotential (η) at a current density of 10 mA cm^{-2} . The overpotential is usually indicated in mV and an electrocatalyst exhibiting an overpotential between 300 and 400 mV is considered an excellent OER catalyst⁴. It is important that we thoroughly understand what overpotential is and how this is calculated. Polarization occurs when the electrode potential deviates from the potential value predicted by the Nernst equation and the degree of polarization is given by the overpotential¹³⁰. The Nernst equation can be used to determine the equilibrium potential (E_{eq}) of the cell as follows:

$$E_{\text{eq}} = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{\text{O}}}{a_{\text{R}}} \quad (10)$$

Where E° is the standard potential, n is the number of electrons transferred and a_{O} and a_{R} are the activities of the oxidized species (O) and reduced species (R)¹³³. The overpotential (η) can then be calculated as:

$$\eta = E_{\text{measured}} - E_{\text{eq}} \quad (11)$$

The equilibrium potential for the oxygen evolution reaction is 1.23 V vs RHE, under standard conditions^{23,81}.

In voltammetric experiments, the potential intended to be applied to the WE may differ from the potential measured by the potentiostat. This is due to series resistance that is affected by factors like the placement of the WE and RE, the surface area and conductivity of the WE and the type and concentration of electrolyte⁸¹. Additional factors such as bubbles on the surface of the electrode or wires in the electrode can also affect the series resistance⁸¹. The uncompensated resistance (R_{u}) of a planar electrode is described by:

$$R_{\text{u}} = \frac{x}{\kappa A} \quad (12)$$

where x is the distance between the WE and RE, A denotes the area of the WE, and κ denotes the conductivity of the electrolyte⁸¹. This resistance is obtained by potenti-electrochemical impedance spectroscopy (PEIS) where the high-frequency x-axis intercept gives R_{u} ^{23,81}. The PEIS experiment is performed by applying a potential in the OER range and scan from 100 Hz to 1 MHz with an amplitude of 10 mV AC⁸¹. Modern potentiostats have the option of correcting for the uncompensated resistance in-situ^{23,81}. According to Ohm's law, the potential required to

overcome this resistance is obtained by iR_u , where i is the current moving through the electrode^{23,81,132}. This potential is referred to as the ohmic potential or IR drop¹³². The measured potential is then corrected according to the equation:

$$E_{\text{compensated}} = E_{\text{measured}} - iR \quad (13)$$

2.9.5.1.1 Cyclic voltammetry (CV)

For CV, the potential applied to the WE is first increased to a maximum and then the direction of the scan is reversed and the potential is returned to the original value. CV, therefore, measures the current response when electroactive species are reduced or oxidized¹²⁸. This results in a triangular waveform in a plot of potential versus time^{128,132}. The minimum and maximum potentials are referred to as switching potentials¹²⁸. During an oxidation reaction, the potential is first increased. This decreases the concentration of the reduced species and the current increases to adjust the surface concentration of the reactant¹²⁸. This current then decreases again as the diffusion layer diffuses further away from the electrode¹²⁸. This presents a current response in the form of a wave, called the oxidation wave. The peak of this wave is at a potential value called the anodic peak potential (E_{pa})¹²⁸. For Ni catalysts, E_{pa} is usually around 1.42 to 1.45 V vs RHE^{12,8,51}. Similarly, the reverse scan results in a reduction wave of which the peak potential is cathodic (E_{pc}). When an electrode reaction is reversible, the size of the oxidation and reduction waves are the same and their peaks are separated by a small difference in potential (ΔE_p)¹²⁸. If the reaction is reversible at 25 °C, ΔE_p can be described by the following equation:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.0592}{n} \quad (14)$$

where n denotes the number of electrons involved in the half reaction¹²⁸. ΔE_p can be small for slow scan rates, but as the scan rate is increased, this value increases if the reaction is irreversible due to sluggish electron transfer kinetics at the electrode^{81,128,132}. Therefore, smaller ΔE_p values for the redox features of electrocatalysts indicate faster charge- and ion-transfer kinetics⁸¹. This could be useful when comparing different electrocatalysts or different environments for the electrocatalysts.

The shape and size of the redox peaks can also provide us with an array of information on the catalyst. For example, it is stated that sharper waves indicate a more homogeneous environment for the catalyst species than broader waves⁸¹. Furthermore, the area under the oxidation or reduction wave can be used to determine the electrochemically active surface area (ECSA) of the

WE^{23,81}. However, this may not always be possible or accurate as the amount of electrons per metal atom has to be known and the redox features may not be reversible⁸¹. If the exact ECSA cannot be determined, the relative size of the redox features can still be indicative of the amount of electrochemically active sites. This can, for example, be indicative of the density of a film. Nardi *et al.* cycled Ni films of various thicknesses and found that the size of the redox features remained the same, indicating that only the outer surface layers are active and that the catalyst film is dense⁸.

CV is therefore a facile way to quickly obtain qualitative information of redox properties as well as quantitative information on kinetics and stability¹²⁸. CV can be employed to evaluate the electrochemical nature of Fe incorporation and how it influences the redox behaviour of Ni electrocatalysts. Previous studies have shown that the anodic peak of the CV shifts gradually to more positive potentials when cycling in Fe-containing electrolyte^{9,5,134}, or when an increasing amount of Fe is present in mixed NiFe electrocatalysts¹². The redox peaks are also reported to decrease in size when Fe is incorporated into the structure of Ni electrocatalysts^{12,8}. In addition, an increase in OER potential is to be expected when cycling these catalysts in KOH containing Fe^{5,9}. The anodic shift is associated with changes in the catalyst structure. In addition, it was found that there is an initial increase in activity upon adding Fe to the electrolyte, but this activity does not increase significantly upon further cycling⁹.

2.9.5.1.2 Linear sweep voltammetry (LSV)

Simply put, an LSV is the forward sweep of a CV. During LSV, the potential is increased linearly from a starting potential to a final potential and the corresponding current response is measured. The scan rate can be defined as the time derivative of the working electrode potential. The scan rate is constant during an LSV. Where CV commonly focuses on redox features, LSV is usually used to evaluate intrinsic activity⁵¹. In addition, Tafel plots can be generated from the LSV (or CV) data to obtain mechanistic information.

2.9.5.1.3 Tafel plots

Tafel analysis involves monitoring the sensitivity of the current response of an electrocatalyst to an applied potential²⁹. Tafel plots can be used to obtain mechanistic and kinetic information about electrocatalysts. From the Tafel equation, two significant parameters can be obtained: the exchange current density and the Tafel slope. The Tafel slope provides us with information on the mechanism of the electrochemical reaction, such as the rate-determining step of multistep reaction mechanisms^{4,29,31,135}. For these multistep reaction mechanisms, the anodic Tafel slope (b_a) can be expressed as:

$$b_a = \frac{d\eta}{d\log(j)} = \frac{2.303 \times RT}{\alpha_{ox}F} \quad (15)$$

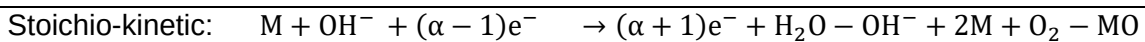
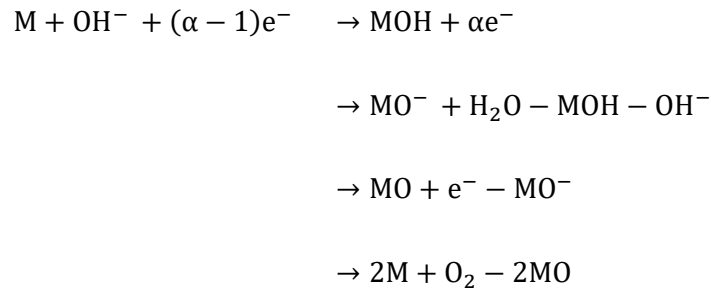
where η is the overpotential, j is the current density (mA cm^{-2}), R is the ideal gas constant and F is the Faraday constant^{136,137}. The slope yields the value of α_{ox} , the composite transfer coefficient of the anodic oxidation reaction¹³⁷:

$$\alpha_{ox} = \frac{RT}{F} \frac{\partial}{\partial E} \ln\{i\}|_{i \approx i_{ox}} \quad (16)$$

Theoretical values for Tafel slopes can be calculated from proposed reaction mechanisms. Experimental Tafel slope values can then be correlated to the theoretical values, assuming different rate-determining steps²⁹. To illustrate how Proposed mechanisms can be used to determine theoretical Tafel slopes at different rate determining steps, the Krasil'shchikov pathway (Table 2-1) will be used as an example.



If the reaction illustrated by equation (17) is the rate-determining step (RDS), then the stoichio-kinetic reaction (where the oxidation reaction is the forward reaction) can be determined and written as follows:



The current can then be written as¹³⁷:

$$\frac{i}{F} = k_{ox}^0 a_{OH^-} a_e^{(\alpha-1)} - k_{rd}^0 \frac{a_e^{\alpha+1} a_{H_2O} a_{O_2}}{a_{OH^-}} \quad (21)$$

The activity of water may be set equal to one and activity coefficients can be absorbed in the rate constants,

$$\frac{i}{F} = k_{ox}^{0'} a_e^{(\alpha-1)} - k_{rd}^{0'} \rho_{O_2} a_e^{\alpha+1} \quad (22)$$

Furthermore, the electrochemical activity of electrons are:

$$\tilde{a}_e = a_e \exp \left[\frac{Z_e F \phi(\vec{r})}{RT} \right] = a_e \exp \left[\frac{-F \phi(\vec{r})}{RT} \right] \quad (23)$$

Where $\phi(\vec{r})$ denotes the electrical potential at the position $\vec{r}$ in space. Factors with no effect on the experiment can be absorbed in constants and the electron activity can be expressed as:

$$a_e = \exp \left\{ \frac{-F(E - E^{0'})}{RT} \right\} \quad (24)$$

When equation (24) is substituted into equation (22), we obtain for the current:

$$\frac{i}{F} = k_{ox}^{0'} c_{OH^-} \exp \left\{ \frac{F(1 - \alpha)(E - E^{0'})}{RT} \right\} - k_{rd}^{0'} \rho_{O_2} \frac{1}{c_{OH^-}} \exp \left\{ \frac{-F(1 + \alpha)(E - E^{0'})}{RT} \right\} \quad (25)$$

If α is assumed to have a value of 0.5, the anodic Tafel slope becomes:

$$b_a = \frac{2.303RT}{F(1 - \alpha)} = \frac{59.1 \text{ mV}}{1 - \alpha} = 118.2 \text{ mV/dec} \quad (26)$$

Each step of the Krasil'shchikov pathway can be rate-determining, and with the equations above, the anodic Tafel slope values can be calculated as²⁷:

$$MOH + OH^- \rightarrow MO^- + H_2O \quad b_a = 2.303 \left(\frac{RT}{F} \right) = 60 \text{ mV/dec} \quad (27)$$

$$MO^- \rightarrow MO + e^- \quad b_a = 2.303 \left(\frac{2RT}{3F} \right) = 40 \text{ mV/dec} \quad (28)$$

$$2MO \rightarrow 2M + O_2 \quad b_a = \left(\frac{RT}{4F} \right) = 15 \text{ mV/dec} \quad (29)$$

The Tafel slope is an important parameter that is commonly used in literature to analyse the OER activity of electrocatalysts¹³⁶. A low Tafel slope is said to be a characteristic of good OER activity⁴. However, Fabbri *et al.* warns against using the Tafel slope as the only activity metric, as two electrocatalysts may exhibit the same Tafel slope but very different current densities at a defined

potential¹³⁶. This is because two lines may have the same slope, but different y-axis intercepts. Since the Tafel plot is a plot of overpotential against current density, it is clear that lines with the same slope but a different intercept has different OER activities. Therefore, an additional activity metric has to be used in parallel with the Tafel slope to evaluate electrocatalytic activity. Fabbri *et al.* suggests that the potential at a defined current density or the current density at a defined potential can be used as additional metric¹³⁶. They mention that the exchange current density can also be used, but not for irreversible reactions such as the OER and ORR¹³⁶.

The exchange current density is a kinetic parameter that describes the rate of electron transfer at equilibrium¹³⁵. Previous studies have used the exchange current density to compare the activities of OER electrocatalysts^{27,47}. However, a study focused on Tafel analysis reported that the use of exchange current density should be approached with caution as the Butler-Vomer equation is not valid in all situations²⁹. Wei *et al.* states that the exchange current density cannot be determined reliably for multiple electron reactions such as the OER²³. It is stated that the value of the exchange current density experimentally determined for irreversible reactions is very inaccurate¹³⁶. The Tafel slope can always be used, but the intercept thereof cannot be assumed to be equal to the exchange current in all cases²⁹. A previous study evaluating the effect of Fe on NiO OER activity found that only the Tafel slopes could be used to evaluate the electrocatalyst activity and that the values of the exchange current density were contradictory to the values of the Tafel slopes²⁷.

Evaluating how the addition of different amounts of Fe affects the rate-determining step can aid the understanding of how Fe kinetically influences Ni and NiO electrocatalysts. Two Tafel regions (low overpotentials and high overpotentials) have been identified for various metals and metal oxides, including Ni, NiO, Fe and NiFe^{138,29,28}. Two Tafel regions are characteristic of Fe-doped Ni thin films⁸. This transition between two Tafel regions can be due to a change in the rate-determining step or a change in surface coverage of the adsorbed intermediates¹³⁸. In a lot of studies only the low overpotential region is mentioned³¹. However, Shinagawa *et al.* recommends that both of the Tafel slopes must be reported in order to obtain a better understanding of the reaction mechanism²⁹. In addition, a recent review strongly recommends that Tafel slopes should not be derived from LSV or CV data, as the mass loading affects these values³¹. This review also states that Tafel slopes not derived from LSV or CV can be used as a method to effectively compare the activity of electrocatalysts³¹. Chronoamperometry (CA) can also be used to determine the Tafel slope. Potential steps held for a specific amount of time is applied to the working electrode and the resultant current response is recorded.

The Tafel equation is normally expressed as follows:

$$\eta = a + b \log j \quad (30)$$

where b is the Tafel slope and a is the intercept related to the exchange current density^{135,29}.

Comparing Tafel slopes can be a useful tool in determining similar mechanisms or rate/determining steps. It is very important to keep in mind that preparation methods and preconditioning of the working electrode has an effect on the value of the Tafel slope²⁸. In addition, the concentration of the alkaline electrolyte and even the type of alkaline electrolyte (cation effect) can alter the Tafel slope¹¹. Determining if the Tafel slope is pH dependent is an additional tool often used to aid researchers to determine mechanisms or rate/determining steps. For example, a recent study found that NiFe LDH and FeOOH-NiOOH both have Tafel slopes of 40 mV/dec, but that the latter does not have a pH-dependent Tafel slope¹¹. Therefore, when the concentration of KOH was increased, the Tafel slope of NiFe LDH decreased, indicating a charge transfer barrier across the bulk film¹¹.

Table 2-5 summarises Tafel slopes reported in literature for Ni and NiFe OER electrocatalyst materials. What is important to note from this table, is that most of the reported Tafel slopes were obtained from Ni samples cycled in unpurified KOH. This could have allowed for unintentional Fe incorporation in these studies and might explain the large deviation in Tafel slope values reported. NiFe electrocatalysts have generally lower Tafel slopes as can be seen in the table. Fe could have had more time to incorporate in certain studies, leading to higher Fe content in the Ni electrocatalyst, which could have lowered the Tafel slopes.

Table 2-5: A summary of Tafel slope values reported in literature for Ni and NiFe OER electrocatalysts.

Transition metal	Electrocatalyst description	Electrolyte	Tafel slope (at 25 °C)	Source
Ni	Ni(OH) ₂ formed in-situ on Ni foam by applying current in 6 M KOH	1 M KOH (unpurified)	39 mV/dec	2020, Wan <i>et al.</i> ¹³⁹
	Polycrystalline Ni cycled for pre-treatment	1 M NaOH (unpurified)	39.4 mV/dec	2008, Lyons & Brandon ²⁶
	Unactivated nickel substrates	Alkaline electrolytes (unpurified)	45-65 mV/dec	1983, LeRoy ²⁰
	Ni(OH) ₂ films cycled and aged in unpurified KOH	1 M KOH (unpurified)	45-55 mV/dec and 40 mV/dec after longer ageing	2015, Klaus <i>et al.</i> ⁶
	Ni(OH) ₂ formed by cathodic electrodeposition of nickel nitrate	1 M KOH (unpurified)	47 mV/dec	2014, Stern and Hu ⁶⁷
	NiO formed in situ using pretreated Ni	1 M KOH (unpurified)	50 mV/dec	2014, Stern and Hu ⁶⁷
	Ni(OH) ₂ nanoparticles	1 M KOH (unpurified)	53 mV/dec	2014, Stern and Hu ⁶⁷
	3D Ni foam upon which a thin NiO nanostructure was grown	1 M KOH (unpurified)	53 mV/dec	2016, Liang <i>et al.</i> ¹⁴⁰
	NiO _x nanoparticles	1 M KOH (unpurified)	54 mV/dec	2014, Stern and Hu ⁶⁷
	NiO treated at 900 °C	0.1 M KOH (purified)	61 mV/dec	2020, Steimecke <i>et al.</i> ¹⁶
	1D NiO hollow nanofibres	1 M KOH (unpurified)	78.8 mV/dec	2020, Silva <i>et al.</i> ⁵¹
	Ni(OH) ₂ films electrodeposited in rigorous Fe free conditions	1 M KOH (purified)	106 mV/dec	2015, Klaus <i>et al.</i> ⁶
	3D NiO nanoparticles	1 M KOH (unpurified)	113.6 mV/dec	2020, Silva <i>et al.</i> ⁵¹

Table continues next page.

Table 2-5 (continued).

	NiO nanoparticles	0.5 M KOH (unpurified)	120 mV/dec	2012, Sadiék <i>et al.</i> ⁴⁷
	NiO nanoparticles	0.5 M KOH (unpurified)	120 mV/dec	2014, Chekin <i>et al.</i> ⁴⁸
	Ni nanofoam	1 M KOH (unpurified)	203.4 mV/dec	2020, Silva <i>et al.</i> ⁵¹
NiFe	NiO cycled in reagent grade and Fe saturated KOH	0.1 M KOH	30 mV/dec at low overpotentials	2015, Nardi <i>et al.</i> ⁸
	Mesoporous Ni cycled in electrolyte containing 1mM Fe (20 CVs)	1 M KOH	33.5 mV/dec	2020, Wang <i>et al.</i> ⁷¹
	NiFe codeposited (both 40 and 20% Fe)	0.1 M KOH (unpurified)	40 mV/dec	2013, Louie and Bell ¹²
	FeOOH-NiOOH (γ -NiOOH with clusters of covalently bonded γ -FeOOH on the surface)	1 M KOH	40 mV/dec	2020, Bai <i>et al.</i> ¹¹
	NiFe LDH	1 M KOH	40 mV/dec	2020, Bai <i>et al.</i> ¹¹
	FeNiO _x H _y nanofoam		40.7 mV/dec	2020, Hu <i>et al.</i> ⁸⁴
	Ni _{0.7} Fe _{0.3} on Ni nanofoam (NiFe LDH formed in-situ)	1M KOH	47 mV/dec	2020, Yang and Liang ⁶⁹
	NiFe co-precipitated	1 M KOH	80 mV/dec	2020, Peng <i>et al.</i> ¹³

2.9.5.2 Electrochemical double-layer (EDL) capacitance

When a potential is applied to the working electrode, the layers of solution immediately adjacent to its surface obtain a charge opposite of the applied potential¹³². This charged solution layer consists of an inner layer and a diffuse layer where potential decreases linearly or exponentially with distance away from the electrode surface¹³². All of these charged species at the metal-

solution interface is referred to as the electrochemical double layer (EDL)¹³². The distribution of the charged species and the formation of the EDL is illustrated in Figure 2-8.

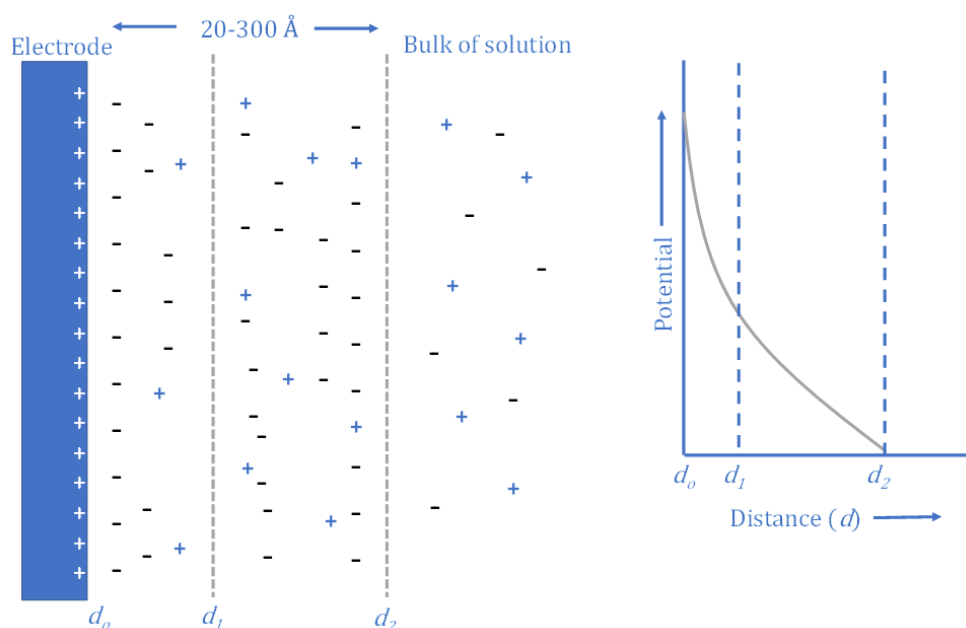


Figure 2-8: The electrochemical double layer that arises due to potential applied to the working electrode¹³².

The capacitance of this double layer can be measured by using cyclic voltammetry or electrochemical impedance spectroscopy. This is referred to as the electrochemical double layer capacitance (C_{DL}). This can be measured when the voltages applied to the cell result in non-faradaic current. This occurs when the electrons do not have enough energy to cross the potential energy barrier at the electrode-solution interface or because electron-transfer is too slow¹³². The electrons in the double-layer rearrange and adjust to the new potential of the electrode and the electrode surface acts as one plate of a capacitor¹³². Therefore, this capacitance can be measured in this non-faradaic region by varying certain related factors. The capacitive current related to double-layer charging is measured by varying the scan rate of CVs in the non-Faradaic potential region¹⁴¹. EIS can also be used by measuring the impedance, which is dependent on the applied frequency¹⁴¹. C_{DL} can be utilised to determine the electrochemically active surface area (ECSA). By dividing C_{DL} with the specific capacitance (C_s) of a sample the ECSA can be obtained¹⁴¹. Previous studies have used this method to determine the ECSA or roughness factor of Ni electrocatalysts. However, since there are no theoretical values available for the specific capacitance of NiO or $Ni(OH)_2$, they used a general value of $25 \mu F cm^{-2}$ to calculate the ECSA of their sample⁶⁷. A double layer capacitance value for electrodeposited NiO was reported as $0.091 mF^{141}$. Previous studies have reported that cycling Ni electrocatalysts in KOH containing concentrated amounts of Fe, results in smaller surface areas that cycling in KOH containing trace

amounts of Fe^8 . Since the electrochemical double layer capacitance is directly related to the surface area, EDL measurements can be used to investigate this further.

2.9.5.3 Electrochemical impedance spectroscopy (EIS)

EIS is yet another powerful tool that can be used to evaluate the performance of OER electrocatalysts. During an EIS measurement, the current response of a working electrocatalyst is measured as a function of applied frequency of AC perturbation voltage^{142,143}. In the field of water electrolysis, EIS is used to determine the charge transfer resistance (R_{ct}), which is an indication of the ability of the electrocatalyst to transfer an electron. R_{ct} can be used as an indication/benchmark of the OER activity in addition to the overpotential at 10 mA cm^{-2} . When the substrate has no contribution to the electrochemical reaction and the electrocatalyst alone is responsible for the reaction (one electroactive interface), the EIS data can be circuit-fitted to a standard Randle's cell¹⁴². This is the case where an electrocatalyst completely covers the substrate surface and there is only one interface. In this case, the Nyquist plot usually occurs as a depressed semi-circle¹⁴². The Randle's circuit can be observed in Figure 2-9.

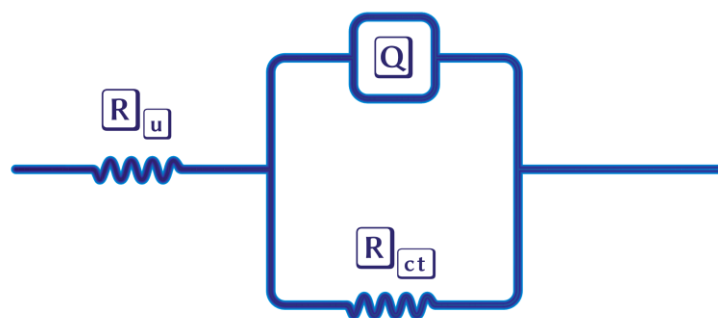


Figure 2-9: A depiction of a standard Randle's circuit.

In this figure, Q denotes a constant phase element (CPE). R_u denotes the uncompensated series resistance and R_{ct} the charge transfer resistance¹⁴². R_{ct} can be calculated by subtracting R_u from the total impedance¹⁴². A previous study focusing on thin films produced with PVD employed the abovementioned circuit, since PVD sputtered thin films cover the entire substrate, yielding a single electroactive interface⁸⁸.

3. METHODOLOGY

In this section the research questions and aim will be revisited, with additional knowledge that is obtained from the literature study. Based on the research questions, the choices for different aspects of the experimental design are explained. This includes why certain chemicals, amounts of reagents in synthesis methods and experimental techniques were chosen. Using the research questions and aim as guideline, an efficient experimental outline can be developed. Specific experimental details pertaining to each unique electrocatalyst will be discussed in subsequent sections.

3.1 Research questions

3.1.1 How is Fe incorporated by Ni electrocatalysts when Fe is present in the electrolyte?

Previous studies have indicated that trace amounts of Fe (<36 ppb) in the electrolyte increases the OER activity of Ni electrocatalysts^{2,5,6}. The addition of mM concentrations of Fe leads to a further increase in the OER activity^{8,9}. In addition, literature reports that there is a certain range of Fe concentrations where the electrocatalytic activity of NiFe electrocatalysts does not increase any further^{9,134}. These results indicate that OER activity is linked to the amount of Fe present in the electrolyte and that there is an Fe saturation point for each Ni electrocatalyst (a Fe concentration beyond which the activity of the electrocatalyst will not increase any further). Therefore, this study differentiates between sub ppm and mM level of Fe present in electrolyte. The effect of electrolytic Fe concentration on activity as well as the structure of the electrocatalyst is examined.

The electrolyte chosen for this study is KOH, since this is the most common alkaline electrolyte used for fundamental studies of transition metal based electrocatalysts. A concentration of 0.1 M KOH was chosen for all electrochemistry experiments in this study. Although a lot of studies use 1 M KOH, this concentration is too high for in-situ Raman spectroscopic studies, since it could lead to corrosion of the instrument. Therefore, to maintain consistency throughout the study, 0.1 M KOH was used for all experiments. In addition, the type of KOH used was SC-grade KOH (99.99%, Sigma Aldrich). Throughout this study, this is referred to as pure KOH when no additional Fe was added. The choice was made not to further purify this KOH by using a previously proposed method that employed precipitated Ni(OH)₂ to absorb Fe⁵. This is because some additional Ni will remain in the KOH and could affect the results of electrochemical and physical analyses. Since this study aims to evaluate rigorously the effect of only Fe on the structure of different Ni electrocatalyst, this could jeopardise answering the research questions. Exploring

other means to purify KOH, such as electrochemical purification¹⁴⁴, was beyond the scope of this study. In addition, using SC-grade KOH will serve the purpose of answering the research questions of this study.

By examining previous studies that investigated electrolytic Fe^{8,9}, the most popular way to dope KOH with known concentrations of Fe, is to add the iron salt, Fe(NO₃)₃·9H₂O. Equation (6) describes the reaction upon adding Fe(NO₃)₃ to KOH electrolyte. Considering the low solubility of Fe(OH)₃, there is the possibility of the formation of FeOOH upon addition of the Fe salt to the electrolyte. Previous reports state that an NiFe LDH structure is formed when ppm levels of Fe is present in the electrolyte^{6,1}. This study evaluates if this is the case or if a separate phase of Fe (FeOOH) is formed, especially for higher concentrations. Therefore, the ultimate composition of the electrocatalyst layer formed on the electrode after addition of sub ppm and 1 mM Fe is characterised. In addition, the structure (composition) is correlated with the OER activity, and it is evaluated how the OER activity is dependent on the structure.

High purity Fe(NO₃)₃·9H₂O (99.9999% trace metals basis, Sigma Aldrich) was used to spike 0.1 M KOH with Fe. A sub ppm range of Fe concentrations were investigated, along with KOH containing a concentrated amount of Fe (1 mM). According to the literature study in section 2, in-situ Raman spectroscopy is a popular technique when it comes to evaluating the OER active structure of NiFe electrocatalysts. Therefore, this technique was employed to monitor structural changes of the Ni nanoparticles under reaction conditions. Each electrocatalyst was evaluated in KOH containing both sub ppm and concentrated (mM) amounts of Fe to observe the influence of the Fe concentration on the electrocatalyst structure. In addition, each electrocatalyst was studied before and after 30 CV cycles in electrolytes containing these different concentrations of Fe. This was done to shed light of the effect of cycling in Fe containing electrolyte, since it is known that the process of electrochemical cycling is said to incorporate more Fe into the Ni electrocatalyst structure.

30 CV cycles in the range 0.2 and 0.8 V vs Hg/HgO at a scan rate of 20 mV s⁻¹ was chosen as preconditioning/activation method for all of the Ni electrocatalysts in this study. The CVs served a threefold purpose. Firstly, performing 30 consecutive CVs is an efficient means to precondition the Ni electrodes, allowing for a stable current response, as well as allowing for Fe incorporation from the electrolyte. Secondly, the CVs in this region provide an efficient means to observe how the OER activity is changing upon each consecutive cycle, which gives an indication of how Fe incorporation influences the OER activity. Lastly, changes in the redox features upon each consecutive cycle as well as changes between electrodes cycled in different concentrations of Fe

can be seen. Therefore, valuable information towards answering the research question is obtained while preconditioning the electrode at the same time.

3.1.2 How does the morphology of Ni-based electrocatalysts influence electrolytic Fe uptake and OER activity?

From the available literature, it is clear that researchers investigate Ni electrocatalysts of various morphologies and oxidation states towards the OER. These factors can potentially influence Fe uptake and therefore OER activity. For electrochemists to synthesise optimum OER electrocatalysts, it is highly beneficial to know which morphologies have the best OER activities and how this is influenced by Fe uptake. The research presented here includes a comparative study on the OER activity of Ni-based electrocatalysts of three different morphologies cycled in Fe doped KOH. The first two morphologies are two different types of nanoparticles, obtained by performing two different syntheses. The third is sputtered thin films obtained through PVD sputtering.

3.1.2.1 An overview of the synthesis methods employed in this study

Two different synthesis methods were employed in this study to produce nanoparticles with two different types of morphology. The first method, will be referred to as the tailored synthesis method, since the reactants and reaction conditions are carefully chosen and controlled to produce nanoparticles of a desired shape and size^{43,44}. To synthesise these nanoparticles, air-free conditions and a carefully controlled temperature program is needed. The reaction used to prepare these nanoparticles can be seen in Figure 3-1.

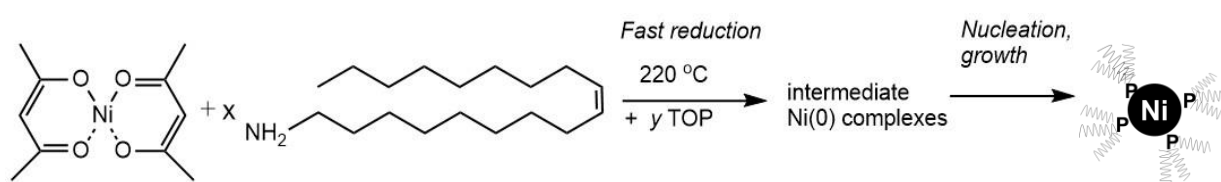
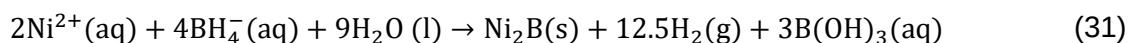


Figure 3-1: Synthesis of colloidal Ni nanoparticles from nickel(II) acetylacetonate, oleylamine and tri-n-octylphosphine (redrawn from⁴⁴).

In this reaction, the stoichiometry of oleylamine (x) and TOP (y) are very important. If x is higher than 4, then all of the nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$) will be consumed and the yield will be close to 100 % versus $\text{Ni}(\text{acac})_2$ ⁴⁴. Increasing the stoichiometry of TOP (y), results in smaller particles since TOP is the surface ligands⁴⁴. These factors were carefully considered when the amounts of reactants were chosen for this synthesis method. After the reaction in Figure 3-1 was completed, the nanoparticles were cleaned with a few consecutive cleaning steps to remove the

phosphines from the surfaces of the Ni nanoparticles. Additionally, all other byproducts were also removed during the cleaning steps, so that we are left with pure colloidal Ni nanoparticles.

The second method will be referred to as the reduction method or simply reduction. This is because the synthesis method only involves a simple reduction step where a Ni nitrate salt is reduced by the strong reducing agent sodium borohydride. The reaction involved in this synthesis method is as follows¹⁴⁵:



As with the previous synthesis method, cleaning steps needed to be applied to the product of this reaction so that pure Ni without any boride could be obtained.

The first analysis method performed on the particles after they have been prepared is powder XRD. This technique was employed to evaluate if the desired crystal structure was obtained. XRD is a facile and efficient screening method to evaluate if the desired electrocatalyst was obtained before moving on to more time consuming and costly techniques such as TEM. The two synthesis methods yield nanoparticles of unique morphologies, which was efficiently analysed by TEM. TEM is an ideal characterisation method often used to visualise the morphology and size of ultrasmall nanoparticles⁴³.

A third morphology was obtained by employing PVD to sputter thin films. Amorphous thin films are produced via sputtering. During sputtering, layers of the desired material are deposited onto a substrate from a target in an ultra-high vacuum (UHV) environment. In this study, both Ni and NiO targets of high purity were used. GC disks are used as the substrate, since they can easily be inserted into a RDE setup for electrochemical analysis. All films were sputtered ~50 nm thick. Ni, NiO and NiNiO films were sputtered.

3.1.3 Is the Ni oxidation state and the electrolytic Fe content interrelated?

Additionally, different oxidation states of each morphology are also evaluated. The different as-prepared oxidation states provide a means to investigate the effect thereof on Fe uptake and OER activity. Furthermore, this study evaluates how Fe incorporation changes each respective oxidation state by employing XPS and SEM-EDX.

The tailored synthesis method produced Ni(0) nanoparticles. To obtain NiO nanoparticles, the Ni(0) nanoparticles were annealed in air. The reduction method produced amorphous Ni nanoparticles. Therefore, to obtain Ni(0) the particles were annealed in 5% H₂/Ar. NiO was obtained by annealing the as-prepared particles in air and a portion of these particles were subsequently annealed in 5% H₂/Ar to produce NiNiO.

With sputtering, Ni films with different oxidation states can easily be deposited onto the substrates by making use of reactive sputtering or different targets.

3.2 Aim

The fundamental aim of this study is to use electrochemistry in parallel with in-situ Raman spectroscopy and other physical characterisation techniques to determine the effect of electrolytic Fe on the structure and OER activity of Ni electrocatalysts. This is done in pursuit of the determination of the OER active structure in NiFe electrocatalysts.

3.3 Experimental outline

Considering the different design choices based on each research question, an experimental outline can be constructed. Firstly, Table 3-1 outlines the different Ni-based electrocatalysts investigated in this study.

Table 3-1: An outline of the electrocatalysts studied

Electrocatalyst	Preparation method	Abbreviation used	Morphology (characterisation technique)	Prepared oxidation state
Colloidal Ni	Tailored synthesis method	Ni coll	Colloidal nanoparticles (TEM)	Ni
Colloidal NiO	Tailored synthesis method and annealing in air	NiO coll	Colloidal nanoparticles (TEM)	NiO
Ni prepared by reduction	Chemical reduction synthesis method and annealing in H ₂ /Ar	Ni red	Nanosheets (TEM)	NiNiO
NiO prepared by reduction	Chemical reduction synthesis method and annealing in air.	NiO red	Nanosheets (TEM)	NiO
NiNiO prepared by reduction	Chemical reduction synthesis method and annealing in H ₂ /Ar and air.	NiNiO red	Nanosheets (TEM)	NiNiO

Table continues next page.

Table 3-1 (continued).

Sputtered Ni	Magnetron sputtering using a Ni target	Ni	Smooth, amorphous thin film (SEM)	Ni
Sputtered NiO	Reactive sputtering using a Ni target and oxygen	NiO	Smooth, amorphous thin film (SEM)	NiO
Sputtered NiNiO	Magnetron sputtering using both Ni and NiO targets	NiNiO	Smooth, amorphous thin film (SEM)	NiNiO

The nature of nanoparticles versus sputtered thin films necessitated unique characterization methods. Therefore, the experimental methods and results will be presented as two separate sections for nanoparticles and sputtered thin films, respectively. The results of both sections will be discussed together, as all of the results contribute to answering the same research questions. To summarise the different experimental techniques used to study the electrocatalysts, two tables have been constructed. Table 3-2 summarises the experiments conducted on nanoparticles, whereas Table 3-3 outlines the experiments on the sputtered samples.

Table 3-2: The experimental techniques that will be used to analyse the electrochemical activity and structure of Ni-based nanoparticles.

Experimental technique	Relevance	Electrolytic Fe concentrations analysed
Physical		
TEM	Determination of morphology and size of nanoparticles.	Only as-prepared nanoparticles.
XRD	To analyse crystal structures of nanoparticles and evaluate if desired products were obtained.	Only as-prepared nanoparticles.
XPS	To evaluate how the oxidation states change due to the presence of Fe and determine the amount of Fe on the surface after CVs.	Pure KOH, 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe.
Electrochemical		
CV	Preconditioning, measure of OER activity, analysis of redox features.	Pure KOH, 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe.
LSV	Determination of OER activity and overpotentials after 30 activation CVs in each respective Fe concentration.	Pure KOH, 0.3 ppm Fe and 1 mM Fe
Tafel analysis	Towards obtaining mechanistic information.	Pure KOH, 0.3 ppm Fe and 1 mM Fe
EDL	Evaluates how electrolytic Fe influences the double layer capacitance.	Pure KOH, 0.3 ppm Fe and 1 mM Fe
In-situ		
Raman spectroscopy	Analyses the electrocatalyst structure under working conditions and how it changes when Fe is present in different amounts.	Pure KOH, 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe

Table 3-3: The experimental techniques that will be used to analyse the electrochemical activity and structure of sputtered Ni-based thin films.

Experimental technique	Relevance	Electrolytic Fe concentrations analysed
Physical		
SEM-EDX	Visualisation of the thin films, analysing the amount of Fe and O in the bulk of the films before and after CVs.	As-prepared, Pure KOH, 0.007 ppm Fe, 0.3 ppm, 0.9 ppm Fe and 1 mM Fe
XPS	To evaluate how the oxidation states change due to the presence of Fe and determine the amount of Fe on the surface after CVs.	As-prepared, Pure KOH, 0.007 ppm Fe, 0.3 ppm and 1 mM Fe
Electrochemical		
CV	Preconditioning, measure of OER activity, analysis of redox features.	Pure KOH, 0.003 ppm Fe, 0.007 ppm Fe, 0.09 ppm Fe, 0.3 ppm 0.9 ppm Fe and 1 mM Fe
LSV	Determination of OER activity and overpotentials after 30 activation CVs in each respective Fe concentration.	Pure KOH, 0.003 ppm Fe, 0.007 ppm Fe, 0.09 ppm Fe, 0.3 ppm 0.9 ppm Fe and 1 mM Fe
Tafel analysis	Towards obtaining mechanistic information.	Pure KOH, 0.003 ppm Fe, 0.007 ppm Fe, 0.09 ppm Fe, 0.3 ppm 0.9 ppm Fe and 1 mM Fe
EDL	Evaluates how electrolytic Fe influences the double layer capacitance.	Pure KOH, 0.003 ppm Fe, 0.007 ppm Fe, 0.09 ppm Fe, 0.3 ppm 0.9 ppm Fe and 1 mM Fe
EIS	Evaluates how electrolytic Fe influences the charge transfer resistance.	Pure KOH, 0.003 ppm Fe, 0.007 ppm Fe, 0.09 ppm Fe, 0.3 ppm 0.9 ppm Fe and 1 mM Fe

From Table 3-3 it can be seen that a wider range of Fe concentrations were studied for the sputtered thin films. This could be done due to the ease of preparation and the reproducibility of

these thin films. A broader range of Fe concentrations will provide useful information about the point where the electrocatalysts are saturated with Fe.

4. NI-BASED NANOPARTICLES

This section deals with the experimental methods pertaining to Ni-based nanoparticles prepared as electrocatalysts, followed by the results obtained by employing these methods. Two synthesis methods were investigated that produced nanoparticles of two different morphologies. These nanoparticles were subsequently investigated.

4.1 Experimental methods

Firstly, this subsection describes the exact procedures followed to prepare colloidal nanoparticles with the tailored synthesis method and nanosheets with the reduction method. Thereafter, the physical characterisation methods used to evaluate if the nanoparticles were successfully prepared (TEM, XRD) are explained, along with XPS used for characterising the electronic structures after cycling.

The electrochemical techniques used to analyse the nanoparticles is subsequently explained. The nanoparticles needed to be dissolved and mixed with a binder to prepare an electrocatalyst ink so that these particles could be drop-casted onto an electrode support. This was done so that these nanoparticles could be used as OER electrocatalysts. Therefore, it is explained how the electrode supports and electrocatalyst inks for each nanoparticle were prepared. Furthermore, the various electrochemical methods are discussed

4.1.1 Synthesis of Ni and NiO nanoparticles

Two different synthesis methods were followed in this study to synthesise nanoparticles with two different morphologies. The first synthesis method was based on a tailored method to produce monodispersed, colloidal nanoparticles using oleylamine (OAm) as the reducing agent and tri-n-octylphosphine (TOP) as a surface stabiliser⁴³. The second is based on the chemical reduction of nickel(II) nitrate hexahydrate with sodium borohydride as reducing agent⁴⁵.

4.1.1.1 The synthesis of colloidal Ni and NiO nanoparticles with a tailored method

50 mL of oleylamine (OAm; technical grade, 70%, Sigma Aldrich) was added to a dried three-neck flask, which was then evacuated and purged with argon. 4 g of nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$; anhydrous, 95%, Sigma Aldrich) was weighed off inside a glovebox into a sample vial which was then sealed. This was then quickly and carefully added to the three-neck flask. This step was crucial since the reaction of the anhydrous reagent with air will not yield the desired product. 14 mL of tri-n-octylphosphine (TOP, 97%, Sigma Aldrich), drawn up by a syringe inside a glovebox, was then injected into the mixture in the three-neck flask. The mixture was heated for

5 minutes at 50 °C and then for two hours at 220 °C while stirring, in an inert environment. A black precipitate was formed and the flask was left to cool down overnight.

The second part of the procedure was cleaning the synthesised nanoparticles. Toluene (anhydrous, 99.8%, Sigma Aldrich) was added to the mixture and then it was transferred to centrifuge tubes, which was filled with toluene and centrifuged for 10 minutes at 10 000 rpm. The supernatant was decanted and the particles was then redispersed in 10 mL isopropanol (IPA, 99.5%, Sigma Aldrich). The tubes were filled to 80% with IPA and the last 20% of each tube was filled with toluene and then centrifuged again for 10 minutes. The supernatant was discarded. The particles were redispersed in 10 mL toluene and the rest of the tubes was filled with acetone and centrifuged. The supernatant was decanted, and the particles were dried in a vacuum oven for 22 hours at 60 °C.

The last part of the procedure involved annealing. For Ni, the particles were used as-prepared. NiO was prepared by annealing a portion of the Ni particles in a tube furnace for 4 hours at 600 °C.

4.1.1.2 Synthesising Ni, NiO and NiNiO nanosheets with the chemical reduction method

2.911 g of nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\geq 97.0\%$, Sigma Aldrich) was added to 100 mL deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, 3 ppb TOC, Milli-Q water) and stirred with a magnetic stirrer for 10 minutes. 1.895 g of NaBH_4 (98%, Sigma Aldrich) was added to 500 mL water and then the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was quickly added to this solution. The solution immediately turned black and bubbled vigorously. The solution was then stirred with a magnetic stirrer for 30 minutes. Then, the solution was centrifuged at 6000 rpm for 8 minutes at a time. Centrifugation was performed until all supernatant could be decanted.

The particles were subsequently cleaned by centrifuging them 3 times at 6000 rpm for 8 minutes at a time with a 1:1 ratio of deionized water and ethanol. The washed particles were dried in a vacuum oven at 60 °C for 20 hours.

The last step was annealing the particles after they were dried. A portion of the particles was annealed in a tube furnace at 500 °C for 6 hours in air to yield NiO. A portion of this NiO was annealed in 5% H_2/Ar at 500 °C for 6 hours to yield NiNiO. To form Ni, the dried particles was annealed in 5% H_2/Ar at 500 °C for 6 hours.

4.1.2 Physical characterisation

4.1.2.1 TEM

The nanoparticles were diluted with IPA and carefully dropped on copper TEM grids (with 300 mesh) with a micropipette. The TEM analysis was performed with a Jeol JEM 2100-LaB6 microscope. The TEM images of the colloidal particles in this study were analysed with ImageJ software. Firstly, the scales of the images were calibrated and thereafter the images were thresholded. Finally, the area of the particles in each image was determined by employing the *Analyze particles* function. The diameter was then calculated assuming that the particles have a spherical shape.

4.1.2.2 XRD

As Ni nanoparticles are to be treated as a toxic gas (for health and safety precautions), the sample preparation method for powder XRD is a unique procedure focused on safe sample handling. A Si-cavity sample holder was used to minimise the amount of powder needed for the analysis. The nanoparticles were carefully placed in the Si cavity before the holder was covered with Kapton foil. This is done to ensure that the nanoparticles do not become airborne and pose a health risk during sample handling.

Powder XRD patterns were obtained for each of the synthesised particles using a Bruker D8 A25 DaVinci X-ray Diffractometer with Cu-K α radiation and a LynxEye™ super-speed detector. For the nanoparticles prepared by reduction, spectra were obtained in the 2θ -range 15-75° with a step size of 0.3° (2θ). For colloidal nanoparticles, spectra were obtained in the 2θ -range 20-80°. The 2θ ranges were selected according to what was previously reported in literature for each morphology in order to successfully characterise them^{43,46}. Grazing Incidence XRD (GIXRD) was also explored as a method to obtain diffraction patterns of the electrocatalysts after they have been electrochemically cycled. Bruker DIFFRAC.EVA software was used to analyse the diffraction patterns obtained and background subtraction was performed by using this software.

4.1.2.3 XPS

XPS was performed by using an Axis Ultra DLD instrument (Kratos Analytical, Manchester, UK). A Mg K α nonmonochromated X-ray source (10 mA, 15 kV) was used to avoid Auger features from Ni in the Fe 2p region, which is present when an Al source is used. The use of a Mg source is critical for detecting small amounts of Fe. To acquire the spectra, a pass energy 40 eV was used to increase signal intensity with a step size of 0.1 eV. As the samples in this study are

magnetic, the electrostatic lens was required for analysis. The samples are conductive due to the GC support and therefore no charge compensation was required.

The GC disks that were analysed are a few nanometers higher than 4 mm, rendering them too high for the conventional sample bars used in the XPS instrument. To solve this, the constant height sample bar was used and the spring disks removed. This allowed for taller samples to be analysed. The glassy carbon disks (4mm length x 5mm diameter) were attached to the constant height bar with carbon tape and inserted into the XPS UHV chamber. The chamber needed to be pumped down to 10^{-10} Pa prior to analysis. Since a lot of carbon was present (carbon tape and GCs) the samples degassed and required a long pump down period (overnight) in order to reach this low pressure.

CasaXPS (Casa Software, Ltd.) was used to analyse the raw XPS data. All binding energies were calibrated using the C 1s peak of adventitious carbon at 284.8 eV in order to compensate for charging effects.

4.1.3 Electrochemistry

4.1.3.1 Electrode preparation

Rotating disk GC electrodes (5 mm diameter, Pine Research) were polished in a figure of 8 for 60 'cycles' using first 0.3 μm and then 0.05 μm alumina (Al_2O_3) suspensions (Allied High-Tech Products, Inc.) on microfiber polishing pads. The electrode was rinsed with DI water between polishing with different particle sizes. After polishing, the GC electrode was sonicated in DI water for 50 seconds and then in 1 M purified KOH for 60 seconds to dissolve any alumina particles left on the surface.

4.1.3.2 Ink formulation

The nanoparticles from both synthesis methods each required a unique ink recipe to ensure optimum dispersion. Both inks contain deionized (DI) water, isopropanol (Sigma Aldrich) and 0.05 mL (5 wt %) Nafion 117 solution (Sigma Aldrich). For the particles prepared via the chemical reduction method, a greater IPA:water ratio was required to ensure dispersion of the particles. First, 0.95 mL of IPA and 0.05 mL of Nafion was used together with 10 mg catalyst. No water was used to ensure dispersion of annealed particles. Although this ink provided excellent dispersion, it proved difficult to drop-cast due to the low viscosity of IPA. A second ink was formulated for these particles containing 0.85 mL IPA and 0.1 mL water together with 0.05 mL Nafion and 10 mg particles. This ink was easier to drop-cast, consequently leading to better reproducibility of the films. This is the ink formulation used for the data reported. The ink prepared for the tailored

particles consisted of 0.75 mL water, 0.25 mL IPA and 0.05 mL Nafion and 10 mg electrocatalyst powder. Both inks were ultrasonicated for 15 minutes to provide a homogeneous dispersion before drop-casting.

4.1.3.3 Preparation of electrolyte

Four electrolytes were used: pure 0.1 M KOH, and 0.1 M KOH doped with 0.007 ppm, 0.3 ppm and 1 mM of Fe. To make a pure 0.1 M KOH solution, 0.561 g semiconductor grade KOH pellets (99.99%, Sigma Aldrich) were weighed and made up to a 1 L solution by adding deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, 3 ppb TOC, Milli-Q water). To avoid Fe contamination, no glass components were used in this process and KOH solutions were stored in plastic containers.

Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9999% trace metals basis, Sigma Aldrich) was added to 0.1 M KOH to obtain 0.007 ppm, 0.3 ppm and 1 mM Fe. 0.404 g was added to 1 L of KOH to obtain a 1 mM Fe solution.

4.1.3.4 Voltammetry techniques

Figure 4-1 shows the classical three-electrode electrochemical cell setup that was used to perform all electrochemical experiments in this study.

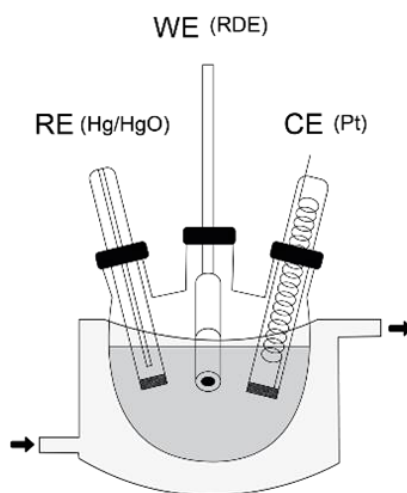


Figure 4-1: The standard three-electrode cell used for electrochemical analyses.

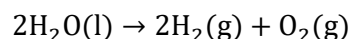
A standard three-electrode electrochemical cell was used to perform all the electrochemical analysis techniques in this study. A Teflon cell was used and was thoroughly cleaned before use and in between experiments to eliminate Fe-contamination. For cleaning, the Teflon cell was

soaked in 1 M sulfuric acid (H₂SO₄) for 3 hours and boiled in DI water 3 times, replacing the water each time.

A Pt wire was used as the CE and a Hg/HgO (Pine research) RE was employed. The GC WE was used as part of a RDE setup (Pine Research). Pt counter electrodes were periodically cleaned by submerging in aqua regia for 1 minute. The electrodes were connected to a Bio-Logic (VMP3) potentiostat controlled with EC-Lab software. The electrolyte was saturated with Ar and all experiments were performed at room temperature (25 °C). The temperature was controlled by using a Julabo F25 waterbath for the jacketed Teflon cell.

The Hg/HgO reference electrode was calibrated by performing a CV at a scan rate of 10 mV s⁻¹ between -1.0 V and 0.9 V in H₂ saturated 0.1 M KOH with a Pt WE and CE. The averaged value of the voltage intercept of the forward and backward scans was 0.87 V. Therefore, 0.87 V is the offset potential used to convert measured potentials to the RHE scale according to equation (9).

For the water electrolysis reaction:



the Gibbs energy change is 474.2 kJ mol⁻¹, and can be used to calculate the null voltage of the reaction as 1.299 V¹³⁷. Thus, in theory, electrolysis of water occurs when the applied potential is 1.299 V vs RHE. Electrochemists have introduced the RHE as universal reference, since it removes the impact of pH on applied potentials by accounting for the pH shift⁷. Thus, the theoretical potential for the HER is always 0 V vs RHE and that of the OER is always 1.299 V vs RHE²³.

The equilibrium potential of a reaction can be calculated by using the Nernst equation (equation (10)). The concentrations of the oxidized and reduced species (O and R) are low and therefore the concentration (c) can be used in the equation instead of the activity.

$$E_{\text{eq}} = E^\circ + \frac{RT}{nF} \ln \frac{c_{\text{O}}}{c_{\text{R}}} \quad (32)$$

At equilibrium, $\Delta G=0$, thus by definition:

$$\frac{RT}{nF} \ln \frac{c_{\text{O}}}{c_{\text{R}}} = 0 \quad (33)$$

Therefore,

$$E_{eq} = E^{\circ} = 1.299 \text{ V vs RHE} \quad (34)$$

This is then the value of the equilibrium potential, which was subtracted from the measured potential to obtain the overpotential, according to equation (11).

The Ohmic (IR) drop was corrected for by using the ZIR function of EC-Lab software. An EIS experiment was performed at high frequencies ($0.1\text{-}10^5$ Hz) and alternative current (AC) perturbation amplitude of 10 mV. The compensation level was 85% of the ohmic resistance measured before the experiment of interest and the IR drop was calculated and compensated in-situ by the software.

In this study, the current density is reported by using the geometric surface area of the WE. ECSA will be influenced by Fe incorporated into the electrocatalyst. This will then affect the reported current density. In addition, Fe is constantly being incorporated in this study as different concentrations of Fe were added to the electrolyte. Therefore, the ECSA could be dynamically changing with each experiment as more Fe is incorporated. For consistency, the geometric surface area is used.

CV experiments were performed between 0.2 and 0.8 V vs Hg/HgO at a scan rate of 20 mV s^{-1} while the WE was rotated at 1600 rpm. This potential range was chosen as it allows for preconditioning, but at the same time shows the OER activity of the electrocatalysts. A scan rate of 20 mV s^{-1} was chosen to produce stable CVs, but also takes a reasonable time to complete.

LSV experiments were performed between 0.2 and 0.8V vs Hg/HgO at a scan rate of 1 mV s^{-1} while the WE was rotated at 1600 rpm. LSV was performed for each electrocatalyst in each electrolyte after 30 CV cycles were completed. The slow scan rate allows for a steady state to be reached, providing more accurate and reproducible results than higher scan rates.

4.1.3.5 Chronoamperometry (CA) for Tafel analysis

In a CA experiment, potential steps are applied to the WE. Each step is held for a certain period of time, allowing the current to reach a steady state. The potential steps used were: 0.5, 0.55, 0.57, 0.6, 0.62, 0.64, 0.66, 0.68, 0.7, 0.72, 0.74, 0.76, 0.78 and 0.8 V vs Hg/HgO). Each step was held for 30 seconds while the current response was recorded. In order to obtain current versus potential curves for Tafel analysis, the steady state current response was plotted against each potential value. The overpotential was corrected for IR drop before plotting it against the current density.

4.1.3.6 Evaluation of the electrochemical double layer capacitance

The first step was to identify the potential range from CV where the current was non-faradaic. This region was identified as 0 V to 0.1 V vs Hg/HgO. After this, CV measurements were conducted at scan rates of 0.005, 0.01, 0.025, 0.05, 0.1, 0.2 and 0.3 V s⁻¹. 10 CV cycles were conducted at each scan-rate to ensure a stable response. The 10th cycle (being the most stable) was then used to obtain the current response at 0.05 V vs Hg/HgO for each scan rate. A plot of current versus scan rate was then constructed to obtain the EDL capacitance from the slope.

4.1.4 In-situ Raman spectroscopy

In-situ Raman spectroscopic analyses were performed within this study. Spectra were recorded using a confocal Raman microscope (WITec alpha300 R) with 5 mW of power delivered by a laser operating at 532 nm. A Zeiss EC Epiplan objective (10×magnification) was used. The instrument was controlled with WITec control scanning and data acquisition software. Prior to each experiment, the instrument calibration was checked against a Si wafer.

The Teflon-sheathed working electrode was mounted within a custom Teflon cell. A Pt counter electrode and a Hg/HgO reference electrode were used for the electrochemical measurements (Figure 4-2). The working, counter and reference electrodes were connected to an (Ivium-n-Stat) potentiostat, which controlled the potential applied to the working electrode in a chronoamperometry experiment. During the CA measurement, potential steps were applied to the working electrode. The potential could not be increased above 0.6 V vs Hg/HgO as this would result in excessive bubble formation due to the OER, which would obscure Raman measurements.

Two sets of samples were investigated: as-prepared samples, and samples that were subjected to 30 CV cycles prior to the Raman analysis. The following potential steps were applied to the as-prepared electrodes: 0.4 V, 0.5 V, 0.55 V and 0.6 V. Each potential step was held for 1000 s in order to obtain a Raman spectrum at a stabilised current. While the different potential values were applied, WITec Control FIVE software was used to program the WITec Raman Instrument to measure Raman Spectra at each potential value. Ten Raman spectra at each of these potentials were recorded to monitor how the structure of the electrocatalyst changed when the potential was increased. After investigating the as-prepared samples, samples that were subjected to CVs were also investigated. After 30 activation CVs in a certain electrolyte, the WE was placed in the custom-made in-situ Raman cell filled with the same electrolyte. The WE was subjected to the following potentials: 0.3 V, 0.4 V, 0.5 V and 0.55 V and 0.6 V vs Hg/HgO, in parallel with an in-situ Raman measurement of the electrocatalyst surface. It was found that 500 s at each potential

was sufficient to obtain a stable current. The potential was allowed more time to stabilise for the electrocatalysts that have not been subjected to CV yet (the as-prepared samples), as these surfaces were less stable. The setup used to perform in-situ Raman spectroscopy can be seen in Figure 4-2.

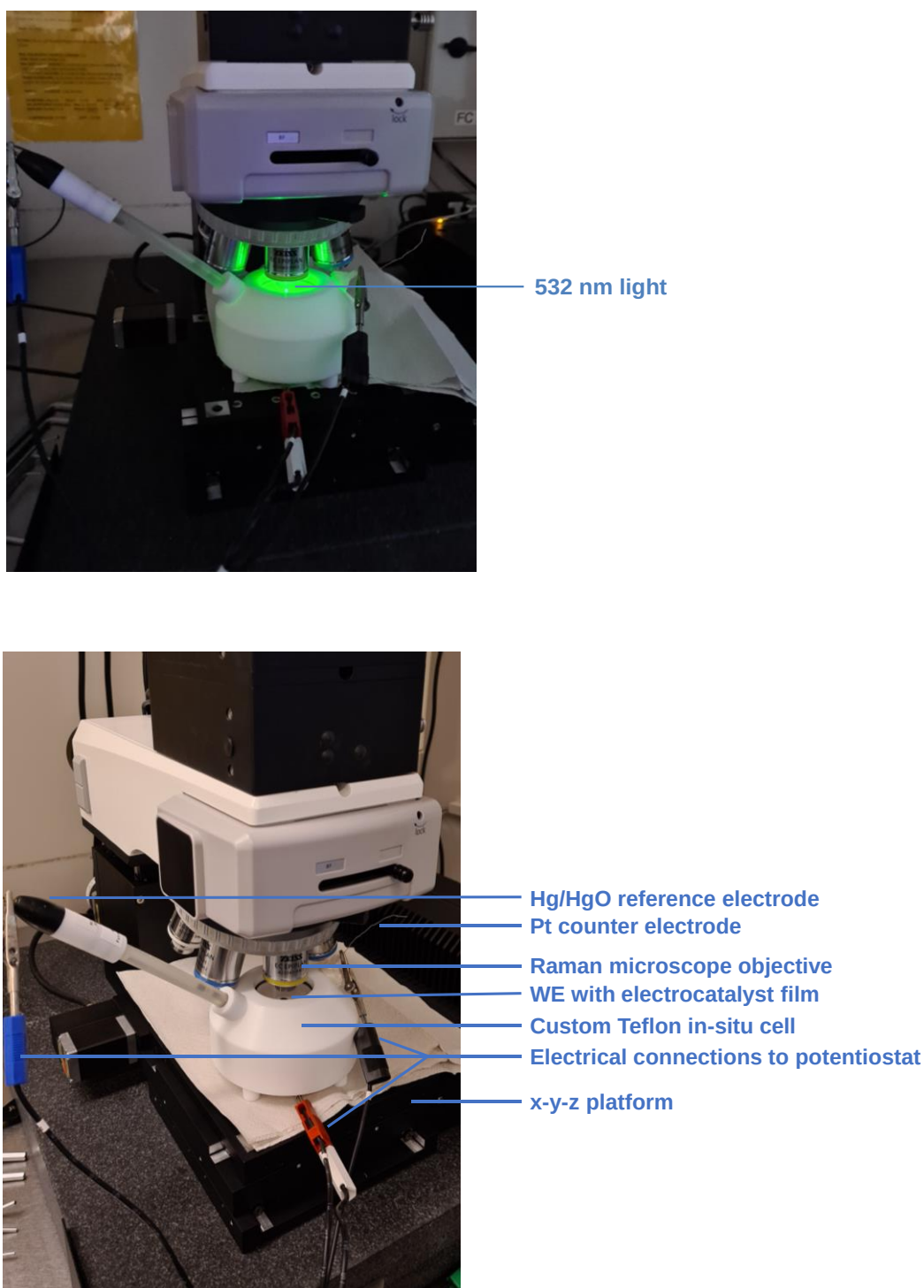


Figure 4-2: The setup used for all in-situ Raman spectroscopic measurements.

The data was analysed with Project FIVE 5.2. software. Savitzky Golay smoothing was applied to the data to remove excessive noise and cosmic ray removal (CRR) was applied when the spectra contained cosmic rays (sharp spikes in the spectra). Cosmic rays normally occur when longer Raman experiments are performed. Cosmic rays also tend to occur when the room where analysis is performed is not dark enough. The advanced fitting tool of the software was used to fit the peaks with a Gaussian function.

4.2 Results

This section will commence by providing the results obtained from the physical characterisation techniques TEM and XRD. These results indicate that the nanoparticles have been prepared as intended. TEM results show that the desired morphologies were obtained whereas XRD results show that the crystal structures (face centered cubic Ni, NiO and NiNiO) have been prepared as intended. Thereafter, XPS results are shown which gives an indication of the oxidation states and Fe concentration in the surface of the nanoparticle electrocatalysts before and after cycling. Then the electrochemistry results are presented, followed by the results obtained from in-situ Raman spectroscopy.

4.2.1 Transmission electron microscopy (TEM) images of Ni-based nanoparticles

TEM images of the tailor synthesised colloidal Ni and NiO nanoparticles can be observed in Figure 4-3.

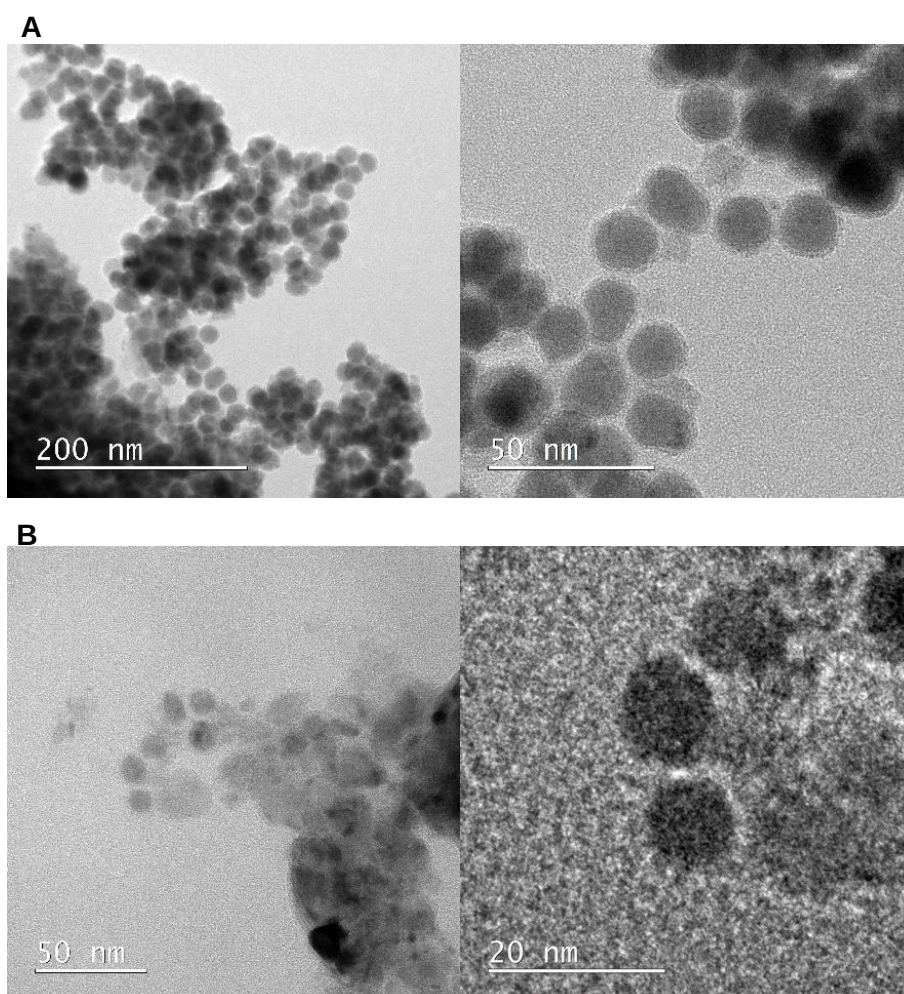


Figure 4-3: TEM images of as-synthesised colloidal (a) Ni and (b) NiO nanoparticles at different magnifications for visualisation of single particles.

As can be observed from Figure 4-3, the nanoparticles synthesised with the tailored synthesis method have spherical morphology. The spheres are not interconnected; individual spheres can easily be identified. The TEM images of the colloidal nanoparticles were analysed with ImageJ. The average diameter of the colloidal Ni nanoparticles is 8.50 nm. The particles have a rather constant size distribution with the smallest diameter being 7.73 nm and the largest 9.41 nm. The average diameter of the colloidal NiO particles is smaller than that of colloidal Ni. The average diameter was determined to be 6.40 nm, with the smallest diameter being 5.74 nm and the largest 7.04 nm.

For the nanoparticles prepared by the chemical reduction synthesis method, it was difficult to find single particles to analyse with TEM. This could only be found for the NiNiO nanoparticles. TEM images of NiNiO nanoparticles prepared by the reduction synthesis method can be observed in Figure 4-4.

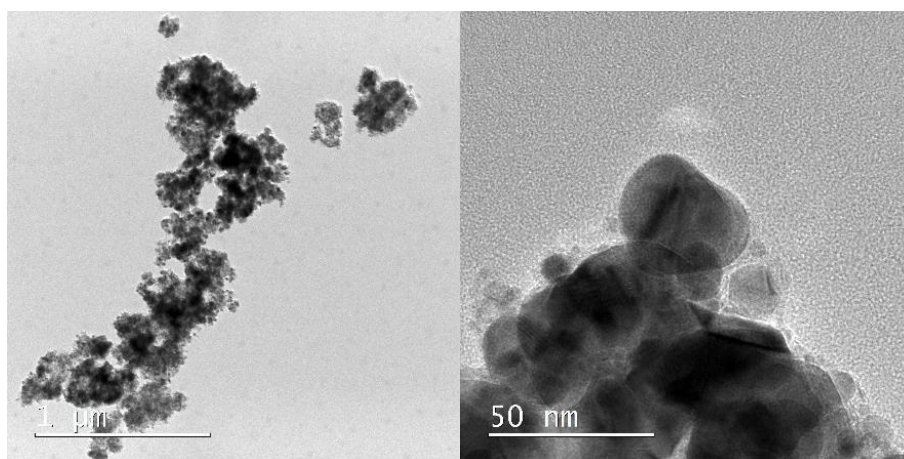


Figure 4-4: TEM images of NiNiO nanoparticles prepared by the chemical reduction method.

Figure 4-4 serves as a representative of the morphology of the nanoparticles prepared by reduction. Since the particles prepared with the chemical reduction method have an irregular shape, their exact diameter cannot be determined. The morphology can be described as curved sheets that are interconnected. This morphology has previously been described as nanosheets⁴⁶.

4.2.2 X-ray diffraction (XRD) results of Ni-based nanoparticles

Powder XRD was used to analyse the crystal structures of the synthesised nanoparticles. The powder XRD patterns for colloidal Ni and NiO are displayed in Figure 4-5. The diffraction pattern of colloidal NiO is displayed in blue, while that of colloidal Ni is displayed in red.

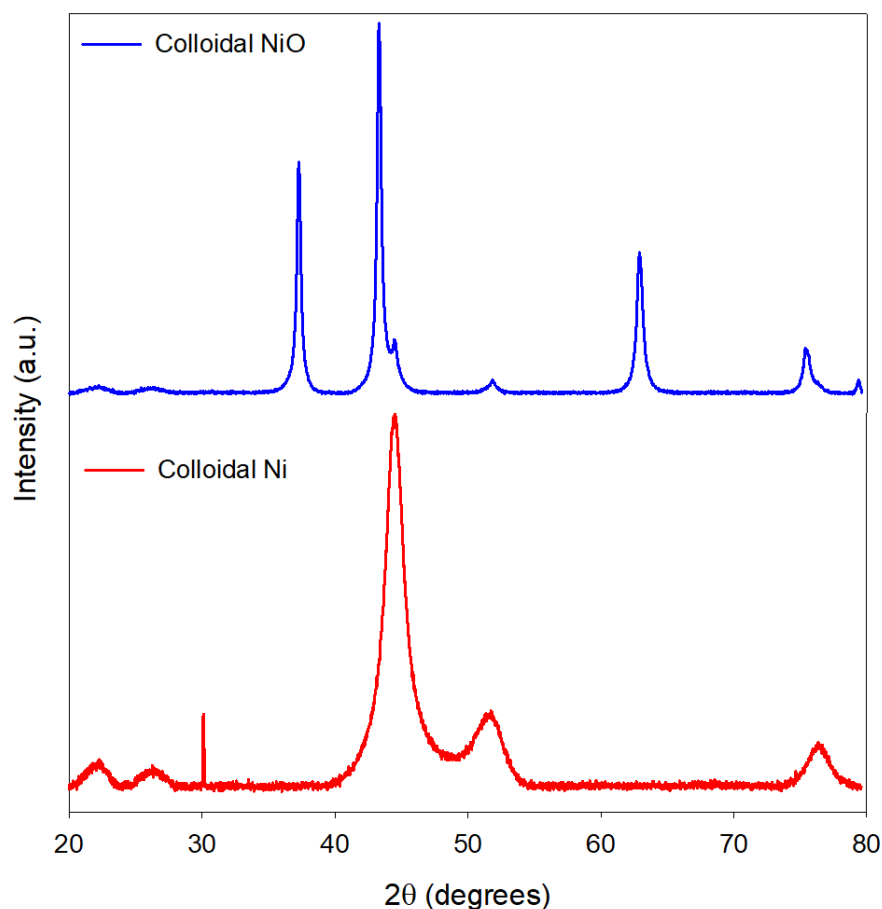


Figure 4-5: Powder XRD patterns of NiO (blue) and Ni (red) prepared by the tailored synthesis.

The diffraction pattern of colloidal NiO nanoparticles in Figure 4-5 shows sharp peaks at 2θ values of 37.2° , 43.2° , 63.0° . These peaks correspond to (111), (200) and (220) phases of face-centered cubic (fcc) NiO as indexed in the standard data (JCPDS card no. 47-1049)¹⁴⁶. In addition, the sample has a peak at 75.6° corresponding to the (311) plane of the fcc phase of NiO¹⁴⁷. The diffraction pattern of colloidal Ni nanoparticles shows peaks at 44.6° , 51.8° and at 76.5° . These three peaks correspond to (111), (200) and (220) of Ni fcc (JCPDS card 04-0850)^{43,147}. In addition, the peaks at 22° and 26° arise due to the Kapton film used in analysis. Figure 4-5 indicates that the desired crystal structures were obtained from the tailored synthesis method for preparing colloidal nanoparticles.

Powder XRD was also used to obtain the crystal structures of the three nanoparticles prepared by the chemical reduction synthesis method. The diffraction patterns for Ni, NiO and NiNiO prepared by reduction can be seen in Figure 4-6.

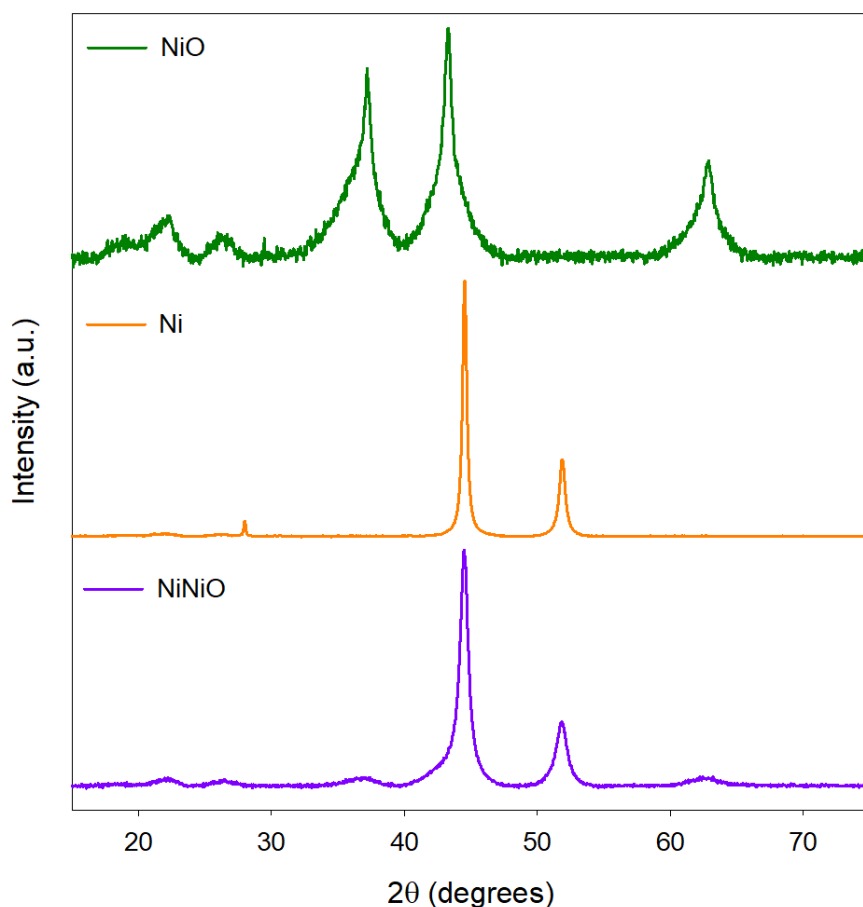


Figure 4-6: Powder XRD patterns of NiO (green), Ni (orange) and NiNiO (purple) prepared by the chemical reduction synthesis.

The XRD pattern of NiO prepared by reduction in Figure 4-6 shows three well-defined peaks at 2θ values of 37.2° , 43.2° and 62.8° . These peaks can be ascribed to (111), (200) and (220) planes of NiO fcc. Furthermore, the diffraction pattern of Ni displays two sharp peaks at 44.5° and 51.8° , corresponding to Ni (111) and Ni (200) crystal planes of Ni fcc (JCPDS card 04–0850)¹⁴⁷. Lastly, NiNiO has peaks at 37.2° , 44.5° , 51.8° and 62.8° , indicating that the diffractogram of NiNiO is the diffractograms of Ni and NiO superimposed. Therefore, the XRD results indicate that the nanoparticles prepared by the chemical reduction synthesis method have been successfully prepared in that the desired crystal structures are apparent from Figure 4-6.

Furthermore, grazing incidence XRD (GIXRD) was performed on as-deposited electrocatalysts on GC electrodes. This was done to determine if post-mortem analysis of the electrocatalysts could be performed after they have been cycled in electrolyte containing different concentrations of Fe. X-rays penetrate all the way to the GC substrate, resulting in the diffraction pattern of carbon. The carbon substrate displays a broad peak at the same position as the largest diffraction

peak of Ni and NiO (43.2°). This can be seen in Figure 4-7, that shows the grazing incidence patterns of Ni, NiO and the GC substrate.

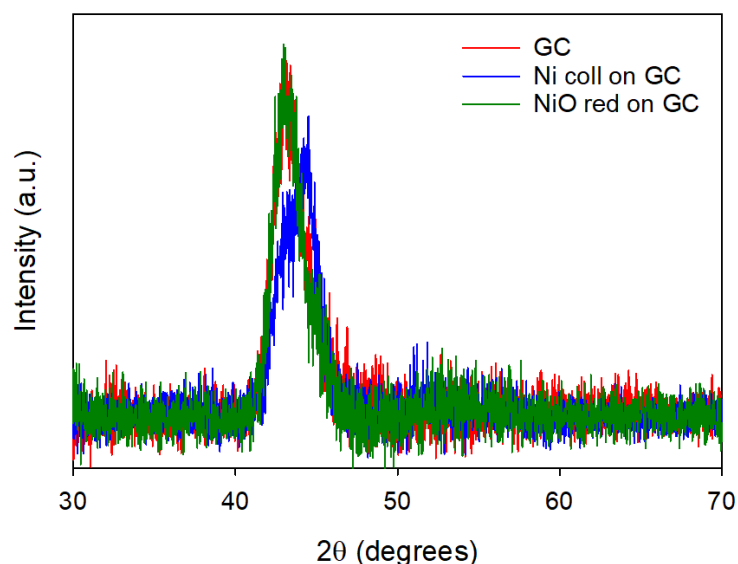


Figure 4-7: X-ray diffraction patterns of GC substrate, colloidal Ni as well as NiO prepared by reduction deposited on the GC substrate.

Seeing as the GC substrate displayed a peak at the exact same position as the (200) plane of fcc NiO, two other substrates were tested. Carbon paper and gold were also tested as substrates to be used for GIXRD analyses. NiNiO was used to test these substrates as it displays diffraction peaks of both Ni and NiO.

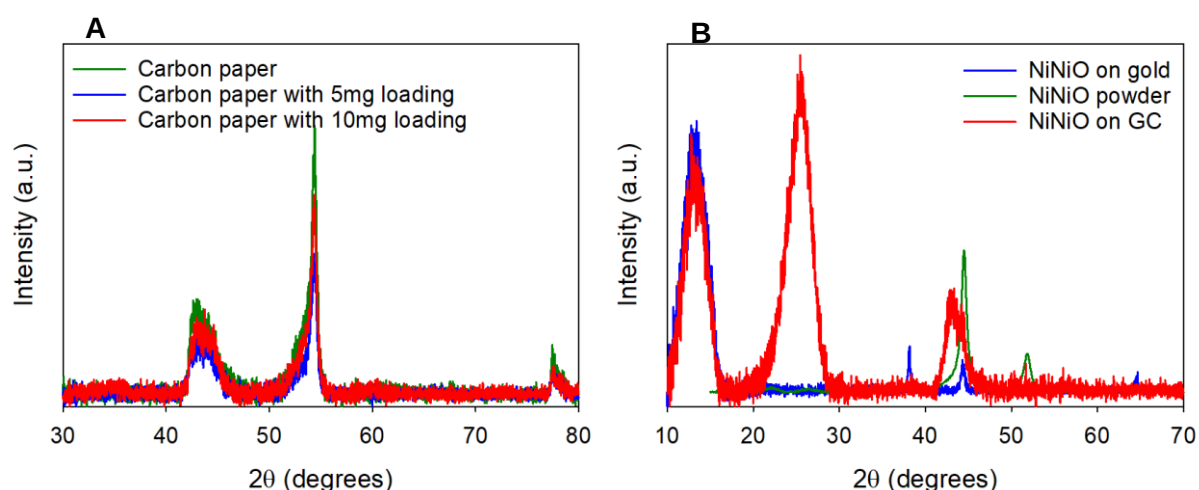


Figure 4-8: Grazing incidence diffraction patterns of (a) carbon paper and (b) gold substrates.

In Figure 4-8 (a), peaks at 43.2°, 54° and 78.5° are observed for the samples and the substrate. These peaks belong to the carbon paper substrate and no peaks for the samples are seen. NiNiO on the GC substrate displayed peaks at 2 θ values of 13.3°, 25.7° and 43.2°. NiNiO on the gold substrate displayed peaks at 13.3°, 38.1°, 44.3° and 64.5°. These peaks can be ascribed to the gold substrate. Gold of the fcc phase exhibits peaks that are at very similar positions as fcc NiO¹⁴⁸. The GIXRD results indicate that it is extremely difficult to investigate thin films of nanoparticles drop-casted on different substrates with XRD. Alternative physical analysis methods were therefore explored for post-mortem analyses. One such method is x-ray photoelectron spectroscopy (XPS).

4.2.3 X-ray photoelectron spectroscopy results of Ni-based nanoparticles after electrochemical cycling in pure and Fe-doped KOH

The Ni nanoparticles were subjected to XPS analysis after 30 CV cycles in KOH containing different concentrations of Fe. After the 30 CV cycles each electrode was gently rinsed with a few drops of DI water to ensure that no electrolyte stuck to the surface.

A survey spectrum of each sample was taken, which indicates all the different elements present in the sample. The survey scans were performed at low resolution as the main purpose of these scans are to obtain a general idea of which elements are present. To obtain information about the electronic states of specific elements present in the samples, regional scans were performed at higher resolution. The XPS results indicate how the electronic structure of Ni changes upon cycling in different concentrations of Fe. Furthermore, XPS is used to evaluate the amount of Fe present in the Ni electrocatalysts after cycling.

In Figure 4-9, the survey spectrum of one of the samples, colloidal NiO cycled in pure KOH, can be observed. Since the samples all contain more or less the same elements (present in different concentrations), only one survey spectrum is included as representative. From the survey spectrum in Figure 4-9, it is immediately clear that a large amount of fluorine (F), is present in the sample. F is present in large amounts in Nafion, which we use as binder to fix the nanoparticles on the surface of the GC electrode. F has a sharp F 1s peak of high intensity compared to other elements in the sample. Nafion is the commercial brand name used for a polymer consisting of a polytetrafluoroethylene (PTFE) backbone with perfluorinated-vinyl-polyether side-chains¹⁴⁹. It contains numerous C-F bonds for -CF, -CF₂ and -CF₃. Therefore, strong correlating XPS peaks are expected for carbon, which will have more positive binding energies than carbon bonded to carbon, oxygen or hydrogen due to the electronegativity of F. Throughout the XPS spectrum, higher binding energies are to be expected for any elements bonded to F.

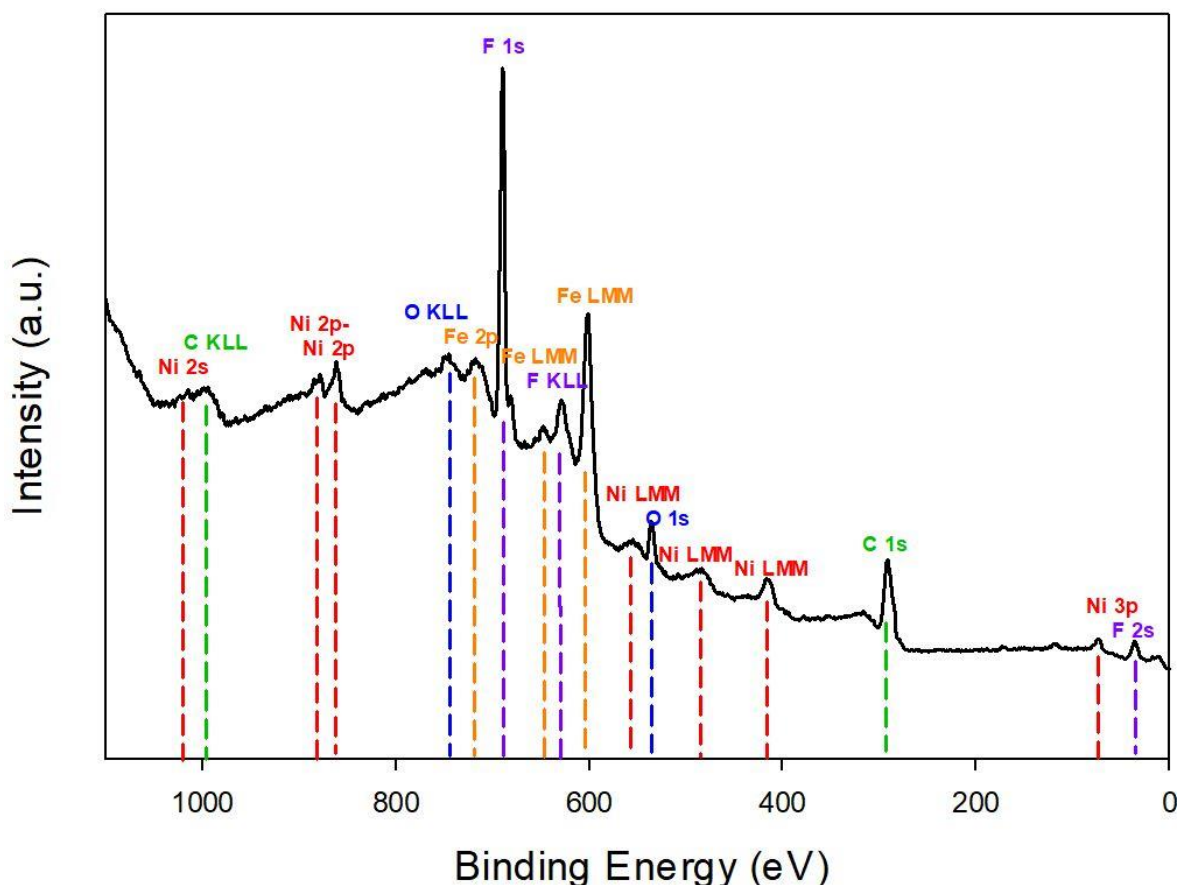


Figure 4-9: XPS survey spectrum for colloidal NiO cycled in pure KOH.

After obtaining a general idea of the elements present in the samples by performing a survey scan, high resolution scans were obtained for the Ni 2p region of all the samples. The spectral fits of these samples can be observed in Figure 4-10 to Figure 4-14.

Figure 4-10 shows the XPS spectra of colloidal Ni after 30 CV cycles in pure KOH, and KOH containing 0.007 ppm Fe, 0.3 ppm Fe, and 1 mM Fe. In this figure, the two main curves of Ni 2p XPS spectra, Ni 2p_{3/2} and Ni 2p_{1/2} can be seen. These curves arise due to spin-orbit coupling and can be fitted to yield component peaks. In addition, a satellite peak is located to the left of each Ni 2p curve. For colloidal Ni, the envelope Ni 2p_{3/2} and Ni 2p_{1/2} curves consist of two component peaks each. In XPS spectra, species with higher oxidation states have higher binding energies. Therefore, the constituent peak located at a lower binding energy is reduced with regards to the peak to its left. For the Ni 2p_{3/2} curve of colloidal Ni, constituent peaks are located at ~857 eV and 860 eV, varying with ± 1 eV, depending on the electrolytic Fe concentration. Using Table 2-4, these binding energy values are ascribed to Ni in the +2 and +3 oxidation states, respectively. Likewise, the constituent peaks of Ni 2p_{1/2} in the XPS spectra of colloidal Ni, located around 876 eV and 879 eV, point to higher Ni oxidation states.

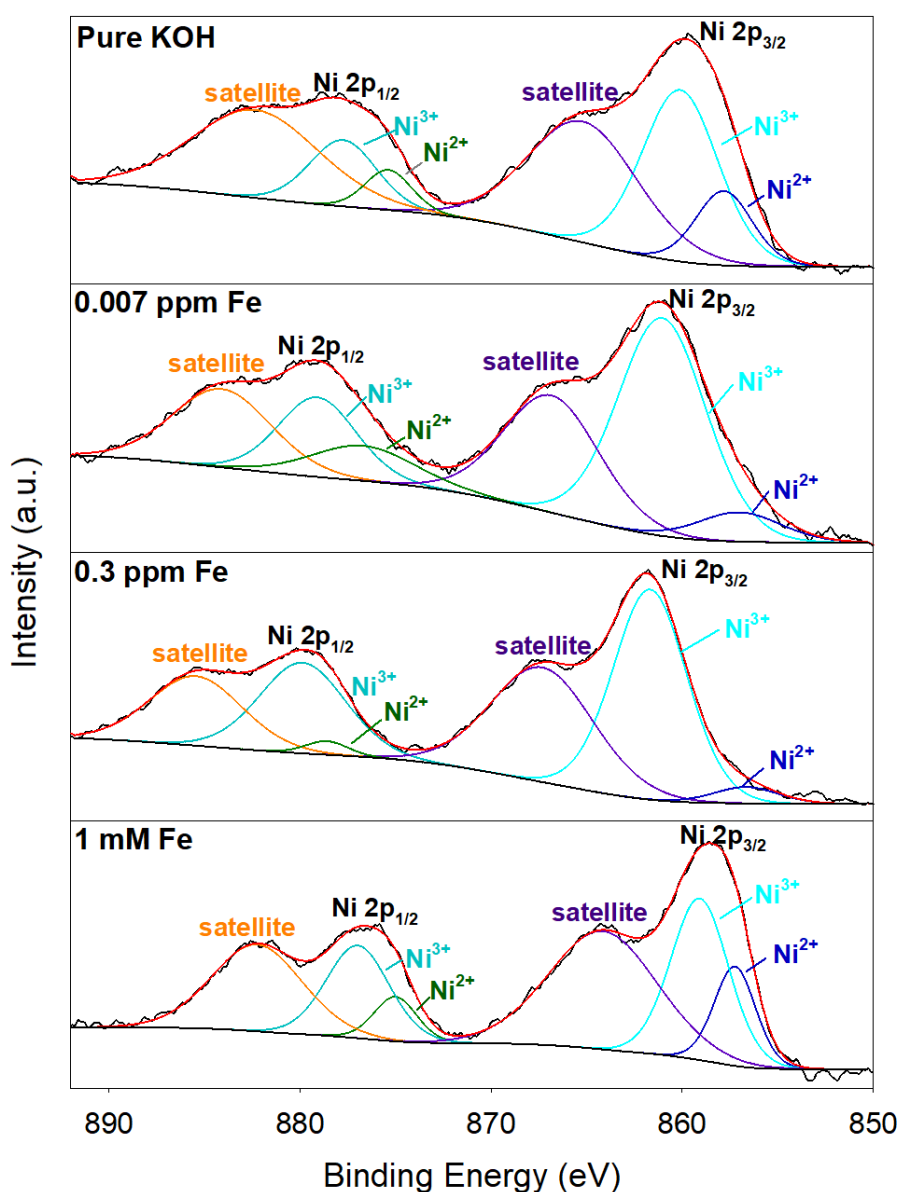


Figure 4-10: Ni 2p XPS spectra of colloidal Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

Furthermore, closer inspection of the Ni $2p_{3/2}$ curves in Figure 4-10, shows that the Ni^{2+} portion is the largest for the samples cycled in pure KOH and 1 mM Fe. This means that colloidal Ni samples cycled in 0.007 ppm Fe and 0.3 ppm Fe are more oxidized than samples cycled in pure KOH or 1 mM Fe. These results are similar to a recent study that used XPS to indicate that Ni samples cycled in KOH containing trace amounts of Fe are more oxidized than Ni samples cycled in KOH concentrated with Fe⁸. The results of the colloidal Ni sample thus indicate that increasing the Fe concentration from trace amounts to concentrated amounts prevents the oxidation of Ni films.

In Figure 4-11, the Ni 2p_{3/2} and Ni 2p_{1/2} curves can be seen in the XPS spectra of colloidal NiO cycled in KOH containing different concentrations of Fe.

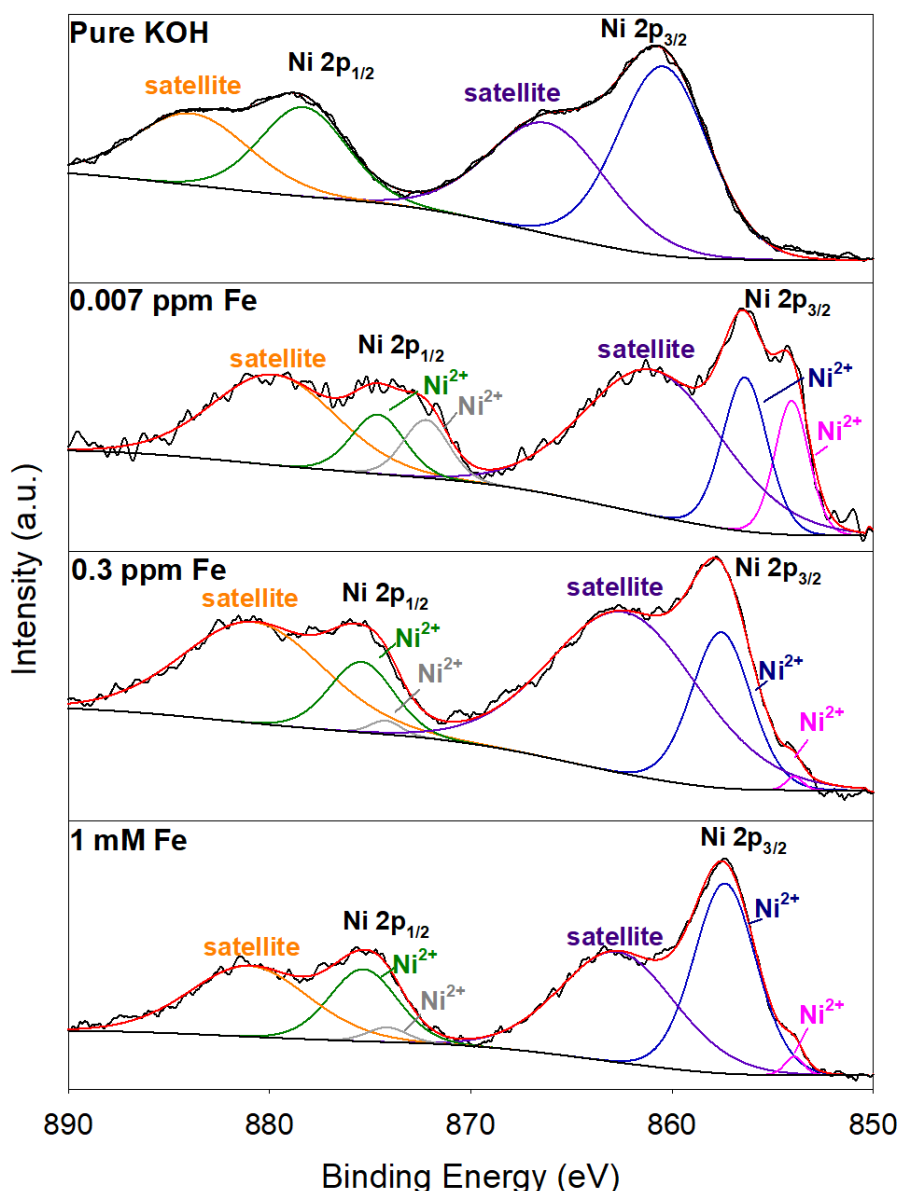


Figure 4-11: Ni 2p XPS spectra of colloidal NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

The Ni 2p_{3/2} and Ni 2p_{1/2} curves of the sample cycled in pure KOH do not contain more than one constituent peak and are found at 861.04 eV and 878.54 eV, respectively. These binding energy values are quite high and could possibly be ascribed to a +3 oxidation state of Ni. Alternatively, this high binding energy could be the influence of F. Furthermore, the Ni 2p_{3/2} and Ni 2p_{1/2} curves of the samples cycled in different Fe concentrations all contain two constituent peaks each. Ni 2p_{3/2} consists of peaks at 854 eV and 857 eV (± 1 eV), which can both be ascribed to Ni in the +2 oxidation state. The peak at lower binding energy corresponds to Ni-O

and the peak at higher binding energy corresponds to Ni-OH. In addition, it can be seen from Figure 4-11 that the colloidal NiO sample cycled in 0.007 ppm Fe has the highest contribution from Ni-O (Ni^{2+}), meaning that this sample is the least oxidized. This is different than what was observed for the colloidal Ni sample, where the samples cycled in pure KOH and 1 mM Fe were the least oxidized.

XPS was also performed on the nanoparticles prepared by reduction. The Ni 2p XPS spectra of Ni nanoparticles prepared by reduction can be observed in Figure 4-12. The figure shows the spectra of Ni nanoparticle electrocatalysts after they were cycled in pure KOH and KOH containing three different Fe concentrations.

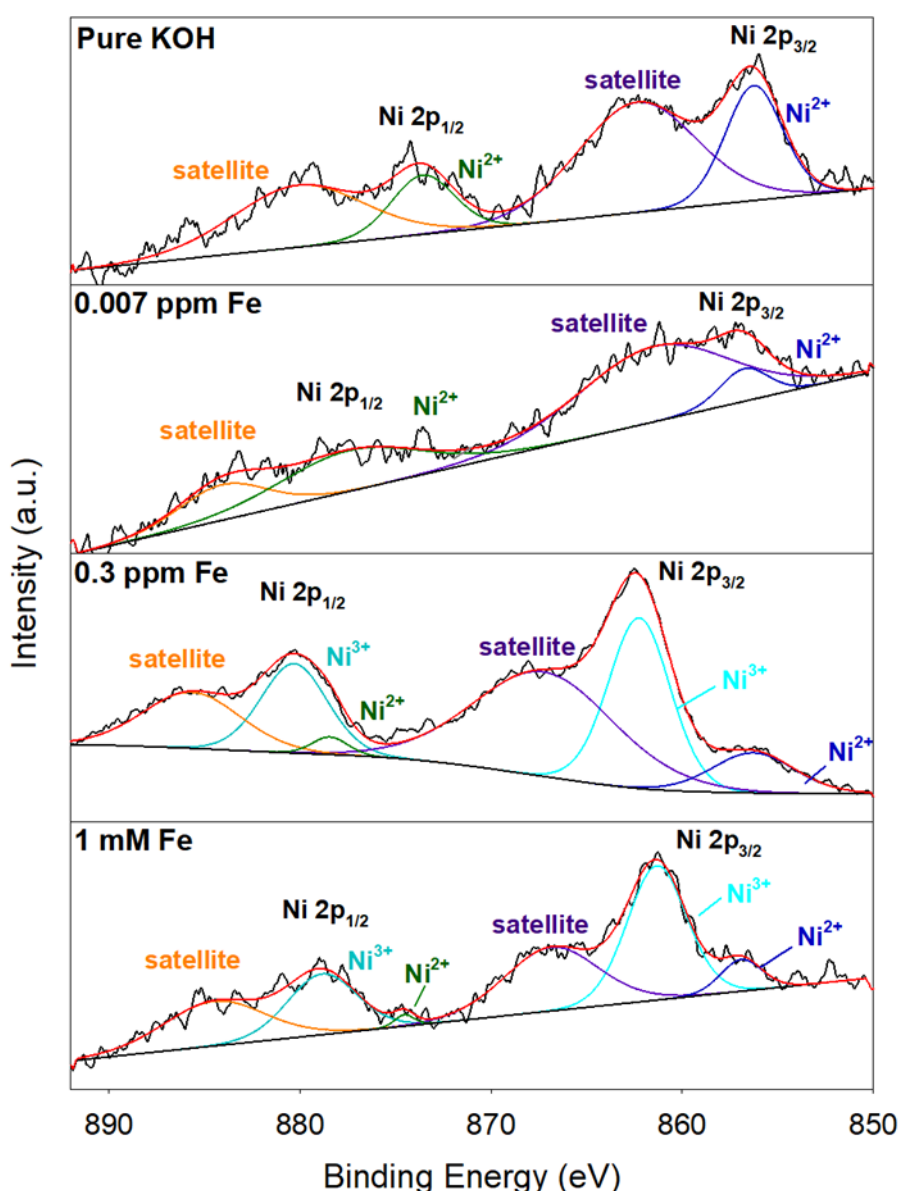


Figure 4-12: Ni 2p XPS spectra of Ni prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

In Figure 4-12, it can be seen that the Ni samples cycled in pure KOH and KOH containing 0.007 ppm Fe, contain only Ni^{2+} . This corresponds to an Ni-OH bond, from $\text{Ni}(\text{OH})_2$. The samples cycled in 0.3 ppm Fe and 1 mM Fe both show large contributions from Ni^{3+} , with smaller contributions from Ni^{2+} . Ni^{3+} peaks arise due to the presence of a more oxidised species, such as NiOOH . In addition, the spectra of Ni prepared by reduction are very noisy. This is because these particles did not disperse well in the electrocatalyst ink and do not cover the substrate surface completely. This causes low concentrations of Ni on the surface.

In Figure 4-13, the Ni 2p XPS spectra of NiO prepared by reduction can be seen.

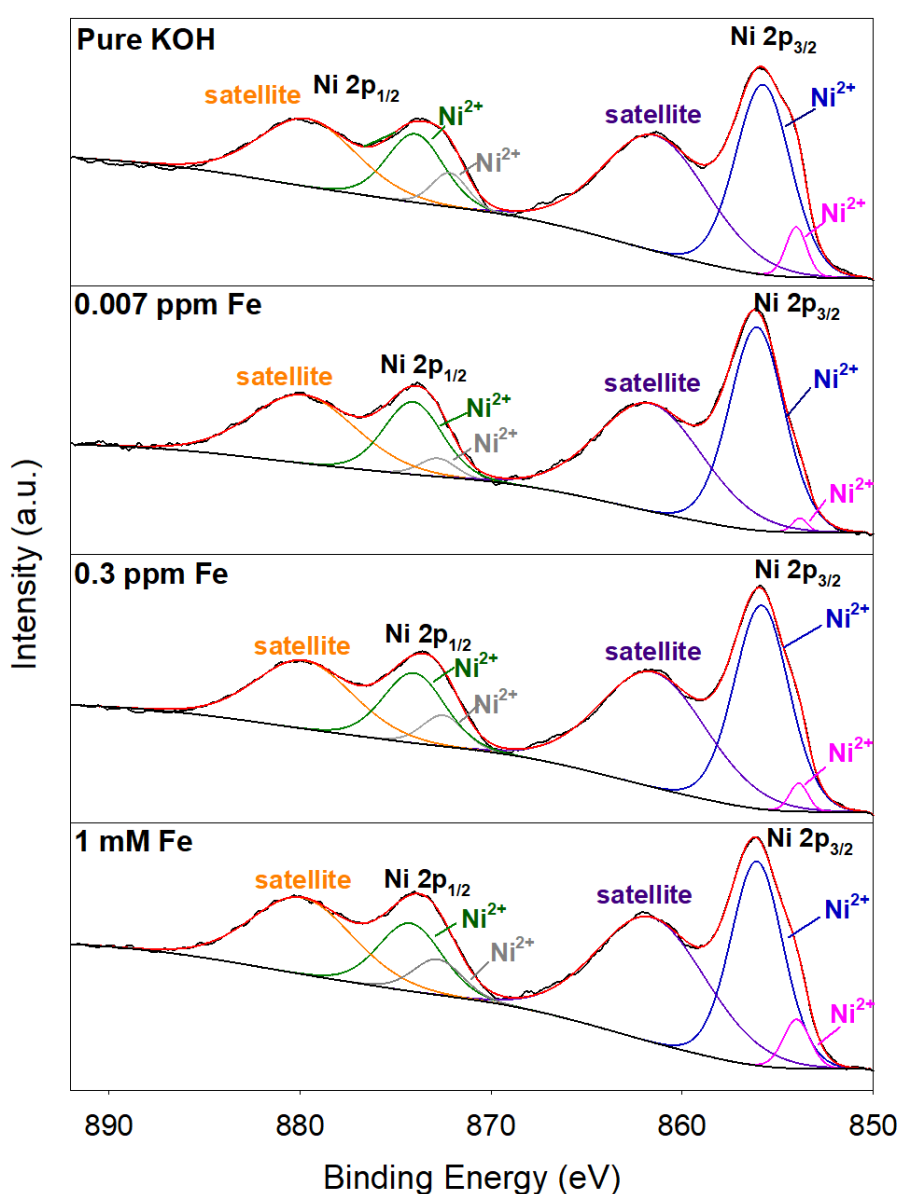


Figure 4-13: Ni 2p XPS spectra of NiO prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM KOH.

The XPS spectra in Figure 4-13 show that NiO samples prepared with the chemical reduction method, contain two Ni peaks representing the +2 oxidation state (Ni-O and Ni-OH) after cycling in pure KOH and KOH containing different concentrations of Fe. This is evidenced by the Ni 2p_{3/2} and Ni 2p_{1/2} curves in the XPS spectra. The Ni 2p_{3/2} curves of all the samples in Figure 4-13 consist of two peaks at ~854 eV and 856 eV, indicating +2 Ni oxidation states corresponding to Ni-O and Ni-OH, respectively. Furthermore, these samples follow the same trend as the colloidal Ni samples, in the sense that the samples cycled in pure KOH and 1 mM Fe are the least oxidized. Lastly, in Figure 4-14 The Ni 2p XPS spectra for NiNiO prepared by reduction can be seen. Only one oxidation state is present for NiNiO prepared by reduction.

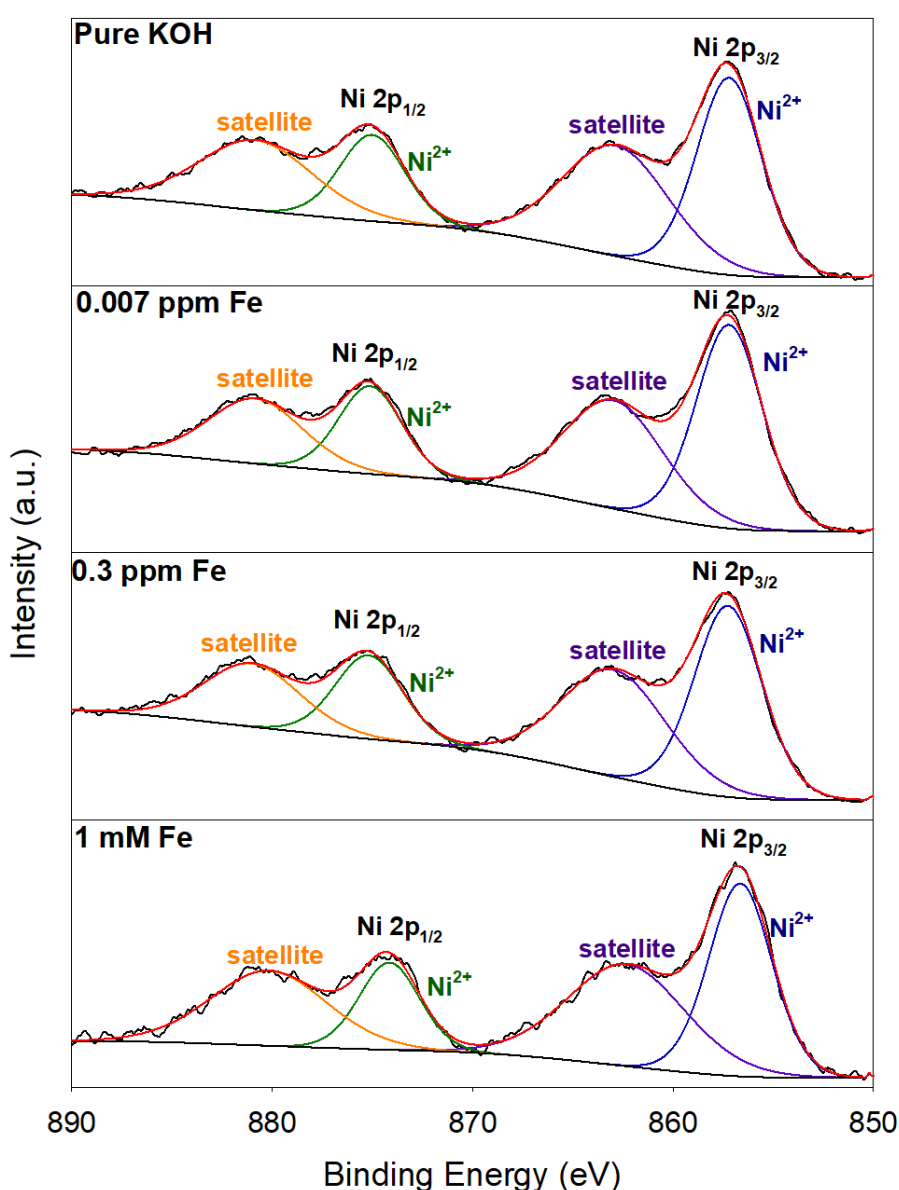


Figure 4-14: Ni 2p XPS spectra of NiNiO prepared by reduction after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

The exact binding energies at which the peaks occur in the Ni 2p XPS spectra of all the nanoparticle electrocatalysts are summarized in Table 4-1.

Table 4-1: Binding energies of the peaks in the Ni 2p XPS spectra of the Ni electrocatalysts cycled in pure and Fe containing KOH.

	Ni 2p _{3/2} (eV)	Ni 2p _{3/2} (eV)	Ni 2p _{1/2} (eV)	Ni 2p _{1/2} (eV)	Satellite (eV)	Satellite (eV)
Ni coll						
Pure KOH	857.82	860.03	875.38	877.60	865.59	882.85
0.007 ppm	857.27	861.05	876.72	878.89	866.72	884.63
0.3 ppm	856.68	861.67	878.60	878.89	867.31	885.25
1 mM	857.27	859.12	875.00	876.35	864.20	882.17
NiO coll						
Pure KOH		860.04		878.31	866.19	883.88
0.007 ppm	854.06	856.38	872.21	873.44	860.95	879.75
0.3 ppm	854.01	857.53	874.23	875.34	862.28	880.82
1 mM	853.92	857.37	874.15	875.09	862.72	880.90
Ni red						
Pure KOH	856.30		873.58		862.35	880.10
0.007 ppm	856.76		877.4		861.45	884.07
0.3 ppm	856.28	862.24	878.44	880.30	867.26	885.69
1 mM	856.90	861.33	874.55	878.85	866.86	884.50
NiO red						
Pure KOH	854.03	855.77	872.20	873.40	861.42	879.56
0.007 ppm	853.84	856.07	872.79	873.81	861.4	879.78
0.3 ppm	853.9	855.76	872.51	873.53	861.59	879.69
1 mM	854.01	856.08	872.78	873.68	861.2	879.83
NiNiO red						
Pure KOH	857.19		875.00		862.86	880.85
0.007 ppm	857.20		875.11		863.0	880.84
0.3 ppm	857.25		875.18		863.0	881.03
1 mM	856.64		874.15		862.34	880.18

By observing the binding energies of the Ni 2p_{3/2} peaks in the Ni 2p XPS spectra of the electrocatalysts, the oxidation states of the catalysts can be determined. The two NiO samples (colloidal and reduction) contain two Ni²⁺ species each, corresponding to Ni in NiO and Ni(OH)₂, respectively. Colloidal Ni and Ni prepared by reduction consists of Ni in the +2 and +3 oxidation states after cycling. NiNiO prepared by reduction contains only Ni²⁺ in the form of Ni(OH)₂. Therefore, the NiO nanoparticles are less oxidized after cycling than Ni nanoparticles. These results are in good agreement with a recent study showing that Ni is more easily oxidized than NiO⁷¹.

Furthermore, it is of interest to quantify the amount of Fe relative to Ni in the nanoparticle electrocatalysts cycled in Fe containing electrolyte. Normally this is done by using the Ni 2p and Fe 2p peaks in the XPS spectrum. However, the F 1s peak from Nafion obscures the Fe 2p peak for all nanoparticle samples in this study. The plasmons of the intense F 1s peak dominate over the Fe 2p region (Figure 4-9). Several survey spectra of Nafion found in literature confirm that it has a peak at the same position as Fe 2p^{150,151,152}. This problem can be resolved to a certain extent by using The Ni 2p and Fe 3p peaks for quantification instead. Nardi *et al.* used Ni 3p and Fe 3p peaks to determine the ratio of Fe in their samples⁸. This is less accurate than using the 2p regions. In addition, the survey spectra had to be used for this analysis since high resolution regional spectra were not obtained. This can also influence the accuracy of the results. However, it is still efficient in obtaining relative amounts of Fe after samples were cycled in different concentrations of Fe. Three spots on the surface of each electrocatalyst were analysed to indicate the homogeneity of the surface. The survey spectra of three spots on each surface were thus used to quantify the Ni 3p and Fe 3p regions and the results can be observed in Table 4-2. Table 4-2 shows that Fe is not homogeneously distributed on the surfaces of these electrocatalysts. Three spots on the same electrocatalyst surface contain varying concentrations of Fe.

Table 4-2: Relative percentages of Fe in the electrocatalyst samples as determined from XPS spectra of Ni 3p and Fe 3p regions.

	Pure KOH (% Fe)	0.007 ppm Fe (% Fe)	0.3 ppm Fe (% Fe)	1 mM Fe (% Fe)
Ni coll	0	1.9	1.9	0
	0	0	0	9.0
	0	3.0	11.8	0
NiO coll	0	7.6	8.8	21.0
	0	0	8.1	17.9
	0	9.4	9.1	18.6
Ni red	-	-	-	-
	-	-	-	-
	-	-	-	-
NiO red	6.4	5.5	4.8	5.5
	5.2	7.6	6.7	5.7
	3.5	4.9	2.7	3
NiNiO red	11.1	7.0	10.3	10.9
	6.3	6.5	5.5	0
	5.1	5.1	7.1	5.0

In addition, the peaks of Ni prepared by reduction were too weak to be detected in the survey spectrum and therefore no quantification could be performed. The percentage of Fe detected for the colloidal Ni and NiO samples cycled in pure KOH is zero. This could also be because the Fe at these spots in the samples were below the detection limit of the quantification via Fe 3p and Ni 3p regions.

4.2.4 Cyclic voltammetry for preconditioning and electrocatalytic activity measurements before and after the addition of electrolytic Fe

CVs of each electrocatalyst were recorded in pure KOH and Fe-containing KOH (0.007 ppm, 0.3 ppm and 1 mM Fe). Each sample was cycled 30 times to precondition the electrocatalyst and provide time for any Fe incorporation. A scan rate of 20 mV s^{-1} was used for all CVs.

4.2.4.1 CVs for colloidal Ni prepared by a tailored synthesis

Figure 4-15 displays the initial 30 CV cycles of colloidal Ni in each electrolyte composition.

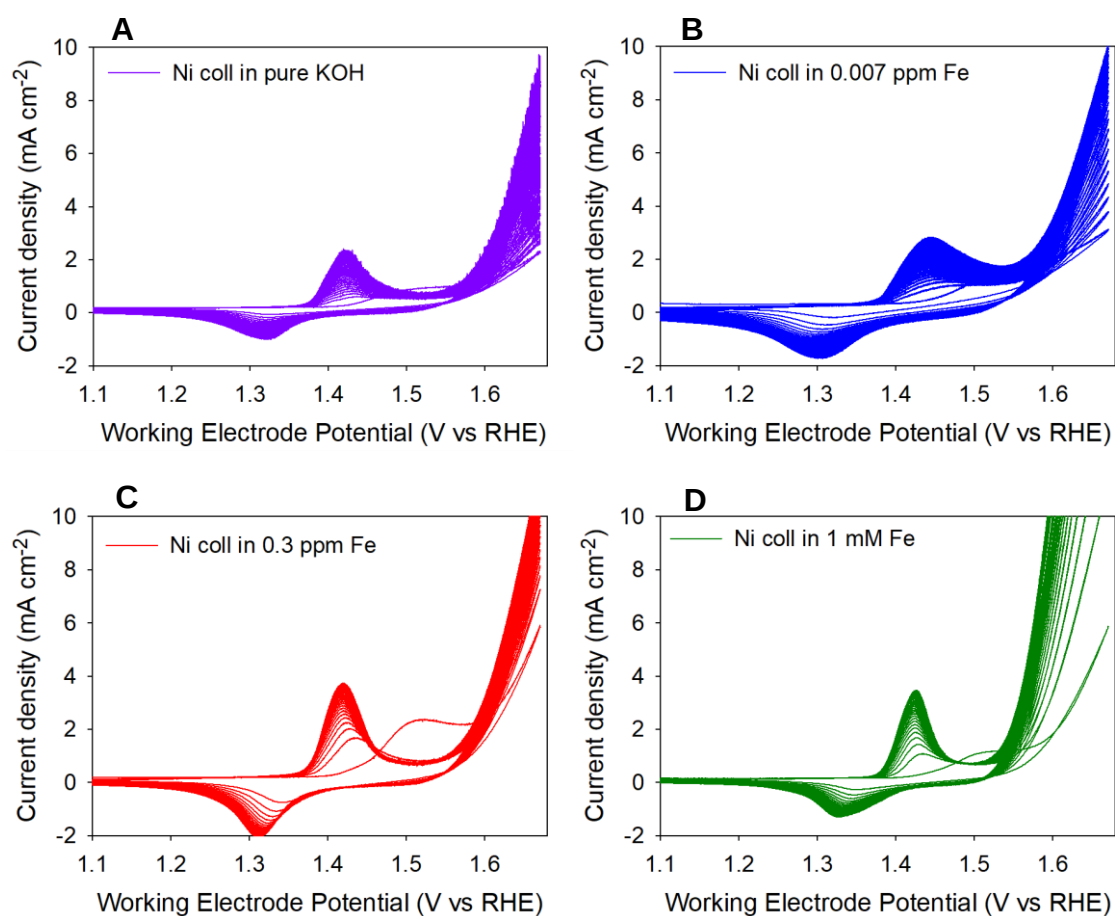


Figure 4-15: 30 CV cycles of colloidal Ni performed at 20 mV s^{-1} in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

After 30 CV cycles at 20 mV s^{-1} , the electrocatalyst starts to stabilise, as indicated by the shape of the CV that does not change anymore. In Figure 4-15 it can be seen that 30 CV cycles is necessary to stabilise the electrocatalysts, since the OER current keeps increasing after each consecutive cycle until more or less the 30th cycle. In order to study the redox features, the scale of the CV graphs is altered in Figure 4-16, and cycles 1, 5, 10, 15, and 30 are shown.

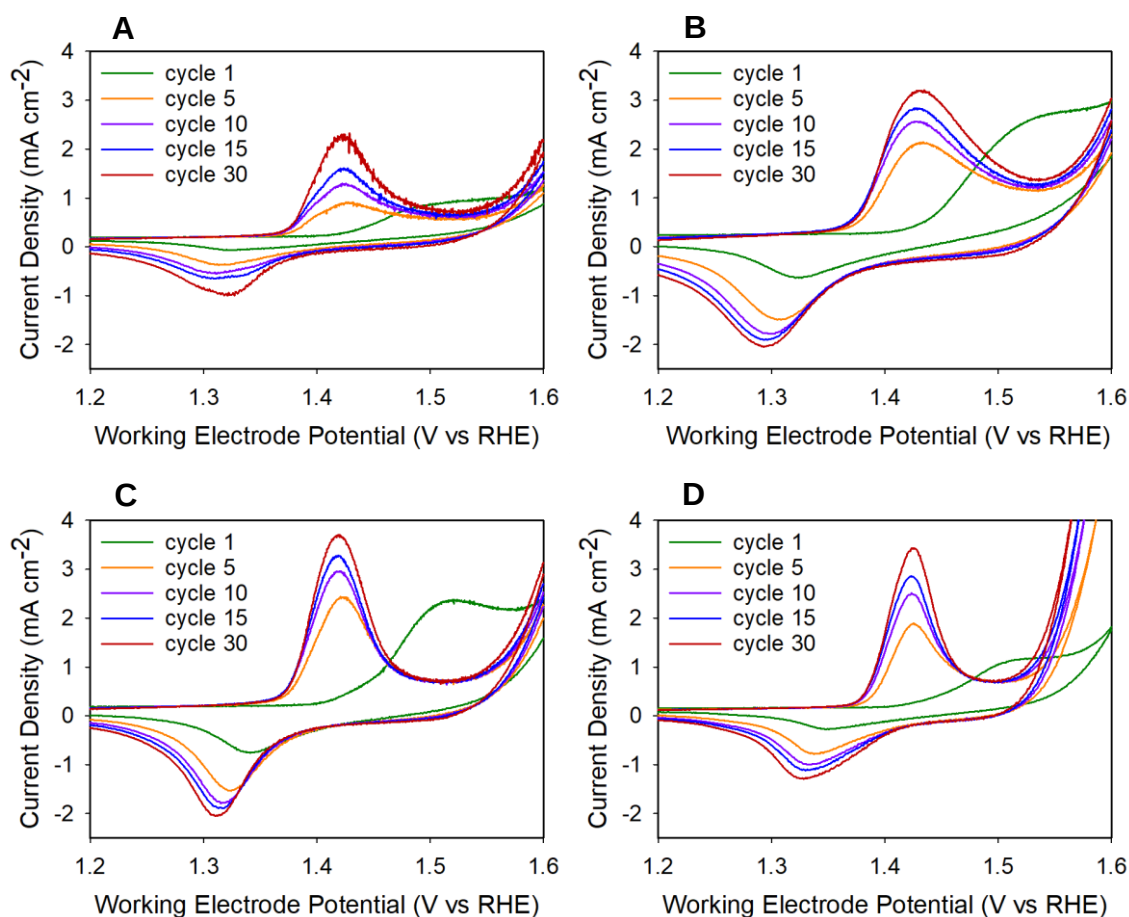


Figure 4-16: Redox features of colloidal Ni performed at 20 mV s^{-1} in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

The first CV cycle of all four samples has a noticeably different shape with an oxidation peak occurring at more positive potentials compared the rest of the cycles. It is clear that the first CV is not stable yet, as it changes significantly after only five cycles. An oxidation wave at $\sim 1.42 \text{ V}$ vs RHE (1.45 V vs RHE in 0.007 ppm) is observed for colloidal Ni samples after 30 CV cycles. This wave can be ascribed to the oxidation of Ni. More specifically, Ni(OH)_2 is oxidized to NiOOH , which is said to be the active phase in OER²⁶. A reduction wave is observed at $\sim 1.32 \text{ V}$ vs RHE (after cycling). This wave indicates the reduction of NiOOH back to Ni(OH)_2 . The oxidation wave is visibly larger than the reduction wave, indicating that not all of the NiOOH species are reduced back to the original oxidation state. This is characteristic of Ni-based electrocatalysts and is

indicative of the formation of layers of NiOOH and Ni(OH)₂¹⁵³. During the anodic sweep, NiOOH is formed, and a top layer of the electrocatalyst surface is reduced back to Ni(OH)₂ during the cathodic sweep. This redox process is therefore not perfectly reversible. The oxidation and reduction waves of the CV also grow upon each consecutive cycle (as the layers of NiOOH and Ni(OH)₂ grow) and stabilises after 30 cycles. The growth of the oxidation wave indicates that more electroactive species (NiOOH) is formed upon each consecutive cycle.

Figure 4-17 overlays the 30th cycle of colloidal Ni in each electrolyte composition. This figure shows the relative sizes of each oxidation wave. In addition, this figure allows the clear observation of the relative OER activity of colloidal Ni in different concentrations of Fe.

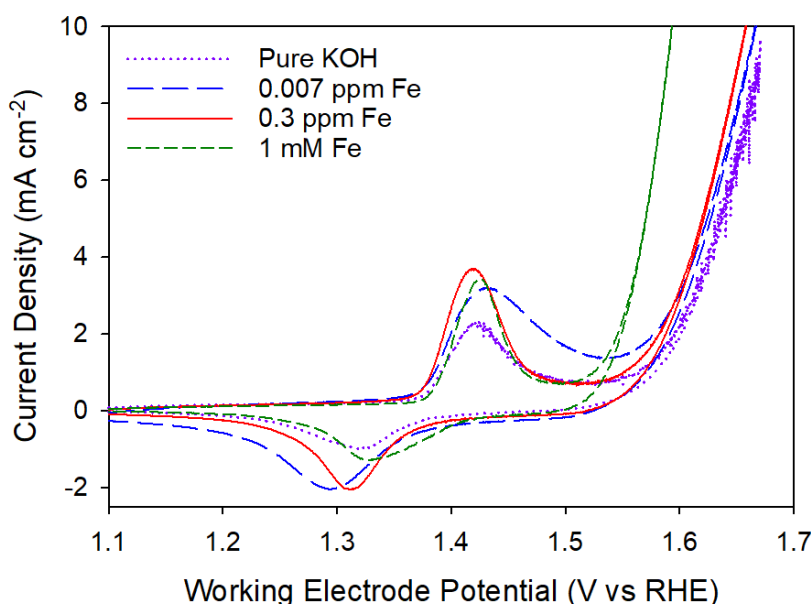


Figure 4-17: 30th CV cycle of colloidal Ni catalyst in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).

The position of the oxidation peak does not shift much after cycling the samples in KOH containing different concentrations of Fe. Previous studies report that the oxidation wave shifts anodically when more Fe is incorporated into the electrocatalyst^{9,5}. In addition, the oxidation peak is larger for the sample cycled in 0.3 ppm than the one cycled in pure KOH. The wave of the sample cycled in KOH containing 1 mM Fe is smaller than the one cycled in KOH containing 0.3 ppm Fe. Previous studies reported that the oxidation wave becomes smaller when increased amounts of Fe is present in Ni electrocatalysts^{9,60,12,8}. This trend is not observed in Figure 4-17 for increasing electrolytic Fe concentrations. A small anodic shift can also be observed from colloidal Ni in 0.3 ppm Fe to colloidal Ni in 1 mM Fe. E_{pa} in 1 mM Fe is 1.426 V vs RHE whereas E_{pa} in 0.3 ppm is 1.418 V vs RHE. E_{pc} in 1 mM is 1.328 V vs RHE where E_{pc} in 0.3 ppm is 1.312 V vs RHE. This

means that ΔE_p is smaller for 1 mM (0.098 V) than for 0.3 ppm (0.106 V), which could indicate faster charge and ion transfer in 1 mM Fe⁸¹.

The current density of colloidal Ni cycled in 1 mM Fe is much higher than that of the other samples in the same potential range. The overpotential at a current density of 10 mA cm⁻² can be used to compare the OER activities of different samples where lower overpotentials point to better OER activity. In pure KOH, the current density does not reach a value of 10 mA cm⁻² in the potential range used, indicating poor OER activity. In 0.007 ppm Fe, the overpotential is 439.50 mV and in 0.3 ppm Fe it is 426.98 mV, at 10 mA cm⁻². In 1 mM Fe, the overpotential decreases to 361.7 mV at 10 mA cm⁻², demonstrating a significant increase in OER activity upon doping the electrolyte with 1 mM Fe.

4.2.4.2 CVs for colloidal NiO prepared by a tailored synthesis

Figure 4-18 displays the initial 30 CV cycles for colloidal NiO in each electrolyte.

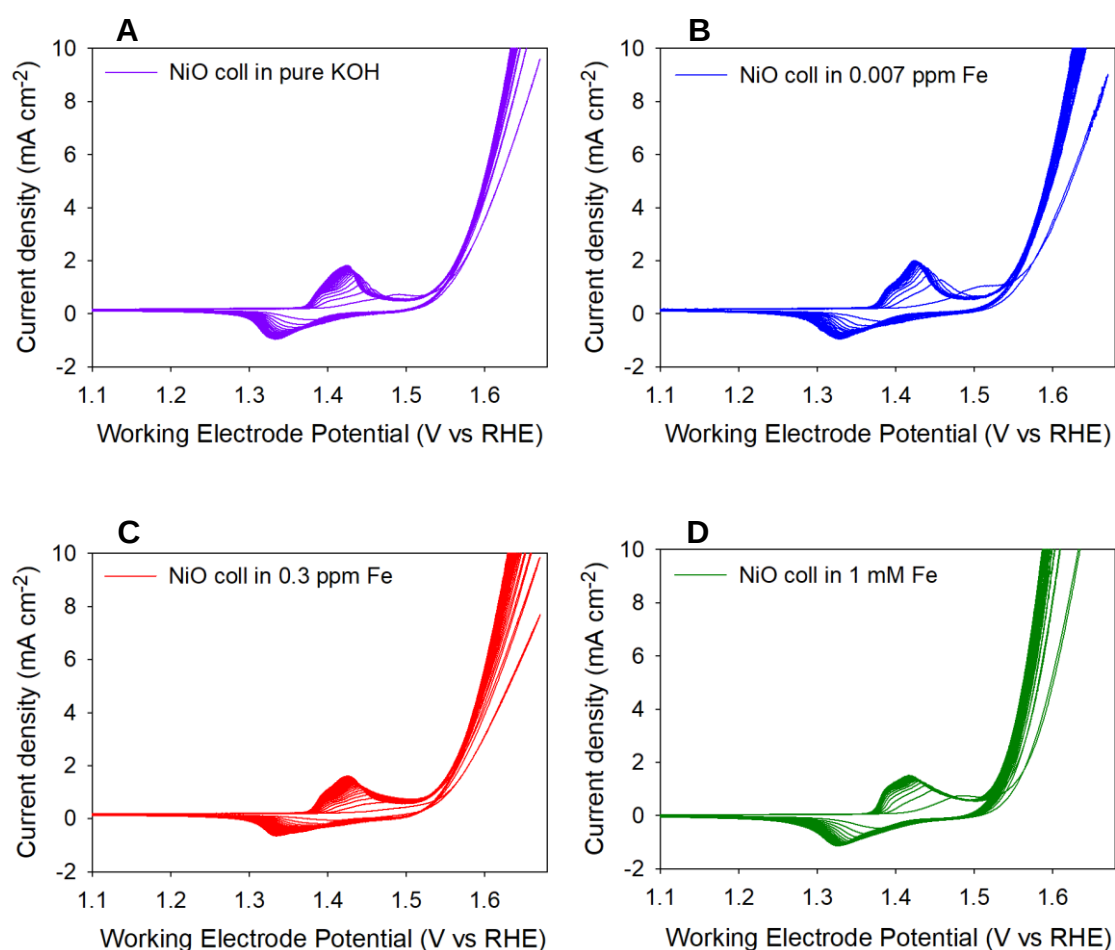


Figure 4-18: 30 CV cycles of colloidal NiO performed at 20 mV s⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

From Figure 4-18, it is visible that less than 30 cycles are required to obtain a stable activity for colloidal NiO. For colloidal NiO in all of the electrolytes, there is a large initial increase in activity. After the initial increase, the activity keeps increasing after a few more cycles, and then stabilises. To observe the redox features of this electrocatalyst in different Fe concentrations, Figure 4-19 has been constructed. In this figure, CV cycles 1,5,10,15 and 30 can be observed.

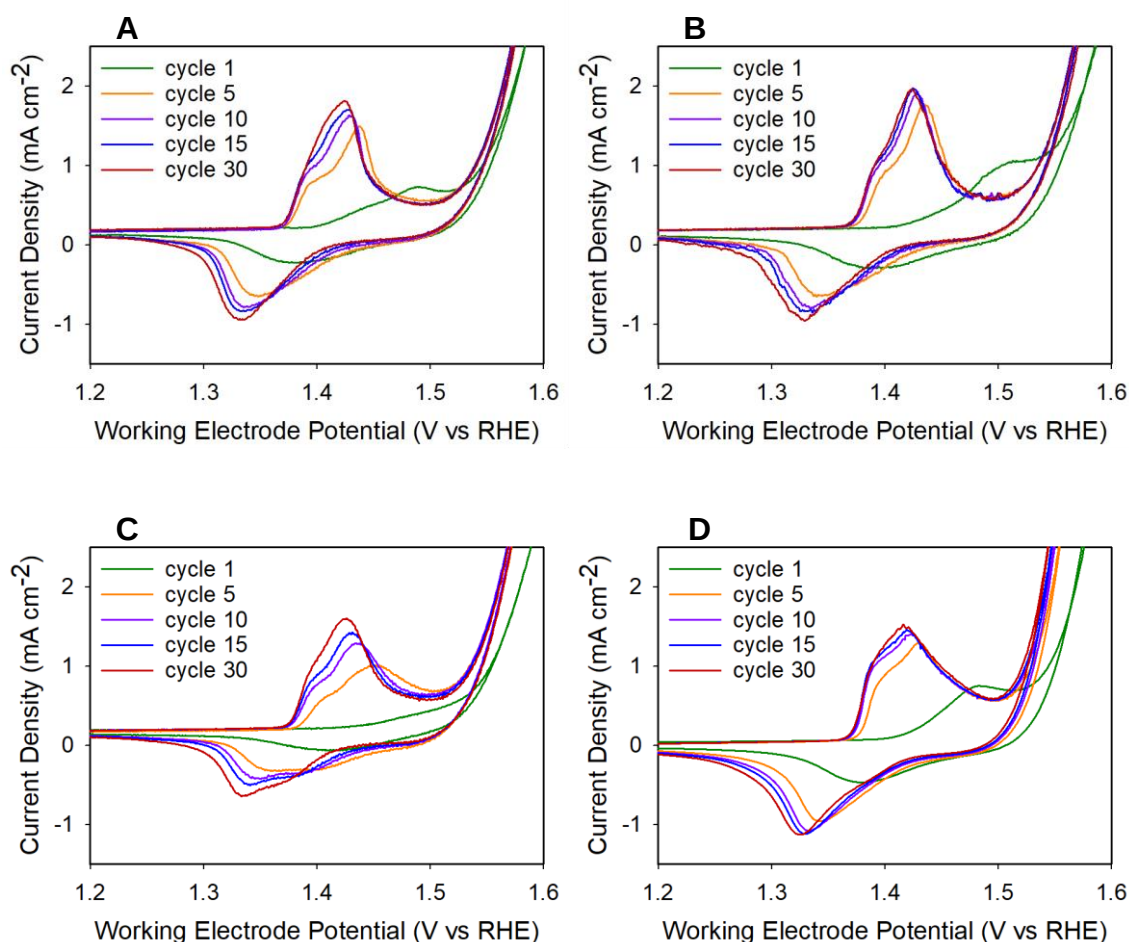


Figure 4-19: The redox features of colloidal NiO in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Figure 4-19 shows that the first cycle for colloidal NiO in each of the electrolyte compositions differs significantly in size and position from the rest of the cycles. It is clear from this figure that the first cycle is not stable yet, and that the redox features change significantly after just five cycles. The redox features continue to grow and change until 30 CV cycles. When the electrocatalyst has been cycled 30 times in each electrolyte, a stable state is reached. For colloidal NiO, two oxidation peaks are observed. The two oxidation peaks are present at similar potentials so that these peaks do not separate completely. A smaller peak is visible to the left of the main oxidation peak and becomes less pronounced as the electrocatalyst is cycled. The two oxidation peaks of colloidal NiO are seen at ~ 1.39 and 1.42 V vs RHE (after 30 cycles) in each

of the electrolyte compositions. Two reduction peaks are observed for the sample cycled in 0.3 ppm Fe at ~ 1.33 and 137 V vs RHE (after 30 cycles). For the other samples, only one reduction peak is present at 1.33 V vs RHE). The oxidation and reduction waves of colloidal NiO are visibly smaller than those of colloidal Ni. In literature, two oxidation peaks has been referred to as an anodic peak doublet¹⁵³. Similarly, two reduction peaks is called a cathodic peak doublet¹⁵³. Two oxidation features could mean that both α -Ni(OH)₂ and β -Ni(OH)₂ are present on the electrocatalyst surface. The peak on the right could be ascribed to β -Ni(OH)₂, since the oxidation thereof occurs at higher potentials²⁶. With cycling, the amount of α -Ni(OH)₂ therefore decreases.

Figure 4-20 displays the 30th cycle of colloidal NiO in each electrolytes containing different concentrations of Fe.

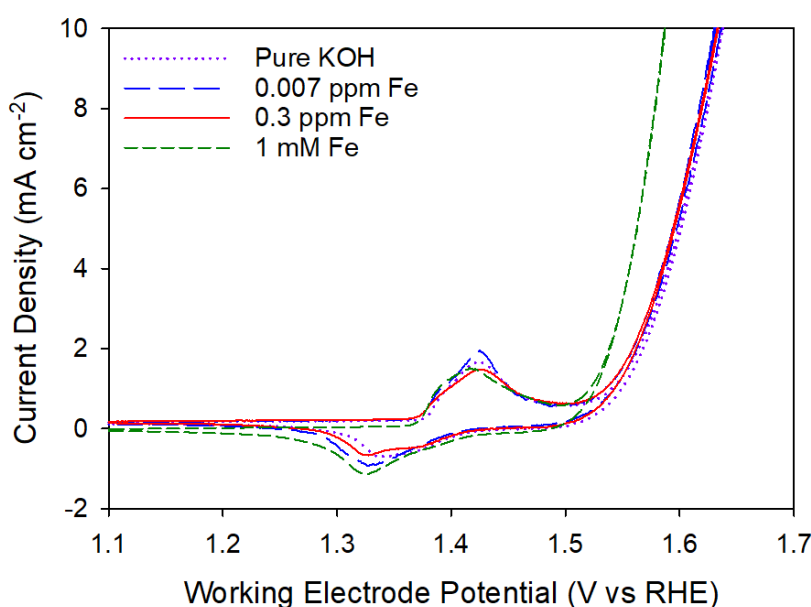


Figure 4-20: 30th CV cycle of colloidal NiO catalyst in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).

In Figure 4-20, where the oxidation waves of the 30th CV cycle of each sample is overlaid, it can be seen that the potential at which these waves occur, as well as the size of the waves, does not differ significantly with increasing electrolytic Fe concentration. In addition, it can clearly be seen that the current density of colloidal NiO cycled in 1 mM Fe is much higher than the current densities of colloidal NiO cycled in the other electrolytes, at the same applied potentials. The overpotentials at 10 mA cm^{-2} are 405.11 mV , 401.12 mV and 402.12 mV in pure KOH, 0.007 ppm Fe and 0.3 ppm Fe, respectively. The overpotential decreases to 356.12 mV at 10 mA cm^{-2} in 1 mM Fe.

4.2.4.3 CVs for Ni prepared by the chemical reduction synthesis method

Ni nanoparticles have been prepared using the chemical reduction synthesis method and the initial 30 CV cycles of this electrocatalyst in pure KOH and Fe containing KOH can be observed in Figure 4-21.

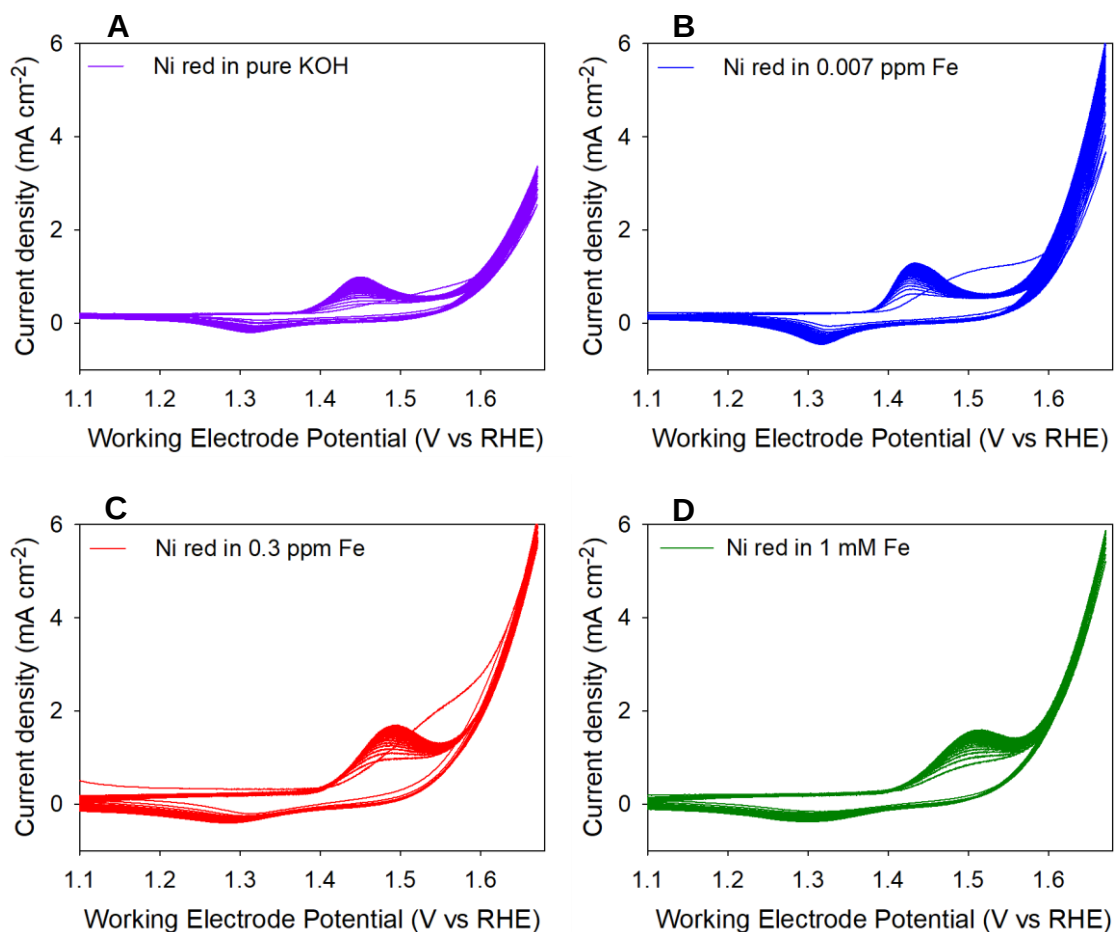


Figure 4-21: 30 CV cycles of Ni prepared by reduction performed at 20 mV s⁻¹ in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Immediately it is clear that the current densities for Ni prepared by reduction are much lower than for the previous two electrocatalyst samples. Even upon cycling in 1 mM Fe, the current density does not increase. Furthermore, upon potential cycling, the current density does not increase much from the first cycle to the 30th cycle. This could indicate that less Fe is incorporating into the structure compared to the other electrocatalyst samples studied, explaining the poor OER activity. In Figure 4-21 it can be better observed how the redox features change with an increasing number of cycles.

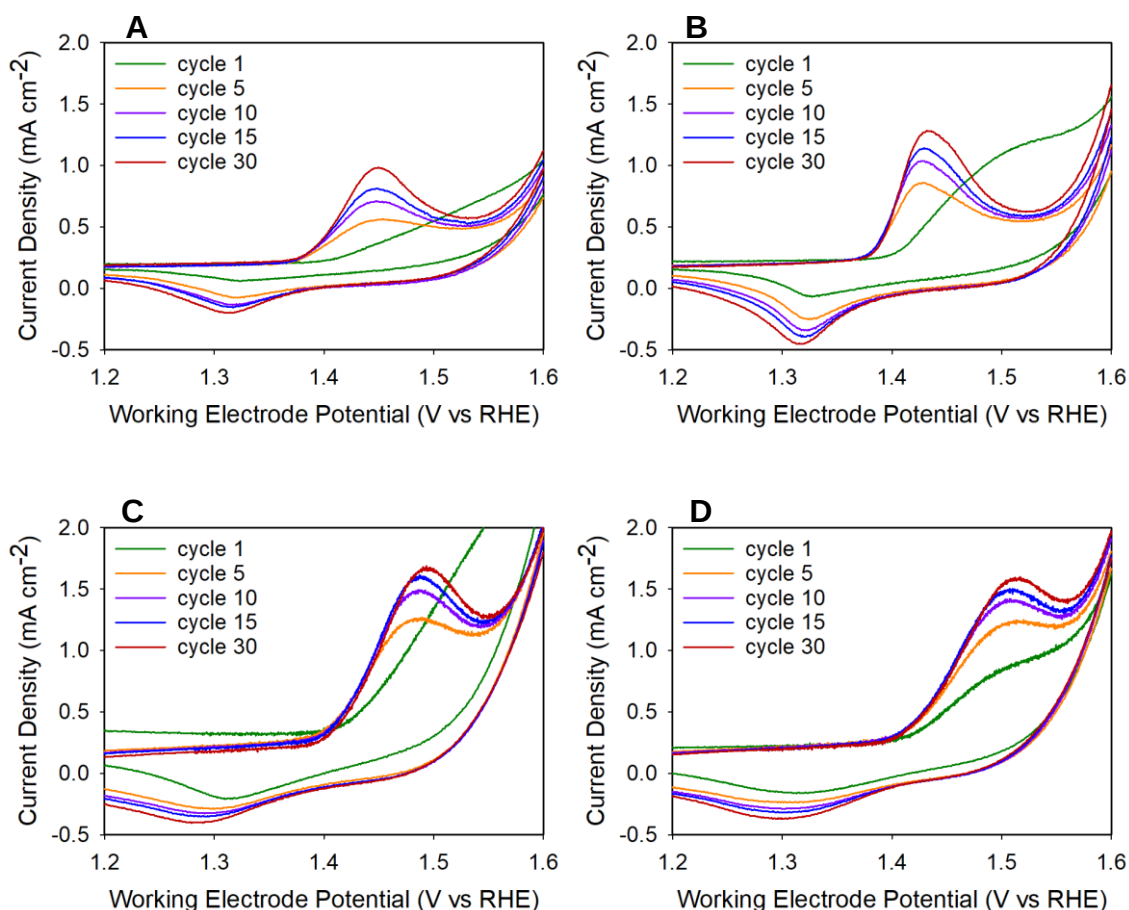


Figure 4-22: The redox features of Ni prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Figure 4-22 shows that the oxidation and reduction waves grow with cycling, and that the first cycle differs the most from the rest. In pure KOH, E_{pa} is 1.45 V vs RHE and E_{pc} is 1.31 V vs RHE, and in 0.007 ppm E_{pa} is 1.43 V vs RHE and E_{pc} is 1.31 V vs RHE. In 0.3 ppm E_{pa} is 1.49 V vs RHE and E_{pc} is 1.28 V vs RHE. Lastly, in 1 mM, E_{pa} is 1.51 V vs RHE and E_{pc} is 1.30 V vs RHE. Therefore, the oxidation peak shifts to more positive potentials as more Fe is added to the electrolyte. This can be better observed in Figure 4-23.

The 30th cycle of Ni prepared by reduction in each electrolyte composition can be observed in Figure 4-23. From this figure it is clear that the increase in current density is limited when the Ni electrocatalyst prepared by chemical reduction is cycled in Fe containing electrolyte.

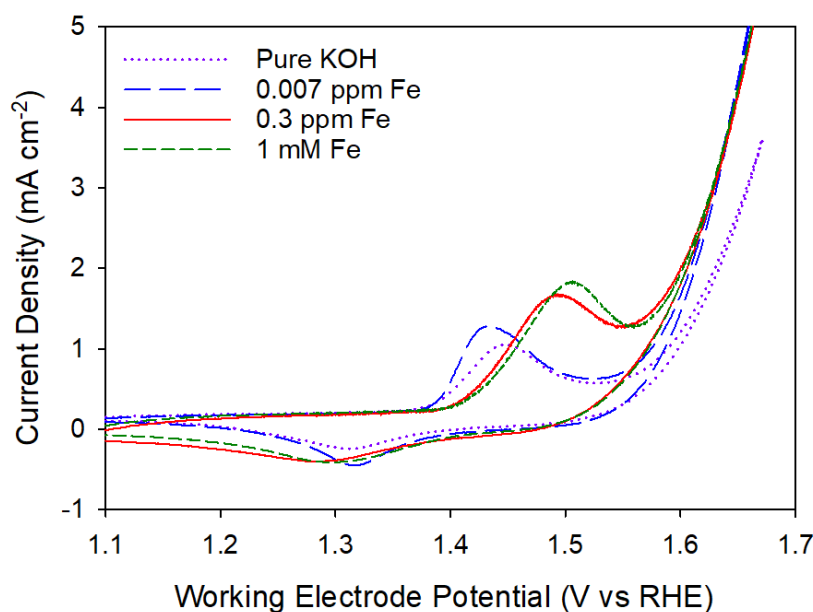


Figure 4-23: 30th CV cycle of the Ni catalyst prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).

The oxidation peaks are not smaller for the samples cycled in increased amounts of Fe. Furthermore, there is a small increase in current density from pure KOH to samples containing Fe, but no further increase in current density when the Fe concentration is increased further than 0.007 ppm. Increased Fe concentrations in the electrolyte has a significant effect on the redox waves, but not the OER activity. Ni prepared by reduction did not reach a current density of 10 mA cm⁻² in any of the electrolytes. In addition, it is important to note that these Ni nanoparticles did not disperse well in the electrocatalyst ink. This also contributes to the poor electrocatalytic activity thereof. Consequently, these particles are not a good indication of how Fe influences the structure and activity of Ni electrocatalysts. Therefore, these particles were only investigated by XPS, CV and in-situ Raman spectroscopy and no further analyses were performed on them.

4.2.4.4 CVs for NiO prepared by the chemical reduction synthesis method

Figure 4-24 displays the initial 30 CVs of NiO prepared by the reduction method.

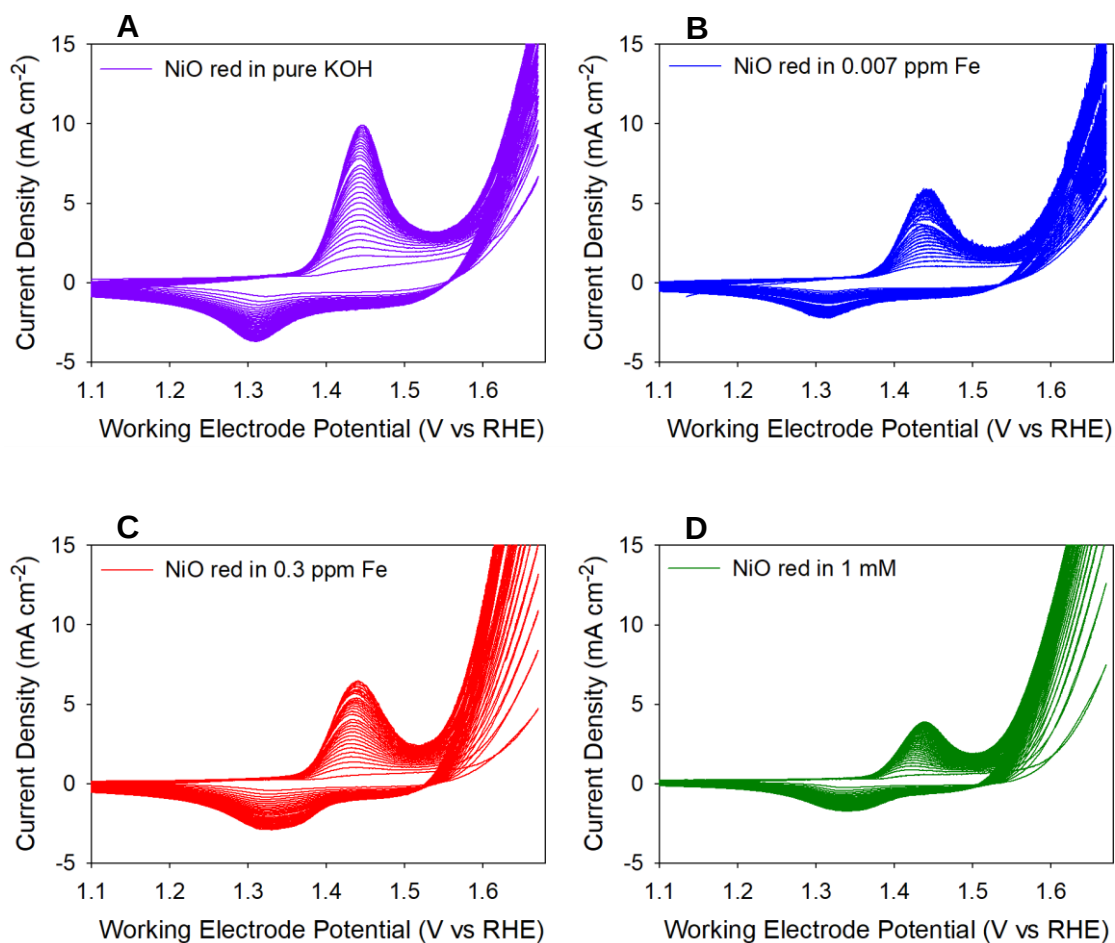


Figure 4-24: 30 CV cycles of NiO prepared by reduction performed at 20 mV s^{-1} in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

In Figure 4-24, it can clearly be seen that there is a large increase in OER current upon potential cycling for all NiO nanoparticles prepared by reduction. At the same potential (1.65 V), the current density increases with $\sim 12 \text{ mA cm}^{-2}$ from cycle one to cycle 30 for NiO prepared by reduction cycled in pure KOH and KOH containing 0.007 ppm Fe. At this potential in KOH containing 0.3 ppm Fe, a current density increase of 29 mA cm^{-2} is observed from cycle 1 to cycle 30. In 1 mM Fe, this increase is 20 mA cm^{-2} . In addition, the redox waves also grow significantly upon potential cycling, indicating that increasingly more active species form upon potential cycling. The redox waves can be better seen in Figure 4-25.

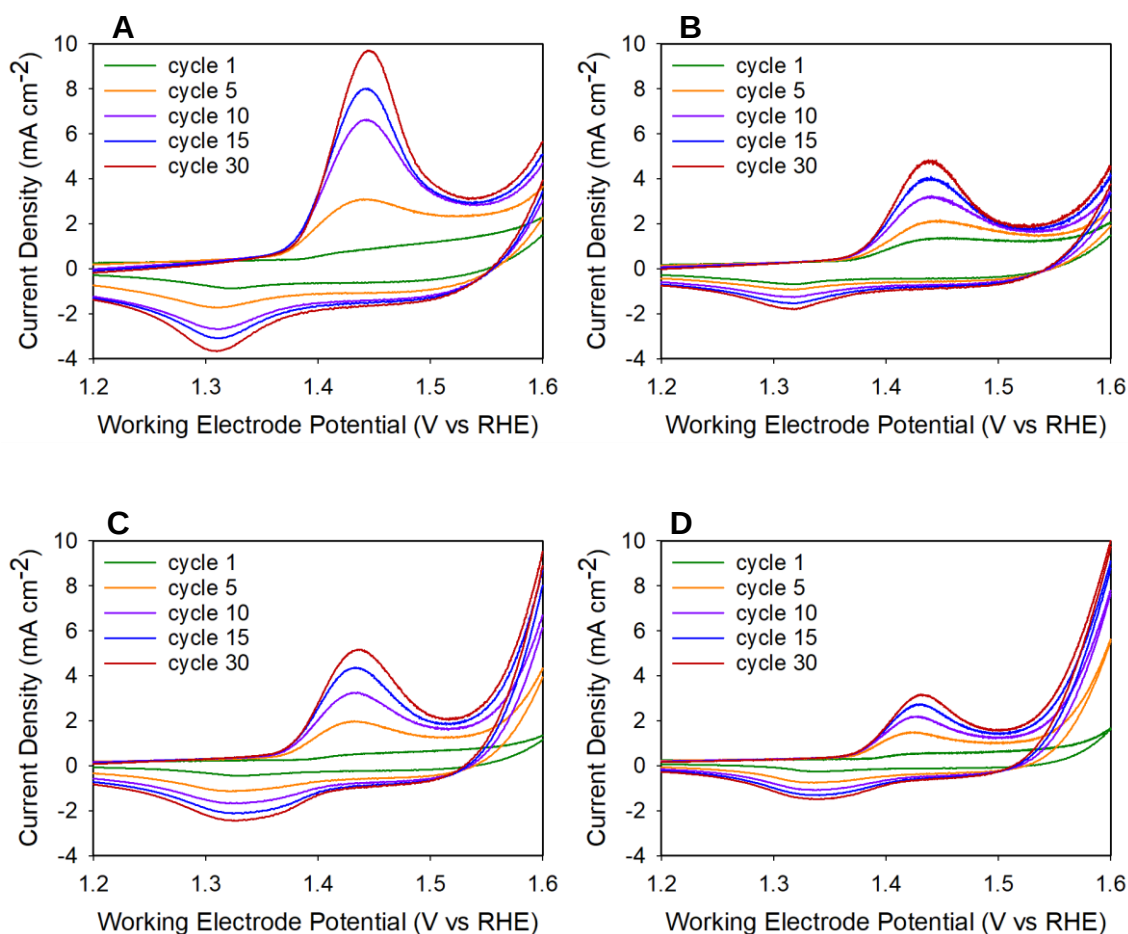


Figure 4-25: The redox features of NiO prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Again, it is clear that the redox features continue growing and stabilising until 30 CV cycles is completed. The first CV cycle is not stable at all, with small redox features occurring at different positions than the rest of the cycles. The oxidation wave for the NiO sample cycled in pure KOH is large (almost 10 mA cm^{-2} in height for the 30th cycle) and centered at 1.44 V vs RHE. The reduction wave for this sample is much smaller (3.5 mA cm^{-2} in height) and is centered at 1.31 V vs RHE. The positions of the oxidation waves of the NiO samples cycled in KOH containing different amounts of Fe are more or less the same as that of the sample cycled in pure KOH. The reduction waves of the samples cycled in 0.3 ppm and 1 mM Fe are centered at 1.32 V vs RHE. To compare the sizes of the redox features and OER activities of NiO prepared by reduction that was cycled in different electrolytes, the 30th CV cycle of each sample is overlaid in Figure 4-26.

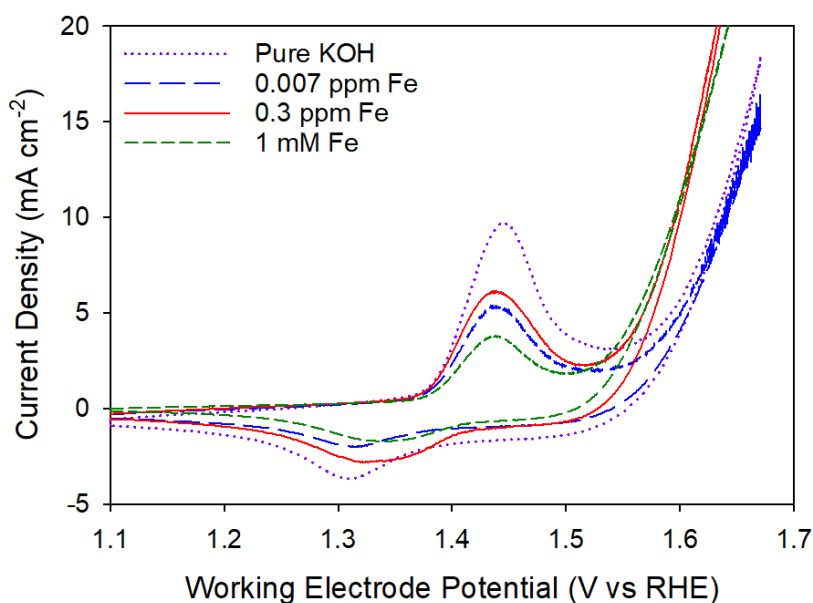


Figure 4-26: 30th CV cycle of NiO prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).

The oxidation wave of NiO cycled in pure KOH is the largest and the oxidation wave of the sample cycled in KOH containing 1 mM Fe is the smallest. The oxidation waves of samples cycled in 0.3 ppm and 0.007 ppm Fe have similar sizes, with the latter being slightly smaller. The current densities of the samples cycled in KOH containing 0.3 ppm and 1 mM Fe are larger than the current densities of the samples cycled in pure KOH and 0.007 ppm Fe. The overpotentials at 10 mA cm⁻² are 403.10 mV and 411.10 mV for the samples cycled in pure KOH and 0.007 ppm Fe, respectively. For NiO prepared by reduction cycled in 0.3 ppm and 1 mM Fe, lower overpotentials of 365.10 mV and 364.10 mV, respectively, are observed.

4.2.4.5 CVs for NiNiO prepared by the chemical reduction synthesis method

Lastly, NiNiO electrocatalysts prepared by the reduction synthesis method was cycled 30 times at a scan rate of 20 mV s⁻¹, and these results can be observed in Figure 4-27. This figure clearly illustrates an increase in current density for NiNiO samples cycled in KOH containing 0.3 ppm and 1 mM Fe. The figure also shows that the current keeps increasing and the redox peaks continue growing upon each consecutive CV cycle until 30 cycles is reached.

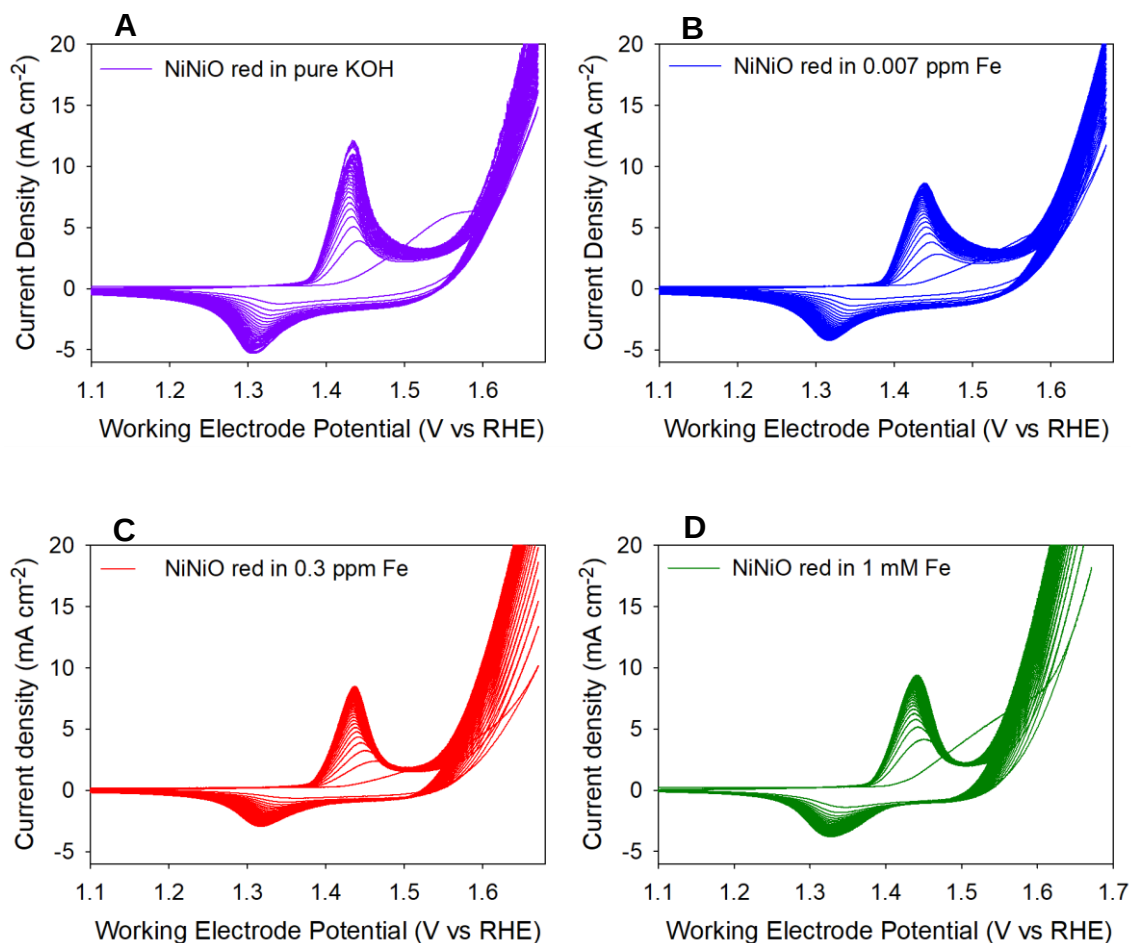


Figure 4-27: 30 CV cycles of NiNiO prepared by reduction performed at 20 mV s^{-1} in (a) pure 0.1 M KOH , and 0.1 M KOH containing (b) 0.007 ppm Fe , (c) 0.3 ppm Fe and (d) 1 mM Fe .

Furthermore, the redox peaks of these samples are very large, and can be better seen in Figure 4-28. In this figure, the first, fifth, tenth, fifteenth and thirtieth CV cycle of the NiNiO electrocatalysts in each of the electrolyte compositions is displayed. The first cycle of each of the samples is the least stable and that the redox peaks keep growing upon each consecutive cycle. The sharp, well-defined oxidation peaks for the samples cycled in pure KOH and 0.007 ppm Fe are centered at 1.43 V and 1.44 V , respectively. Both of these peaks have a corresponding reduction peak at 1.31 V , which is significantly smaller than the corresponding oxidation peak. The samples cycled in 0.3 ppm and 1 mM Fe both have oxidation peaks at 1.44 V and reduction peaks at 1.30 V and 1.32 V , respectively.

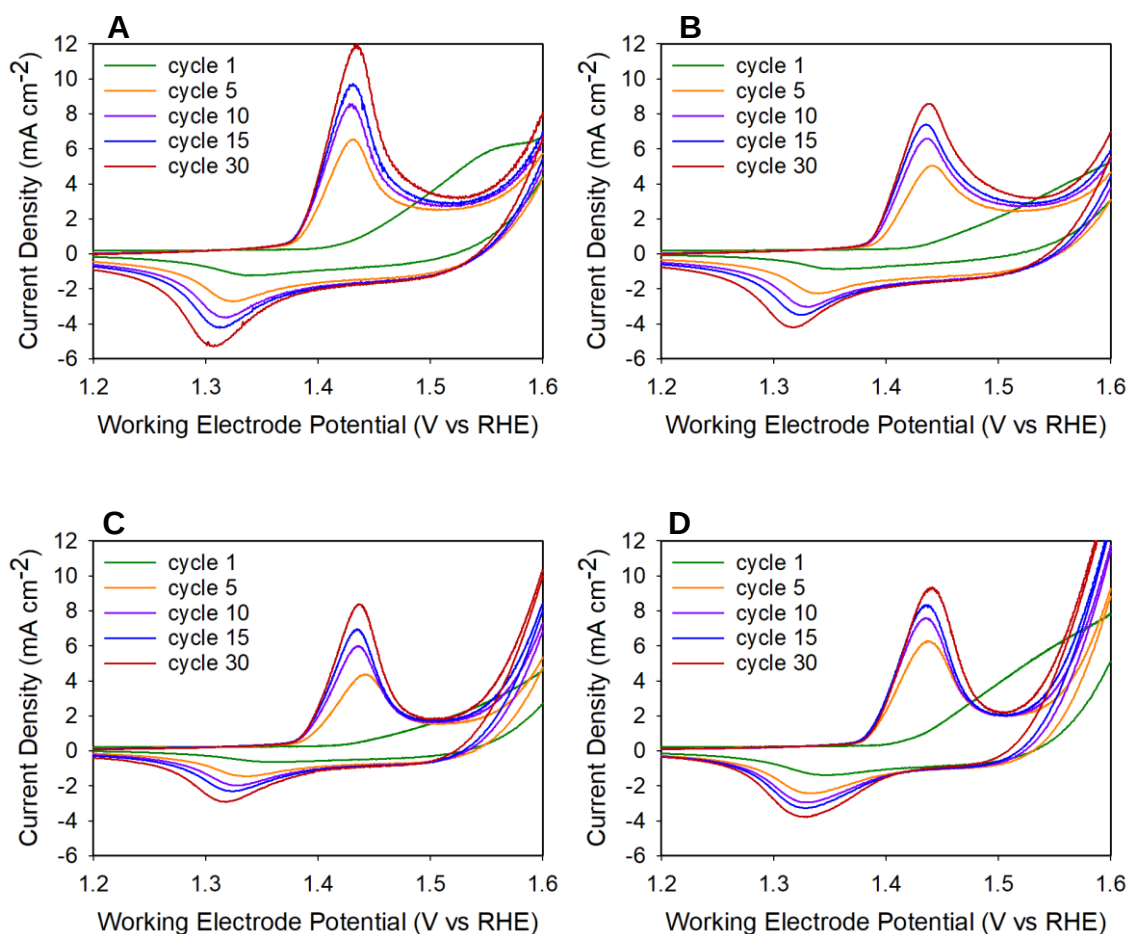


Figure 4-28: The redox features of NiNiO prepared by reduction in (a) pure KOH and KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

The 30th cycle of each of these samples are overlayed in Figure 4-29. In this figure, the increase in current density when cycling NiNiO in KOH containing 0.3 ppm and 1 mM Fe is visible. The overpotentials at 10 mA cm⁻² are 382.6 mV, 391.6 mV, 355.6 mV and 346.6 mV for NiNiO cycled in pure KOH, 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe, respectively. The oxidation peaks of the samples cycled in pure KOH and KOH containing 1 mM are similar in size. The oxidation peaks of the samples cycled in 0.007 ppm and 0.3 ppm are similar in size, and smaller than the former. It can also be seen that no anodic shift is observed for the oxidation peaks of samples cycled in KOH containing higher concentrations of Fe.

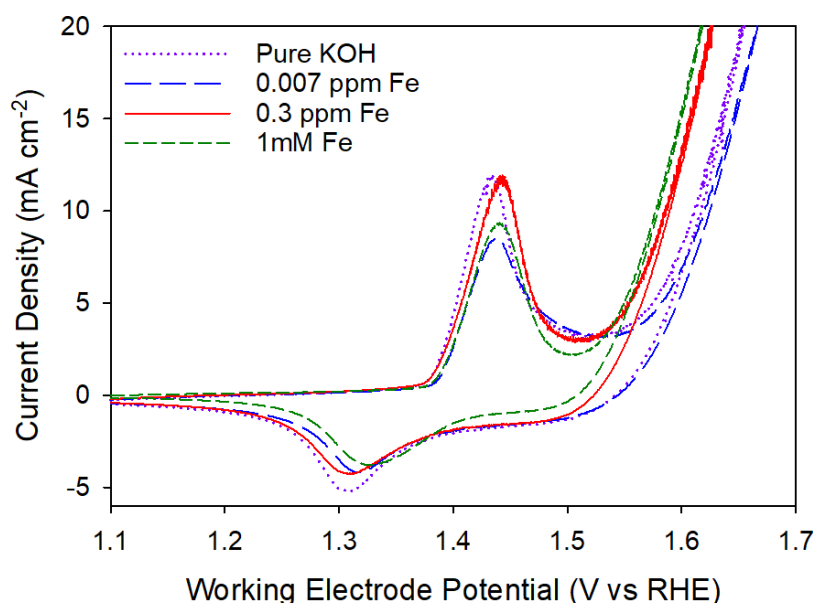


Figure 4-29: 30th CV cycle of NiNiO prepared by reduction in pure KOH (purple), and KOH containing 0.007 ppm Fe (blue), 0.3 ppm Fe (red) and 1 mM Fe (green).

4.2.5 Linear sweep voltammetry and Tafel analysis of Ni-based nanoparticles

LSVs of the nanoparticle electrocatalysts were performed in pure KOH, KOH containing 0.3 ppm Fe and KOH containing 1 mM Fe, after the samples were cycled 30 times in each electrolyte. A scan rate of 1 mV s⁻¹ was used to investigate the OER activity of these electrocatalysts. A slower scan-rate allows for a steady-state current to be reached and is said to provide more reproducible results. In Figure 4-30, LSVs of the nanoparticle electrocatalysts can be observed. From the LSVs for colloidal Ni and NiO (Figure 4-30 a and b), it is apparent that a significant increase in OER activity is observed when 1 mM Fe is present in the KOH. Figure 4-30 b and c show that the current response for NiO and NiNiO prepared by reduction cycled in 0.3 ppm Fe and 1 mM Fe are much higher than for the samples cycled in pure KOH. This means that the OER activity is significantly better for the samples cycled in 0.3 ppm Fe and 1 mM Fe.

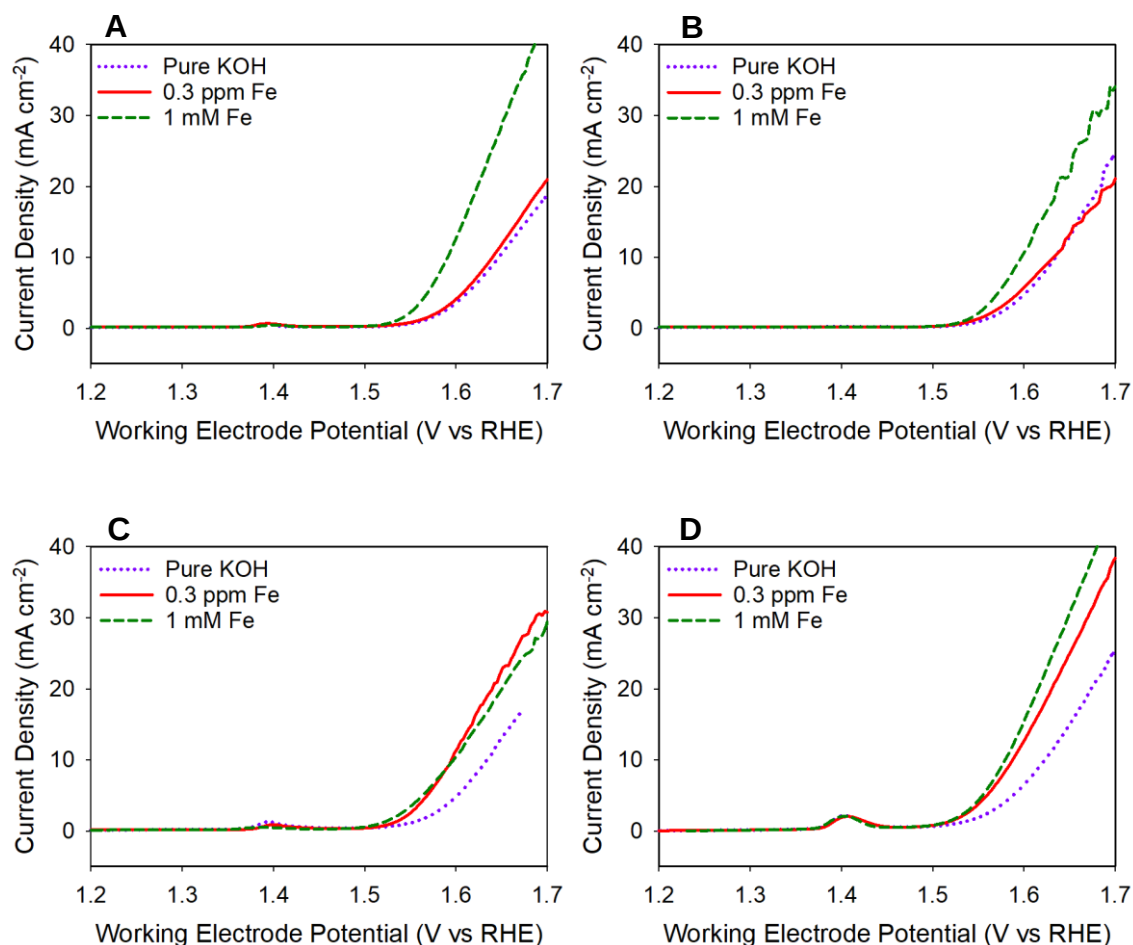


Figure 4-30: LSV performed at 1 mV s^{-1} of (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction.

From the LSVs, the overpotential at 10 mA cm^{-1} of each electrocatalyst cycled in each electrolyte can be obtained. The overpotentials are summarised in the form of a bar chart in Figure 4-31. At 10 mA cm^{-1} , the overpotentials of colloidal Ni are 415 mV, 409 mV and 360 mV, in pure KOH and KOH containing 0.3 ppm and 1 mM Fe, respectively. The overpotentials of colloidal NiO are 406 mV, 403 mV and 366 mV for the samples cycled in pure KOH and KOH containing 0.3 ppm and 1 mM Fe, respectively. According to an OER electrocatalyst merit system outlined by Tahir *et al.*⁴, the colloidal Ni and NiO electrocatalysts can be described as a “good” OER electrocatalyst after 30 CV cycles in pure KOH and 0.3 ppm Fe. After 30 CV cycles in 1 mM Fe, these electrocatalysts can be described as “excellent”⁴. Furthermore, the overpotentials (at 10 mA cm^{-1}) of the samples cycled in pure KOH and 0.3 ppm Fe are in good agreement with that of Ni samples in pure KOH with no effect of Fe⁵. The benchmarking overpotential of sample cycled in 1 mM Fe agrees well with that of Ni samples that have incorporated Fe⁵.

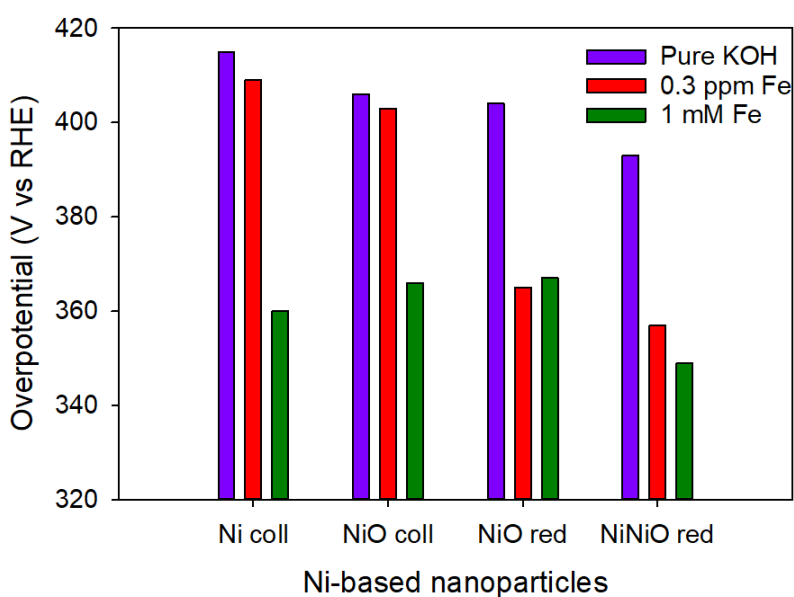


Figure 4-31: A bar chart indicating the overpotentials of each Ni-based electrocatalyst cycled in pure KOH (purple), 0.3 ppm Fe (red) and 1 mM Fe (green).

For NiO prepared by reduction, the overpotentials at 10 mA cm^{-1} are 404 mV, 365 mV, 367 mV for samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. For NiNiO prepared by reduction, the overpotentials at 10 mA cm^{-1} are 393 mV, 357 mV and 349 mV for samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. Therefore, NiO prepared by reduction can be classified as “good” after cycling in pure KOH, and “excellent” after cycling in both 0.3 ppm and 1 mM Fe⁴. NiNiO cycled in all three electrolytes can be regarded as an “excellent” OER electrocatalyst⁴. However, it is clear that the OER activity is significantly higher for samples cycled in 0.3 ppm Fe and 1 mM Fe. The overpotential values of the samples cycled in 0.3 ppm Fe and 1 mM Fe are in good agreement with Ni electrocatalysts tested in reagent grade KOH (containing Fe impurities)⁶⁷ or NiFe electrocatalysts¹³.

Chronoamperometry was used for Tafel analysis to obtain steady-state current responses for applied potentials. From the chronoamperometry data of the nanoparticle electrocatalysts, Tafel plots are constructed and can be seen in Figure 4-32. In this figure it can be seen that different Tafel slopes are obtained when the nanoparticle electrocatalysts are cycled in KOH containing different concentrations of Fe. The different Tafel slope values could be indicative of different rate-determining steps being apparent when the electrocatalyst are cycled in KOH containing varying concentrations of Fe. However, it is more likely that an entirely different mechanism is the reason for the differing Tafel slopes. This is because the presence of Fe on the surface of the electrocatalyst films can result in two electroactive species being present, and thus a different

mechanism. This mechanism is referred to in literature as a bifunctional mechanism, where both Ni and Fe are active sites¹¹.

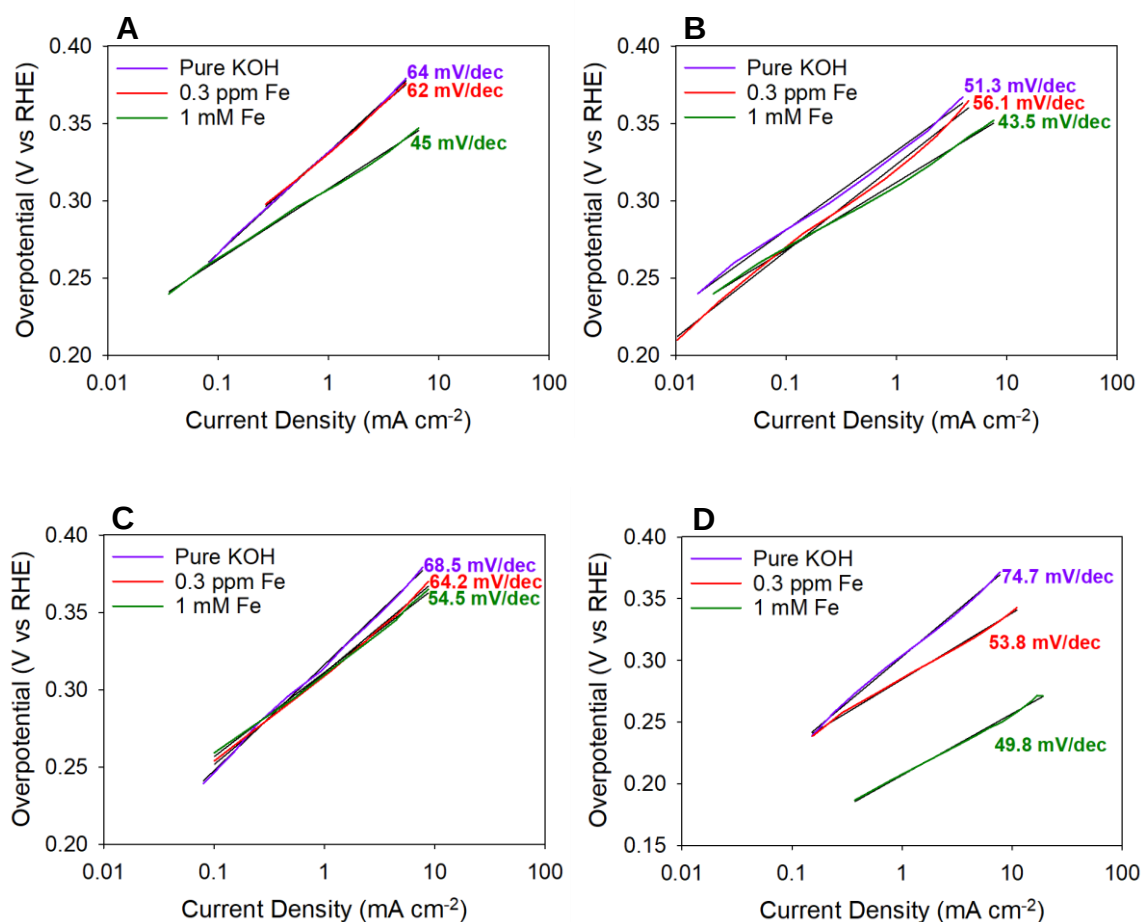


Figure 4-32: Tafel plots for (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction after cycling.

Figure 4-33 serves as a means to better compare the different Tafel slope values. The slopes obtained from the Tafel plots are similar for the colloidal Ni samples cycled in pure KOH and 0.3 ppm Fe. Tafel slopes of 64 mV/dec and 62 mV/dec are observed for the samples cycled in pure KOH and 0.3 ppm Fe, respectively. In Table 2-5, different Tafel slope values obtained from literature are summarised. From this table, it can be seen that the Tafel slope values of colloidal Ni cycled in pure KOH and 0.3 ppm Fe agree well with Ni electrocatalysts that have been electrochemically tested in purified KOH¹⁶. Furthermore, the Tafel slope of the sample cycled in 1 mM Fe is 45 mV/dec, which is in good agreement with the values for NiFe samples or Ni that has been electrochemically tested in KOH containing Fe^{6,67,69}.

Tafel slopes of colloidal NiO are 51.3 mV/dec, 56.1 mV/dec and 43.5 mV/dec for samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. The Tafel slopes of the samples cycled in pure KOH and 0.3 ppm Fe are found to be in agreement with Ni samples in previous studies that

have been cycled in unpurified KOH^{67,140}. The Tafel slope of the sample cycled in 1 mM Fe, is again in agreement with that of NiFe electrocatalysts or Ni electrocatalysts cycled in electrolyte containing Fe^{6,67,69}.

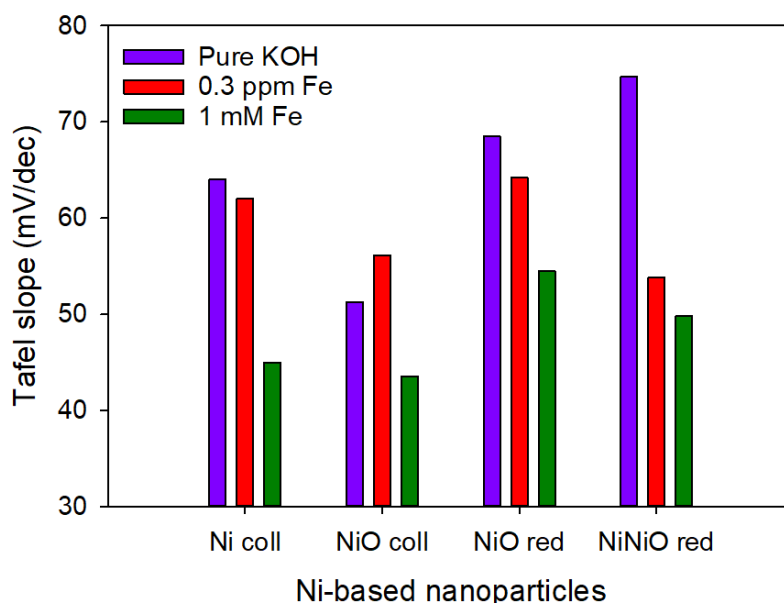


Figure 4-33: A bar chart illustrating the Tafel slope values of Ni-based nanoparticle electrocatalysts after 30 CV cycles in pure KOH and KOH containing different concentrations of Fe.

The Tafel slopes of NiO cycled in pure KOH and KOH containing 0.3 ppm Fe are quite high, with values of 68.5 mV/dec and 64.2 mV/dec, respectively. Using Table 2-5, one can see that these values are similar to Tafel slopes of Ni-based electrocatalysts cycled in purified KOH¹⁶ or unpurified KOH⁵¹. The Tafel slope of the sample cycled in 1 mM is 54.5 mV/dec. This value is similar to Tafel slopes reported in literature for Ni electrocatalysts cycled in unpurified KOH^{67,140}.

The Tafel slope of NiNiO cycled in pure KOH is the highest, with a value of 74.7 mV/dec. Previous studies have reported Ni-based electrocatalysts tested in unpurified KOH with a similar Tafel slope⁵¹. The Tafel slope of the sample cycled in 0.3 ppm Fe is 53.8 mV/dec, which also agrees with studies reporting Tafel slopes of Ni tested in unpurified electrolyte^{67,140}. The Tafel slope of the sample cycled in 1 mM Fe is 49.8 mV/dec and is similar to Ni electrocatalysts cycled in unpurified KOH⁶⁷ or NiFe electrocatalysts⁶⁹.

4.2.6 Determination of the electrochemical double layer capacitance of Ni-based nanoparticles through cyclic voltammetry

The electrochemical double-layer capacitance was measured by using cyclic voltammetry. The scan-rate dependent capacitive current was measured in a non-Faradaic region which is associated with double-layer charging¹⁴¹. Equation (35) can be used to determine the double-layer capacitance¹⁴¹:

$$i_c = \nu C_{DL} \quad (35)$$

where i_c denotes the charging current, ν is the scan rate and C_{DL} is the double-layer capacitance. An example of the CVs performed in the non-faradaic region towards obtaining the double layer capacitance can be seen in Figure 4-34.

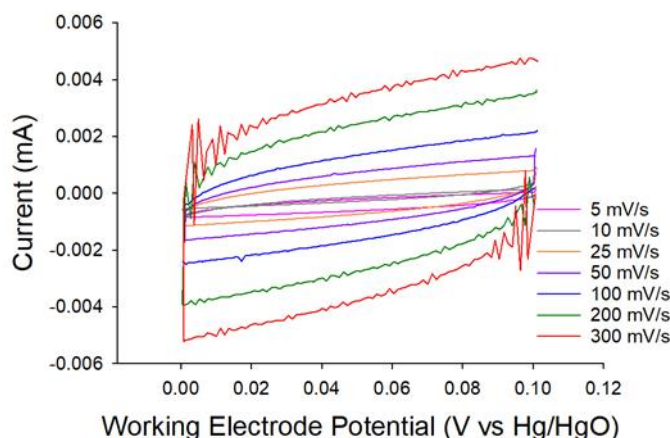


Figure 4-34: CVs of colloidal Ni in pure KOH performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

Ten CV cycles were performed at each scan-rate and the 10th cycle of each is shown in the figure. The CVs of colloidal Ni in pure KOH are shown as representative. The CVs toward double layer capacitance determination of all the samples can be found in Figure A-1 to Figure A-3 in Appendix A. According to equation (35), a plot of the current at a chosen potential of 0.05 V vs Hg/HgO (i_c), against the scan rate (ν), will yield a straight line where C_{DL} can be obtained from the slope. Since CVs have an anodic and a cathodic sweep, two straight lines are obtained. Figure 4-35 shows the plots of current versus scan rate for the nanoparticle electrocatalysts. The values obtained from the slopes of the straight lines in this figure are the electrochemical double layer capacitance values of the Ni-based nanoparticle electrocatalysts cycled in different electrolytes. For each sample, two straight lines are obtained: one with a positive slope and one with a negative slope. This is due to CVs consisting of both a negative and a positive current response (that should be equal in value and opposite in sign) at a certain potential in the non-Faradaic region. Therefore,

the absolute value of the average of the two slopes yields the value of the electrochemical double layer capacitance of each sample.

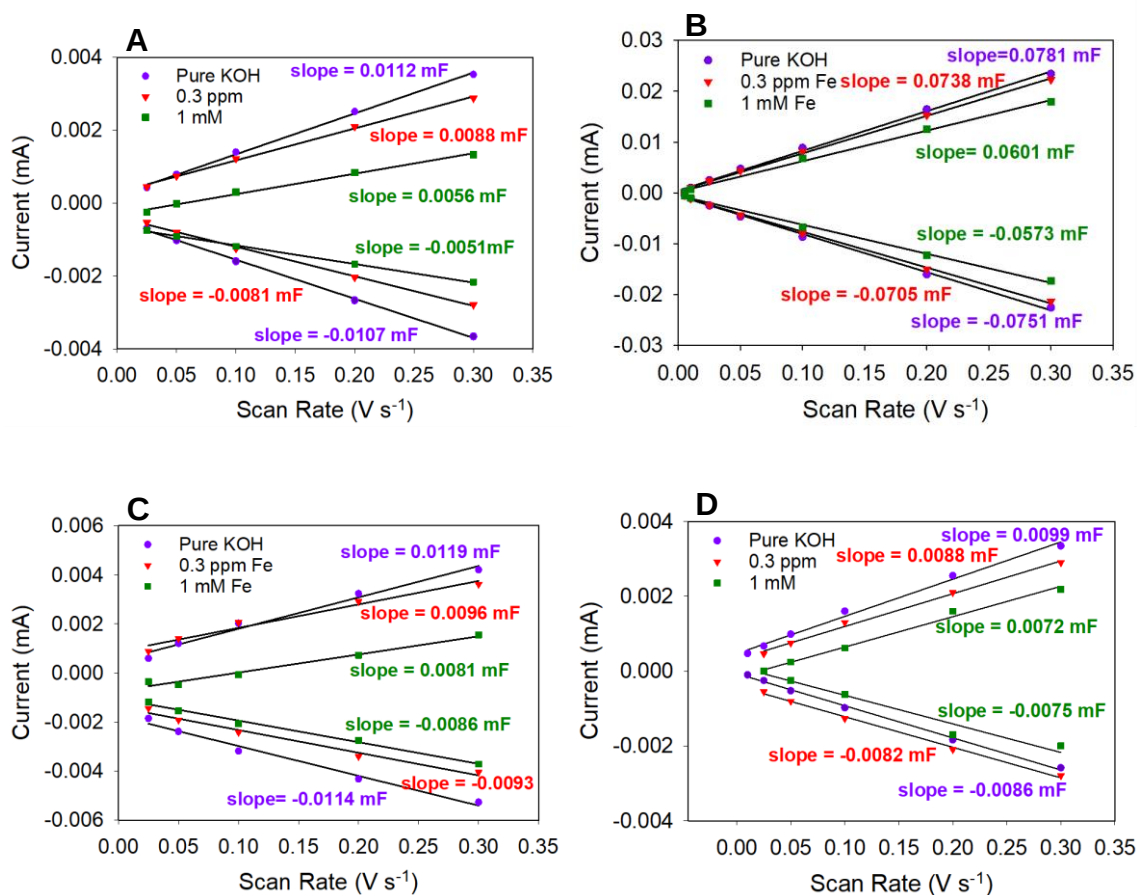


Figure 4-35: A plot of scan rate against the current response at 0.05 V vs Hg/HgO for (a) colloidal Ni, (b) colloidal NiO, (c) NiO prepared by reduction and (d) NiNiO prepared by reduction.

Thus, for colloidal Ni, double layer capacitance values of 0.0109 mF, 0.0085 mF and 0.0054 mF are obtained for samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. The electrochemical double layer capacitance therefore decreases as the Fe concentration is increased. These results agree with a study that found that the surface area of Ni samples cycled in KOH containing trace amounts of Fe were higher than that of samples cycled in KOH containing concentrated amounts of Fe⁸. For colloidal NiO, the electrochemical double layer capacitances are found to be 0.0766 mF, 0.0722 mF and 0.0587 mF for the samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. Again, it is observed that the electrochemical double layer capacitance decreases as the Fe concentration increases. Furthermore, NiO samples prepared by reduction have electrochemical double layer capacitances of 0.0117 mF, 0.0094 mF and 0.0083 mF when the samples are cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe respectively. A decrease in the values are observed as the Fe concentration increases, similar to the previous two samples. Lastly, the electrochemical double layer capacitance values for NiNiO prepared by

reduction re 0.0092 mF, 0.0085 mF and 0.0074 mF for samples cycled in pure KOH, 0.3 ppm Fe and 1 mM Fe, respectively. To visualise the values of the electrochemical double layer capacitances of all of the nanoparticle samples together, Figure 4-36 has been constructed.

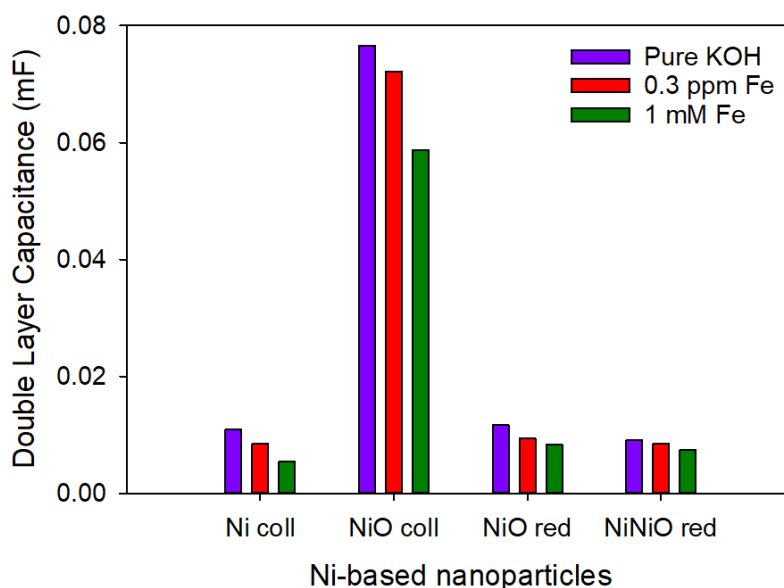


Figure 4-36: A bar chart of the electrochemical double layer capacitance values of Ni-based nanoparticles cycled in pure KOH, and KOH containing 0.3 ppm and 1 mM Fe.

It should be noted that the loading for all samples was the same (subsection 4.1.3.2). From Figure 4-36, it can be seen that colloidal NiO samples have the largest double layer capacitance, which is almost one order of magnitude larger than that of the rest of the samples. Colloidal Ni and NiNiO prepared by reduction have the smallest double layer capacitances.

4.2.7 In-situ Raman spectroscopy in pure and Fe-doped electrolyte before and after electrochemical cycling

In-situ Raman spectroscopy was used to investigate the effect of different concentrations of Fe within the electrolyte on the structure of the electrocatalysts, specifically the active material. At first, the Raman spectra of as-prepared electrocatalysts, which have undergone no previous electrochemistry, were obtained in the different electrolyte compositions. However, by observing how much the CVs of the electrocatalysts changes and stabilises after 30 cycles, it is clear that in-situ Raman spectra should also be obtained after the electrocatalysts have been subjected to potential cycling. Upon potential cycling, more active species are formed, as indicated by the growth of the oxidation feature. In addition, potential cycling allows for the incorporation of Fe, as evidenced by the increase in current density for samples cycled in Fe containing electrolyte.

Therefore, a more accurate representation of the active species can be obtained from the Raman spectra of cycled electrocatalysts. An example of the chronoamperometry used to apply potentials to the as-prepared and cycled electrocatalysts can be observed in Figure 4-37. This is the CAs for a colloidal Ni electrode and serves as representation of the CAs for all as-prepared samples.

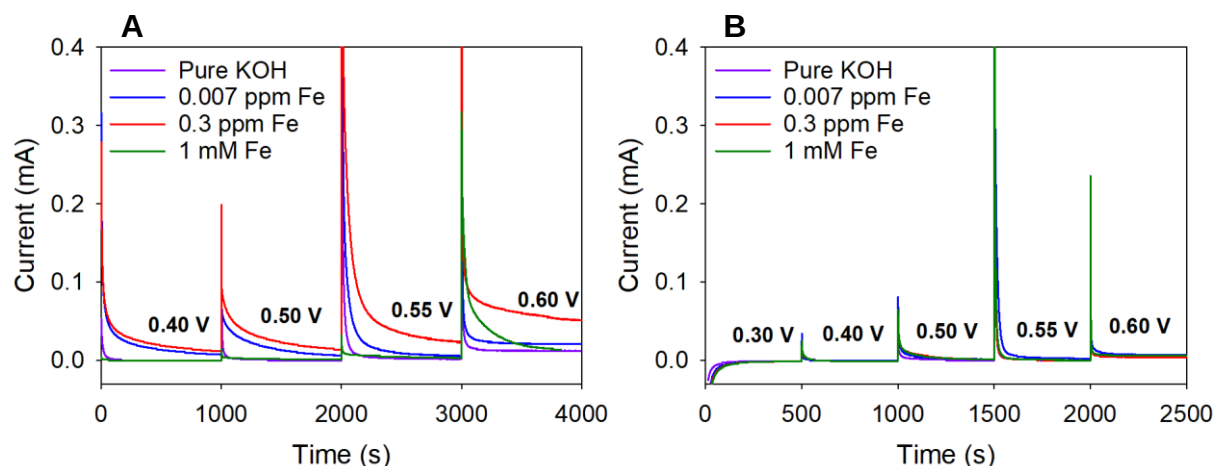


Figure 4-37: The current response observed for the potentials applied to the colloidal Ni working electrode in different electrolyte compositions in parallel with in-situ Raman spectroscopy (a) before and (b) after 30 CV cycles.

From Figure 4-37, it is clear that the sample that has been cycled has a stable current response whereas the as-prepared sample is clearly not yet stable.

In the following subsections, the in-situ Raman spectra of the nanoparticle electrocatalysts before and after electrochemical cycling are discussed. Note that all potentials referred to in this section are versus the Hg/HgO reference. The spectra are depicted from 100 cm^{-1} to 1000 cm^{-1} , which is where the important Raman features ascribed to transition metals and transition metal oxides occur. The full spectra can be seen in the Figure A-5 to Figure A-13 in Appendix A.

4.2.7.1 In-situ Raman spectra of colloidal Ni before and after cycling

The in-situ Raman spectra of colloidal Ni (prior to any previous electrochemistry) in pure KOH, and KOH containing 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe can be observed in Figure 4-38.

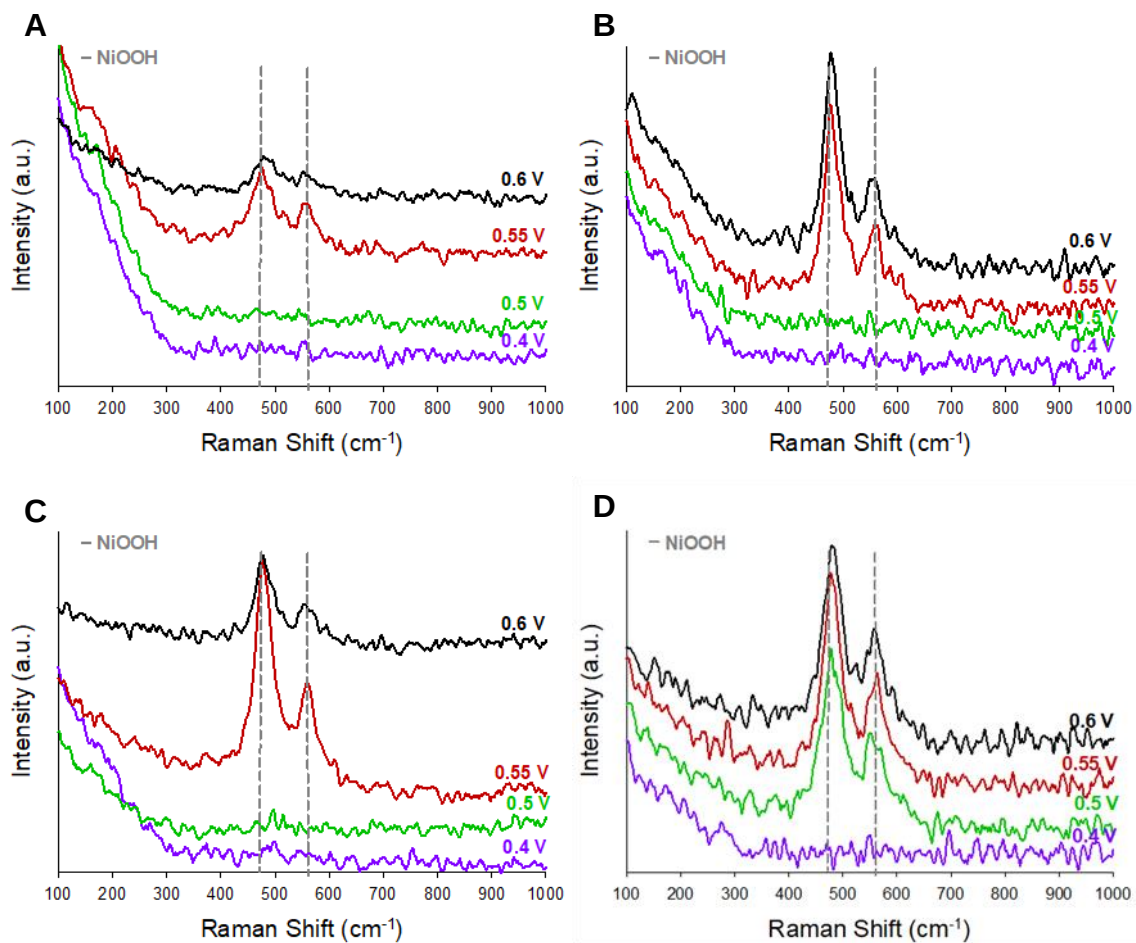


Figure 4-38: Raman spectra of as-prepared colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

In pure KOH, Raman peaks at 480 and 560 cm^{-1} first appear at a potential of 0.5 V. In both 0.007 ppm and 0.3 ppm they first appear at 0.55 V. Lastly, in KOH containing 1 mM Fe, the two peaks appear at 0.5 V. These two peaks are ascribed to NiOOH and indicate that $\text{Ni}(\text{OH})_2$ (which is not present in the spectra due to low Raman cross-section) is oxidised to NiOOH.

In Figure 4-39, Raman spectra of colloidal Ni after 30 CV cycles in different concentrations of Fe electrolyte can be observed.

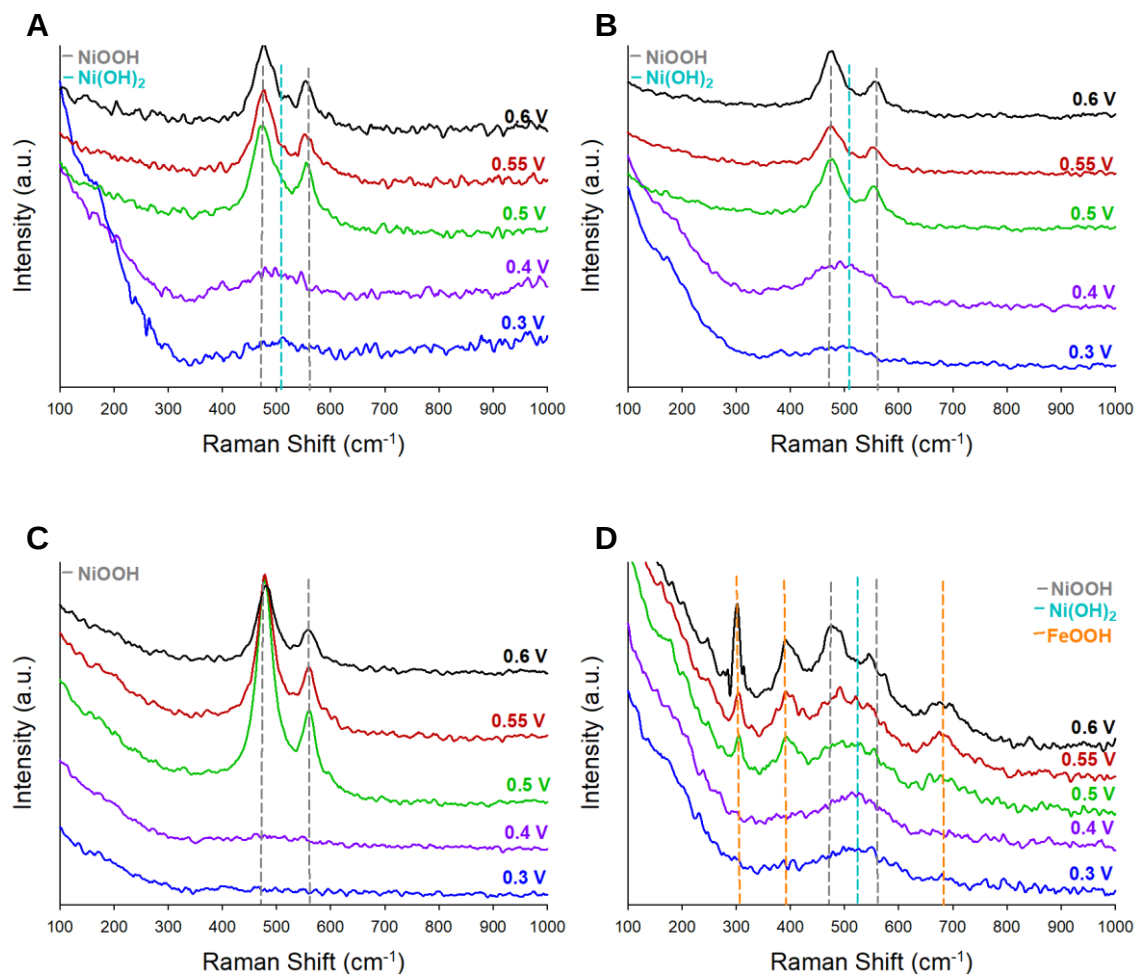


Figure 4-39: Raman spectra of colloidal Ni after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

In pure KOH, 0.007 ppm Fe and 0.3 ppm Fe, the 480 and 560 cm^{-1} peaks start to appear at 0.5 V vs Hg/HgO. The peaks seen at 500 cm^{-1} in figures (a), (b) and (d) are due to Ni(OH)_2 that forms in-situ on the surface of Ni. This could also possibly be NiO, that forms on the surface of Ni upon contact with air. Ni(OH)_2 and NiO have Raman peaks at similar positions. A peak for Ni(OH)_2 is present in these spectra, and not in the spectra displayed in the previous figure, because more Ni(OH)_2 is formed during cycling, as seen in the CVs. The higher concentration of Ni(OH)_2 on the surface of these samples result in peaks of higher intensity. In 1 mM, 3 new peaks are observed, that is not observed for samples cycled in lower Fe concentrations. These peaks are also not present in the Raman spectra of the as-prepared sample in any of the electrolyte concentrations, including 1 mM. These peaks are located at around 302, 400 and 678 cm^{-1} . The peaks start to appear from 0.5 V and are also present at 0.55 V and 0.6 V.

4.2.7.2 In-situ Raman spectra of colloidal NiO before and after cycling

In Figure 4-40 the in-situ Raman spectra of colloidal NiO can be seen. These spectra are taken in each respective electrolyte before any previous electrochemical analyses were performed on the samples.

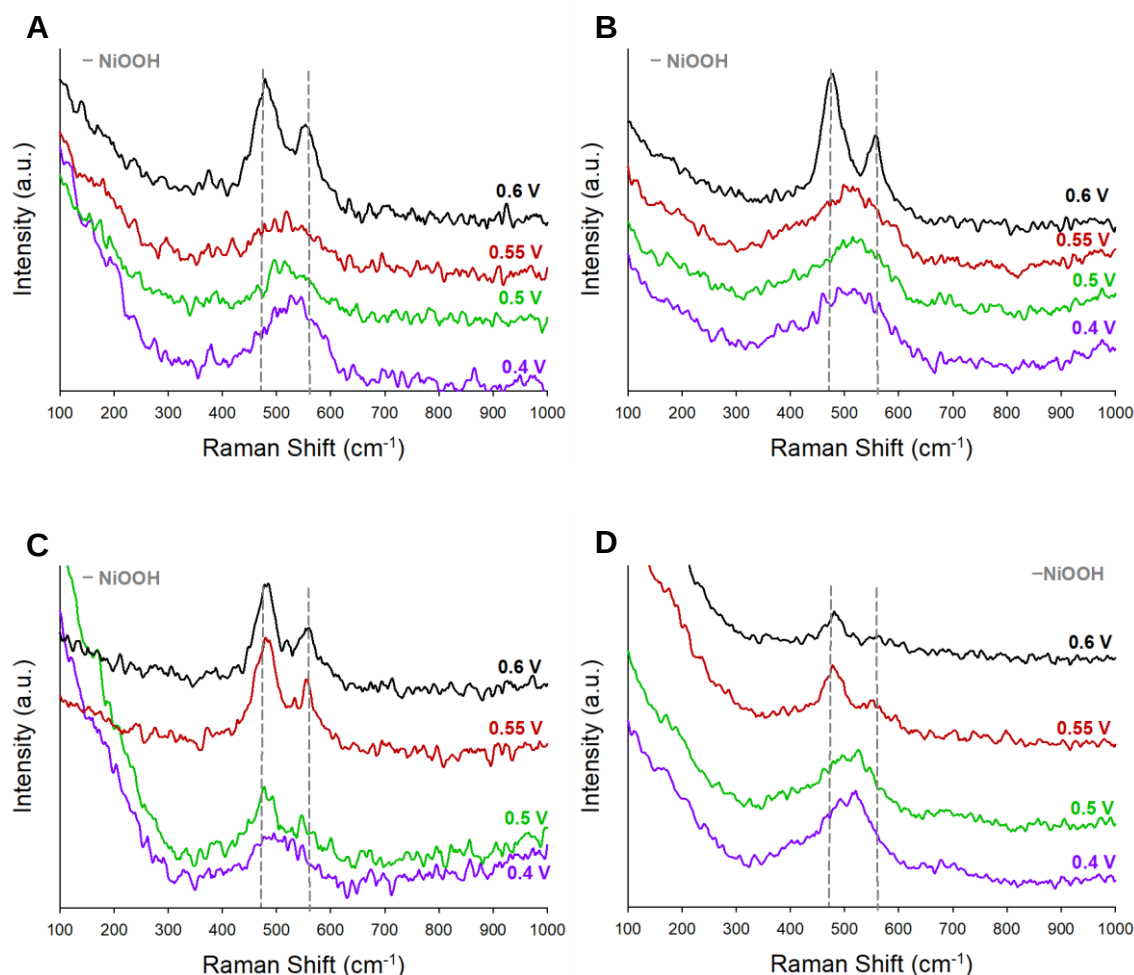


Figure 4-40: Raman spectra of as-prepared colloidal NiO in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Figure 4-40 shows that peaks corresponding to NiOOH emerge when 0.6 V potential is applied for samples analysed in pure KOH and 0.007 ppm Fe. In 1 mM Fe, the doublet peaks emerge at 0.55 V. The sample analysed in KOH containing 0.3 ppm Fe displays NiOOH peaks for applied potentials of 0.5 V and above. In addition, a peak at 500 cm⁻¹ is seen for all samples before the NiOOH peaks emerge. This peak can be ascribed to NiO or Ni(OH)₂. Likely, this peak arises due to the inherent NiO structure of the sample, as not prior electrochemistry have been done on these samples yet and the Ni(OH)₂ concentration is still low.

Spectra of colloidal NiO films after 30 CV cycles in pure KOH, and KOH containing 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe can be seen in Figure 4-41.

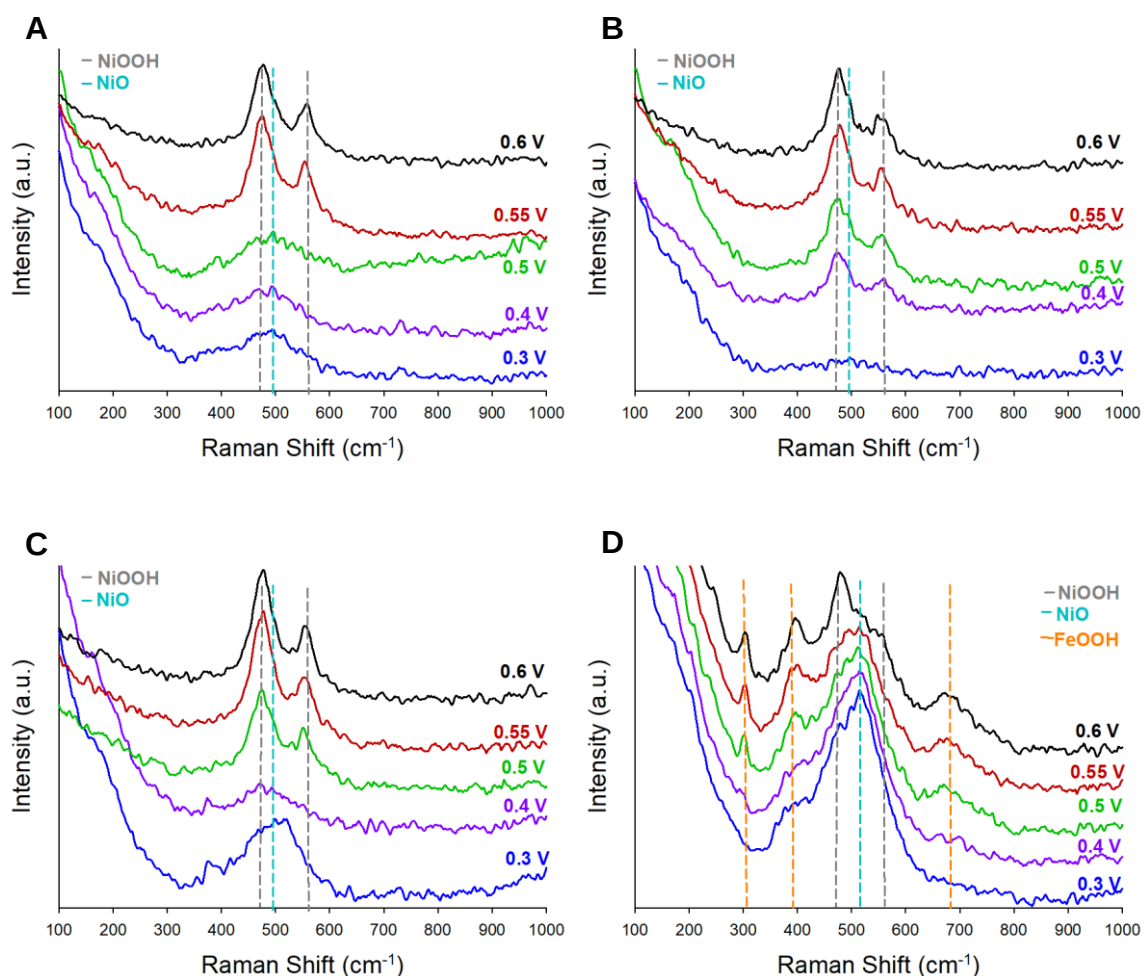


Figure 4-41: Raman spectra of colloidal NiO after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

The twin peaks at ~ 480 and 560 cm^{-1} appear first at 0.55 V in pure KOH. In KOH containing 0.007 ppm Fe, they appear at for the first time at 0.4 V. Furthermore, in 0.3 ppm Fe, they appear at 0.5 V. In KOH containing 1 mM Fe, however, three peaks at ~ 300 , 400 and 675 cm^{-1} appear at 0.5 V and are present at 0.55 V and 0.6 V. These peaks were also seen in the spectra of colloidal Ni cycled in 1 mM Fe. A large peak at around 500 cm^{-1} is seen in figures (a), (c) and (d). This peak likely arises due to the presence of NiO in the bulk of the sample. The intensity of the peak also suggests that a large concentration of NiO or Ni(OH)_2 are present in the samples.

4.2.7.3 In-situ Raman spectra of Ni prepared by reduction before and after potential cycling

The 3 nanoparticle samples prepared by the chemical reduction method were also analysed by in-situ Raman spectroscopy before and after 30 CV cycles. Firstly, the spectra of as-prepared Ni can be seen in Figure 4-42.

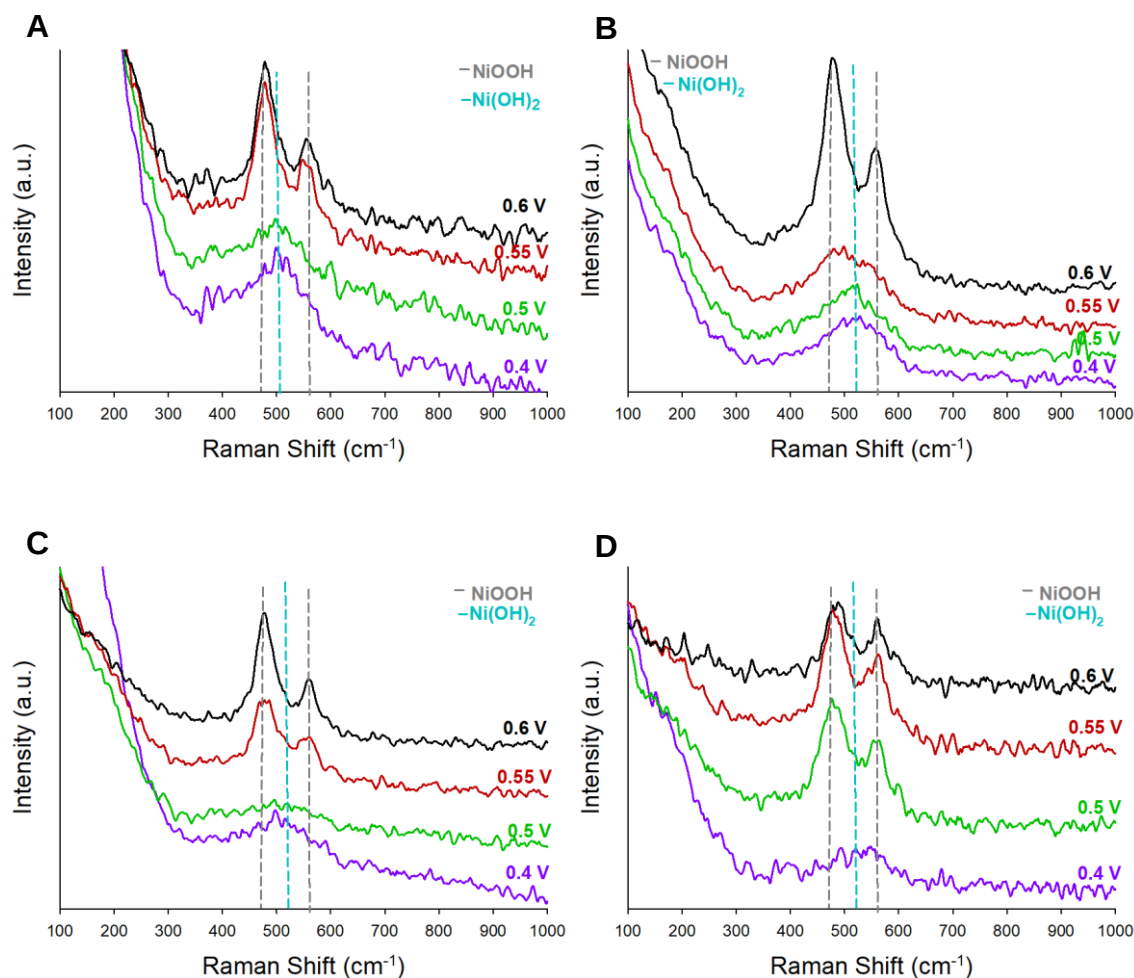


Figure 4-42: Raman spectra of as-prepared Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

A small broad peak centered around 500 cm^{-1} can be observed at potentials lower than those where the 480 and 560 cm^{-1} peaks appear. This peak may be ascribed to the Ni-O stretching vibration of NiO which forms on the surface of Ni, or Ni(OH)_2 that forms upon contact with electrolyte. For Ni prepared by reduction in pure KOH and 0.3 ppm, the two NiOOH peaks appear from 0.55 V. For 0.007 ppm they only appear at 0.6 V, whereas in 1 mM Fe, they already appear at 0.5 V.

The in-situ Raman spectra were also taken after the samples have been cycled 30 times in pure KOH and KOH containing each of the mentioned Fe concentrations. These spectra for Ni prepared by reduction can be seen in Figure 4-43.

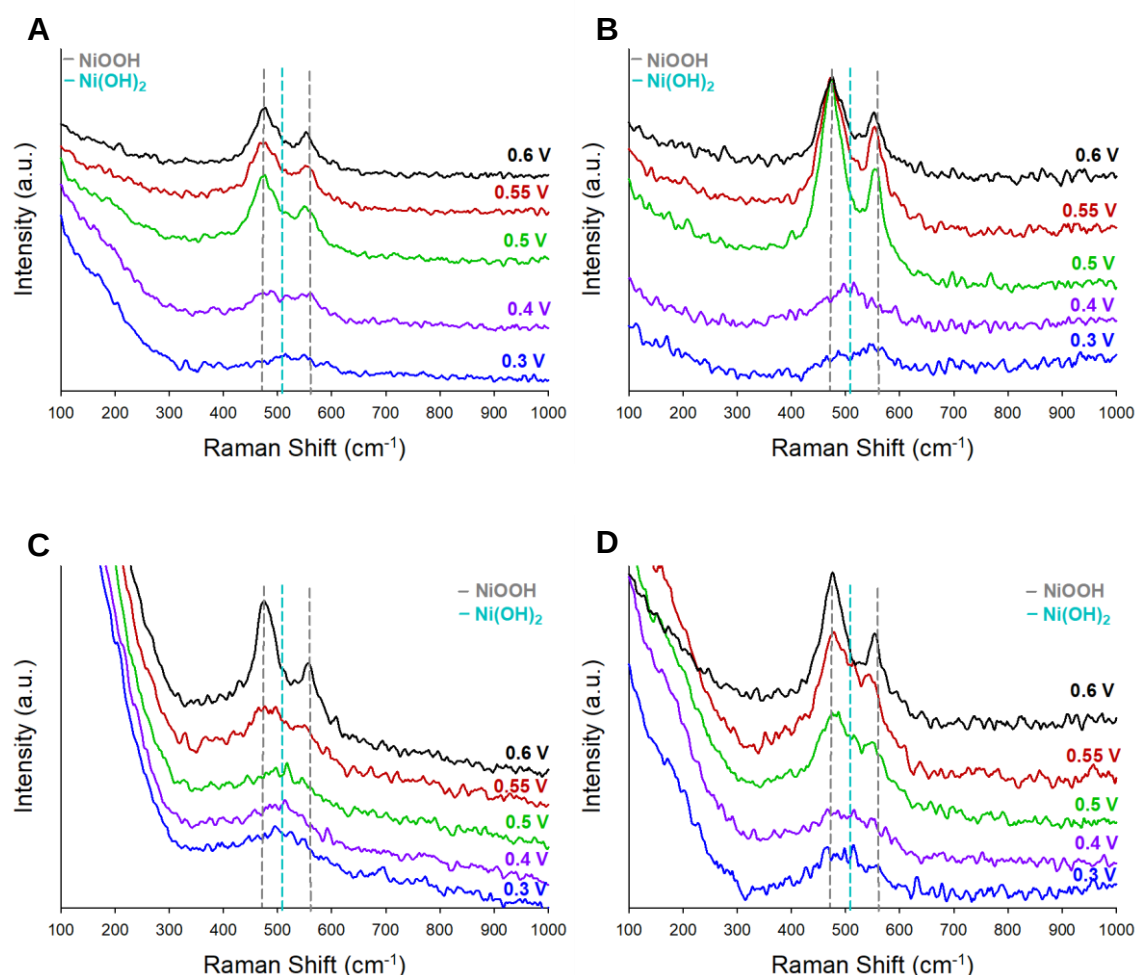


Figure 4-43: Raman spectra of Ni prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

From the in-situ Raman spectra in Figure 4-43, it can be seen that the 480 and 560 cm^{-1} peaks appear at 0.5 V in pure KOH and in 0.007 ppm Fe. In 0.3 ppm Fe, these two peaks are only seen at 0.6 V. In 1 mM Fe they are visible at 0.5 and 0.55 V, but not well-defined, and at 0.6 V they are clearly visible.

4.2.7.4 In-situ Raman spectra of NiO prepared by reduction before and after potential cycling

Figure 4-44 depict the results of the in-situ Raman experiment conducted on NiO prepared by reduction before any prior electrochemical analyses have been conducted on these samples.

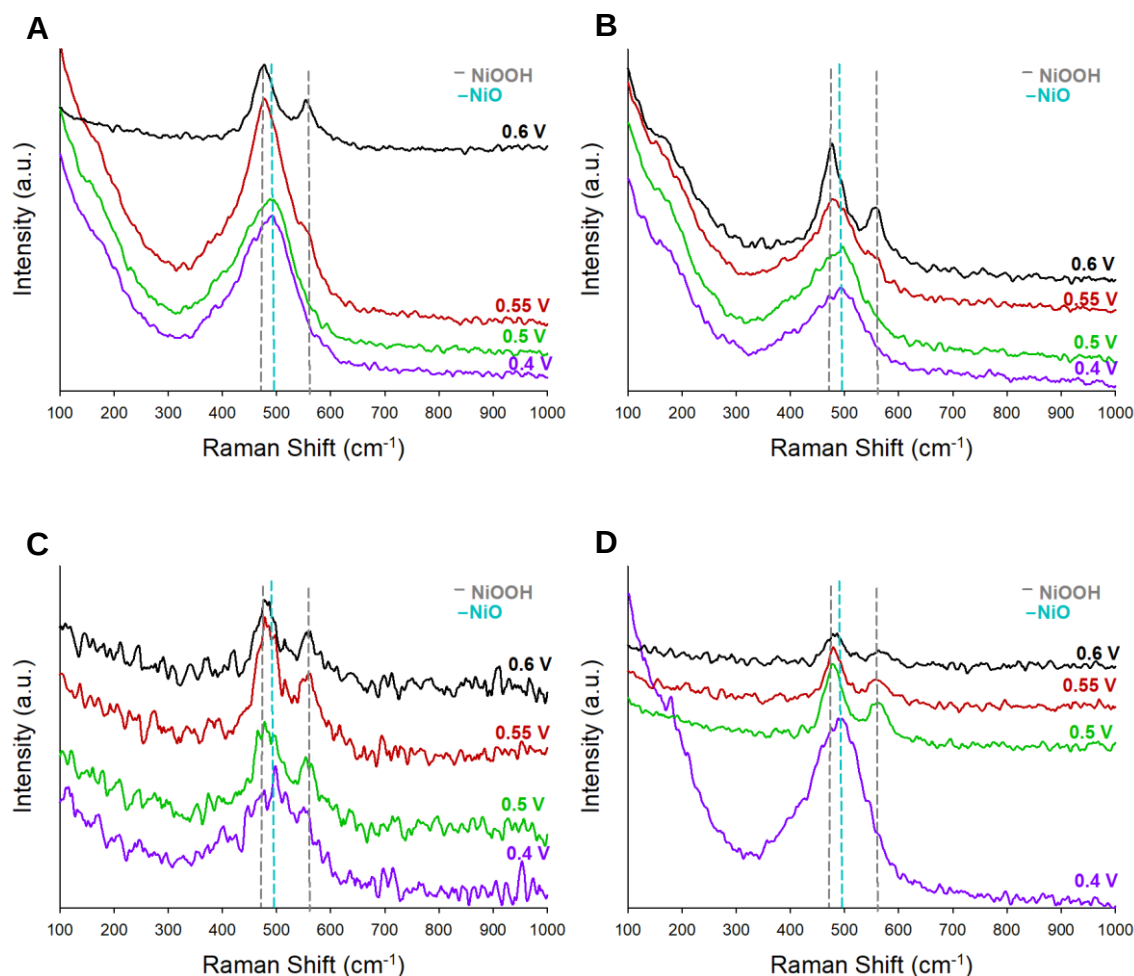


Figure 4-44: Raman spectra of as-prepared NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

In the Raman spectra in Figure 4-44, intense peaks centered at about 495 cm⁻¹ can be seen at potentials of 0.4 to 0.55 V. This peak arises due to a large concentration of NiO present in the sample. For the catalyst in pure KOH and 0.007 ppm Fe, the 480 and 560 cm⁻¹ peaks start to appear at 0.6 V. In 0.3 ppm and 1 mM, these peaks already appear at 0.5 V.

The Raman spectra of the in-situ experiments performed on NiO prepared by reduction after stabilisation cycles in each electrolyte composition, can be seen in Figure 4-45.

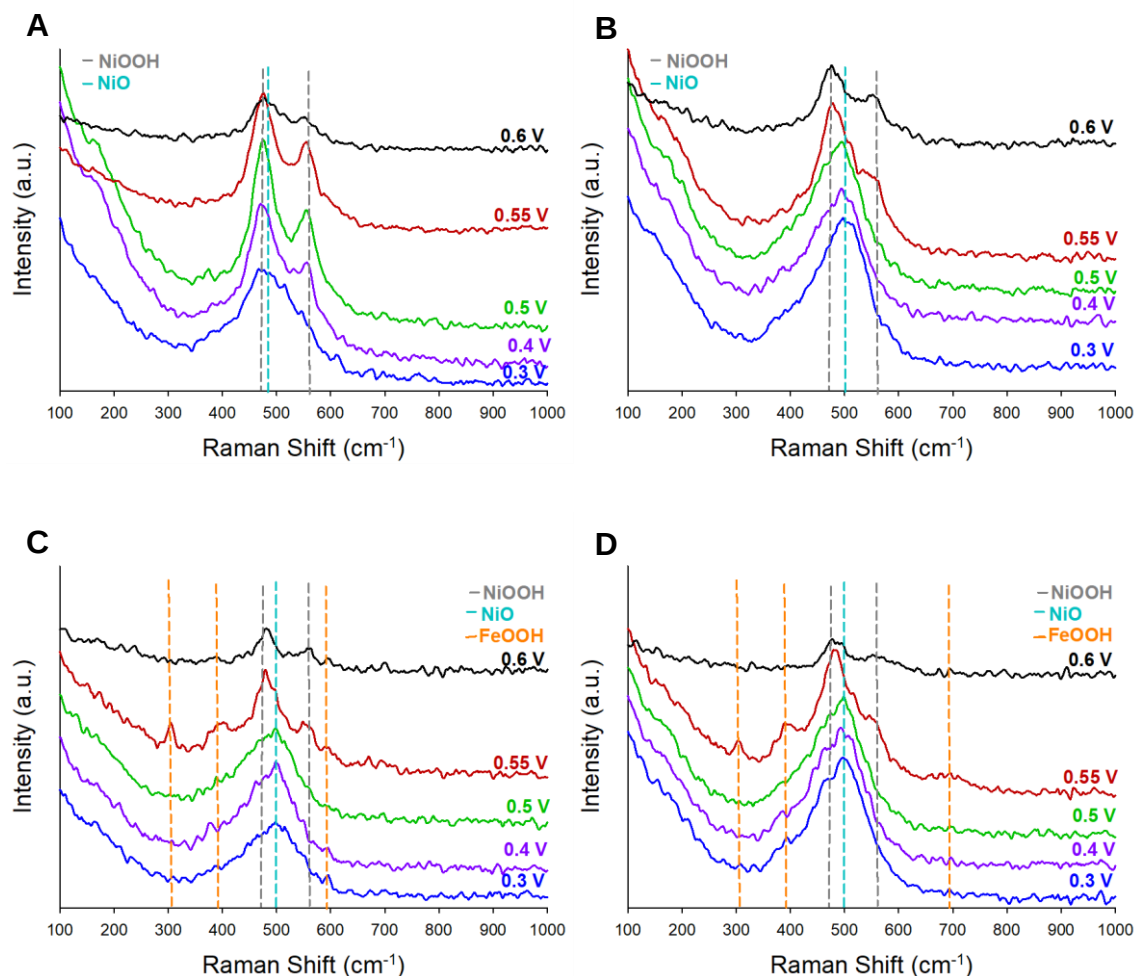


Figure 4-45: Raman spectra of NiO prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

In pure KOH, the 480 and 560 cm^{-1} peaks appear at 0.4 V vs Hg/HgO. In 0.007 ppm, a peak with a shoulder appears around 500 cm^{-1} at 0.55 V vs Hg/HgO and the 480 and 560 cm^{-1} peaks are seen at 0.6 V vs Hg/HgO. For the samples cycled in 0.3 ppm and 1 mM, the three peaks at ~ 300 , 400 and 675 cm^{-1} appear at 0.55 V.

4.2.7.5 In-situ Raman spectra of NiNiO prepared by reduction before and after potential cycling

In Figure 4-46, the in-situ Raman results for as-prepared NiNiO prepared by reduction can be seen. Again, the peak at 495 cm^{-1} is observed at lower potential values and the 480 cm^{-1} and 560 cm^{-1} pair at higher potentials. In pure KOH, the pair emerge at 0.55 V and in 0.007 ppm at 0.6 V. In 0.3 ppm the doublet starts to develop at 0.5 V and in 1 mM at 0.4 V.

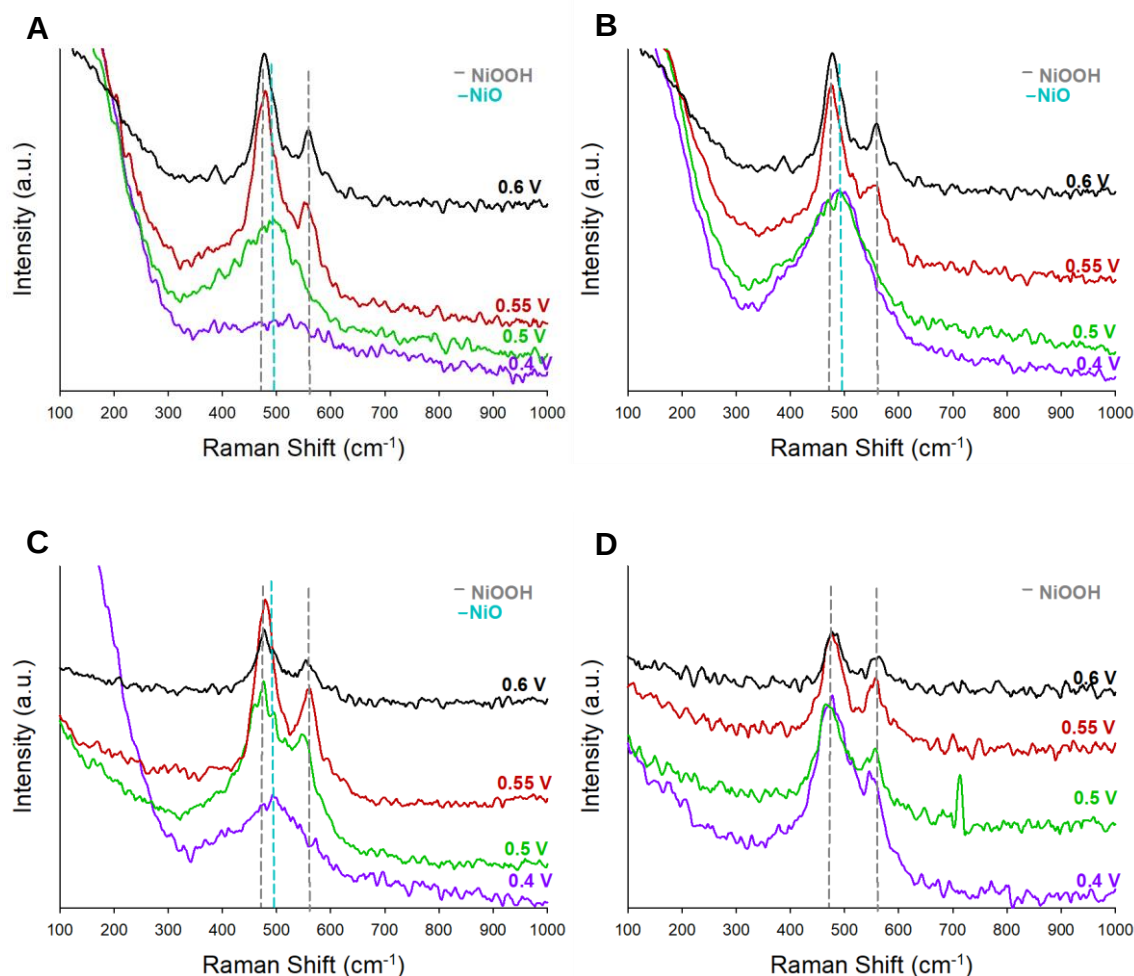


Figure 4-46: Raman spectra of as-prepared NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1 mM Fe.

Figure 4-47 shows the in-situ Raman experiment performed on NiNiO prepared by reduction after 30 activation CVs in each electrolyte composition. In pure KOH, the peaks at 480 and 560 cm^{-1} appear at 0.55 V and in 0.007 ppm Fe they already appear at 0.3 V. For the NiNiO sample in KOH containing 0.3 ppm Fe, a peak at 480 cm^{-1} with a shoulder at 560 cm^{-1} is visible at 0.3 V. At 0.4 V and 0.5 V, two well pronounced peaks are present at 480 and 560 cm^{-1} . At 0.55 V these peaks are weaker and at 0.6 V the 560 cm^{-1} peak is again reduced to a shoulder. A peak at 623 cm^{-1} is observed at 0.55 V and 0.6 V. A peak at 985 cm^{-1} is observed at all the potential values and one at 1065 cm^{-1} is seen from 0.4 V (Figure A-13). By observing peak positions and relative intensities, the peaks at 985 and 1065 cm^{-1} could possibly be ascribed to Nafion in the film¹⁵⁴. However, FeOOH also has peaks at these positions. Lastly, for the NiNiO sample in 1 mM Fe, peaks at 300 cm^{-1} , 400 cm^{-1} and 685 cm^{-1} are observed at 0.3 V, 0.4 V and 0.5 V. At 0.55 V and 0.6 V, 480 and 560 cm^{-1} peaks are present.

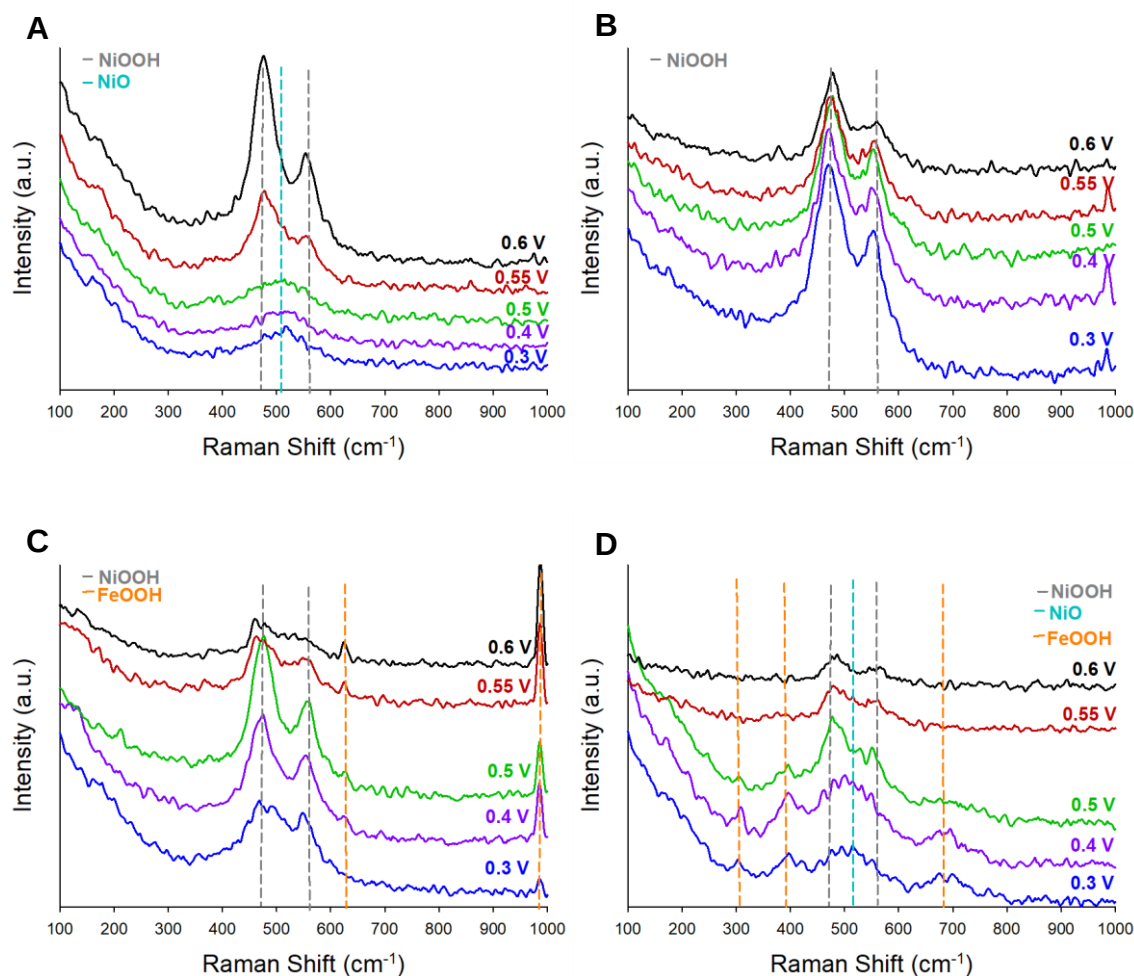


Figure 4-47: Raman spectra of NiNiO prepared by reduction after 30 CV cycles in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe.

4.2.7.6 Tables summarising the in-situ Raman results

In previous studies, the peak height ratio of the $480\text{ cm}^{-1}/560\text{ cm}^{-1}$ peaks have been used to verify if a NiFe LDH structure is present after Fe incorporation into the bulk⁵⁶. Fe that incorporates into the bulk $\text{Ni}(\text{OH})_2/\text{NiOOH}$ structure will result in larger intersheet spacing, which will reduce the $480\text{ cm}^{-1}/560\text{ cm}^{-1}$ peak height ratio and cause peak broadening. In addition, the Raman shift (peak position) of peaks in the Raman spectra are also very important to analyse these spectra. Therefore, WITech Project Five software was used to fit the peaks in the Raman spectra and the peak positions and peak height ratios are tabulated in Table 4-3 for as-prepared samples and Table 4-4 for cycled samples.

Table 4-3: Peak positions and peak height ratios obtained from the in-situ Raman spectra of as-prepared samples.

	Peak 1 (cm ⁻¹)	Peak 2 (cm ⁻¹)	Ratio
Ni coll			
Pure KOH			
0.55 V	477.6	556.3	2.2
0.6 V	480.7	558.1	2.2
0.007 ppm			
0.55 V	480.0	558.0	2.6
0.6 V	480.5	554.9	2.6
0.3 ppm			
0.55 V	480.4	556.7	2
0.6 V	481.3	557.2	2
1 mM			
0.5 V	479.7	556.2	2
0.55 V	489.0	560.2	2
0.6 V	481.8	558.0	2
Ni red			
Pure KOH			
0.55 V	479.2	554.0	2
0.6 V	478.0	556.1	2
0.007 ppm			
0.4 V	512.0		
0.5 V	502.0		
0.55 V	491.9		
0.6 V	481.8	555.0	1.6
0.3 ppm			
0.55 V	479.6	557.1	1.6
0.6 V	479.5	555.0	2
1 mM			
0.4 V	520.0		
0.5 V	484.6	554.0	1.6
0.55 V	486.8	556.0	1.6
0.6 V	485.7	562.0	1.6

Table continues next page.

Table 4-3 (continue).

NiO red			
Pure KOH			
0.4 V	478.0		
0.5 V	474.0		
0.55 V	477.8		
0.6 V	478.0	553.8	2
0.007 ppm			
0.4 V	480.0		
0.5 V	476.0		
0.55 V	479.2		
0.6 V	477.0	555.0	2
0.3 ppm			
0.4 V	490		
0.5 V	484.0	555.0	1.7
0.55 V	483.9	553.4	1.6
0.6 V	481.4	555.0	1.6
1 mM			
0.4 V	478.6		
0.5 V	480.2	558.6	1.7
0.55 V	482.7	559.5	1.8
0.6 V	484.8	556.0	2.3
NiNiO red			
Pure KOH			
0.5 V	476.0		
0.55 V	478.0	552.0	1.9
0.6 V	479.0	558.0	2.1
0.007 ppm			
0.4 V	479.0		
0.5 V	475.0		
0.55 V	478.0	548.4	1.5
0.6 V	479.4	558.8	2.4
0.3 ppm			
0.4 V	487.0		
0.5 V	477.7	538.0	1.5

Table continues next page.

Table 4-3 (continue).

0.55 V	479.5	557.4	2
0.6 V	481.0	556.0	2
1 mM			
0.4 V	477	546.7	1.5
0.5 V	476.6	546.0	1.5
0.55 V	478.2	552.8	2
0.6 V	482.0	559.6	2

Table 4-3 summarises the peak positions and peak height ratios of the relevant peaks observed in the Raman spectra of the as-prepared samples. At voltages above 0.5 V, a Raman peak between 476 and 484 cm^{-1} and one between 553 and 560 cm^{-1} are observed for the electrocatalysts. Therefore, the oxidation of the Ni or NiO catalysts to NiOOH are observed in these Raman spectra. No trend is apparent for the 480/560 cm^{-1} peak height ratio with increasing concentration of Fe. The ratio seems to vary uniquely for each catalyst in each composition. Studies similar to this one often analyse and compare the 480/560 cm^{-1} peak height ratio at 0.6 V vs Hg/HgO. At this potential, the colloidal Ni sample exhibits peak height ratios of 2.2, 2.6, 2 and 2 for the samples cycled in pure KOH, 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe, respectively. For Ni prepared by reduction, the ratios are 2, 1.6, 2 and 1.6, in the order of increasing electrolytic Fe concentration. The ratios for NiO prepared by reduction are 2, 2, 1.6 and 2.3, in the same order. Lastly, for NiNiO prepared by reduction the ratios are 2.1, 2.4, 2 and 2. From these values, it is clear that no trend is apparent in the peak height ratios. Since cycling the electrocatalysts in the various electrolytes stabilises them, in-situ Raman spectroscopy was also conducted after the samples were cycled. The peak height ratios and peak positions for the nanoparticles after cycling are summarised in Table 4-4.

Table 4-4: Peak positions and peak height ratios obtained from the in-situ Raman spectra of cycled samples.

	Peak 1 (cm ⁻¹)	Peak 2 (cm ⁻¹)	Ratio	Other peaks (cm ⁻¹)
Ni coll				
Pure KOH				
0.5 V	477	553	2	
0.55 V	477	555	2	
0.6 V	478	554	2	
0.007 ppm				
0.3 V	481.5			
0.4 V	489.3			
0.5 V	475.0	551.0	2	
0.55 V	476.3	551.0	2	
0.6 V	476.6	555.0	2	
0.3 ppm				
0.5 V	478.9	558.5	2.7	
0.55 V	480	558	2.9	
0.6 V	480.8	559	2.3	
1 mM				
0.3 V	513.8			
0.4 V	510.7			
0.5 V	486.0			303.44, 395.7, 678.2
0.55 V	499.0			303.0, 397.3, 675.2
0.6 V	480.7	541.9	2	301.2, 400.8, 676.0
NiO coll				
Pure KOH				
0.4 V	469.0			
0.5 V	492.0			
0.55 V	476.0	553.7	1.7	
0.6 V	478.0	554.0	1.7	
0.007 ppm				
0.4 V	477.0	555.0	2	
0.5 V	477.0	553.0	2	
0.55 V	478.0	556.0	2	
0.6 V	478.0	554.0	2	

Table continues next page.

Table 4-4 (continue).

0.3 ppm			
0.3 V	494.4		
0.4 V	479.5		
0.5 V	475.7	551.0	2
0.55 V	476.0	551.0	2
0.6 V	476.0	551.0	2
1 mM			
0.3 V	504		
0.4 V	500		
0.5 V	500		300.9, 398.2, 671.0
0.55 V	500		300.7, 400.3, 672.0
0.6 V	482.2		302.0, 400.4, 673.7
Ni red			
Pure KOH			
0.3 V	518.0		
0.4 V	482.0	548.0	1
0.5 V	477.0	551.0	1.5
0.55 V	478.0	548.0	1.5
0.6 V	478.0	552.0	1.8
0.007 ppm			
0.3 V	512.1		
0.4 V	506.0		
0.5 V	480.0	553.3	1.4
0.55 V	478.8	552.6	1.4
0.6 V	478.0	557.0	2
0.3 ppm			
0.55 V	481.0	542.0	1.4
0.60 V	478.0	555.0	2
1 mM			
0.4 V	488.0		
0.5 V	483.1	543.0	1.6
0.55 V	483.1	540.0	1.6
0.6 V	478.0	550.0	1.6

Table continues next page.

Table 4-4 (continue).

NiO red					
Pure KOH					
0.3 V	479.0				
0.4 V	476.9	552.0	1.6		
0.5 V	476.5	552.0	1.6		
0.55 V	477.0	551.2	1.6		
0.6 V	483.1	548.0	1.6		
0.007 ppm					
0.3 V	488.0				
0.4 V	482.0				
0.5 V	481.0				
0.55 V	477.0	540.0	1.6		
0.6 V	480.4	542.0	1.6		
0.3 ppm					
0.3 V	485.3				
0.4 V	480.4				
0.5 V	479.6				
0.55 V	481.9	552.0	2	304.0, 400.3, 670.0	
0.6 V	481.0	555.0	2		
1 mM					
0.3 V	487.5				
0.4 V	485.0				
0.5 V	479.9				
0.55 V	484.5			303.0, 678.0	
0.6 V	483.0	556.4	2		
NiNiO red					
PureKOH					
0.3 V	502.0				
0.4 V	504.0				
0.5 V	500.0				
0.55 V	481.6	550.0	1.5		
0.6 V	478.0	552.0	2		
0.007 ppm					
0.3 V	473.0	548.9	1.4		

Table continues next page.

Table 4-4 (continue).

0.4 V	476.0	552.0	1.4	
0.5 V	478.3	551.0	1.6	
0.55 V	477.0	554.0	1.6	
0.6 V	478.0	554.0	2	
0.3 ppm				
0.3 V	482.3	549.3	1	
0.4 V	474.4	552.0	1.5	986.0, 1062.3
0.5 V	475.0	555.0	1.6	986.0, 1060.0
0.55 V	479.3	549.1		986.0, 1062.0
0.6 V	478.8			987.0, 1062.0
1 mM				
0.3 V	500.8			302.4, 396.0, 685.0
0.4 V	500.8			303.7, 397.6, 677.0
0.5 V	483.2	552.0	1.5	304.7, 393.0, 663.0
0.55 V	489.2	550.0	1.5	
0.6 V	485.0	554.2	1.5	

The peak positions and peak height ratios in the Raman spectra of post-cycled samples are summarised in Table 4-4. For the samples containing two peaks (NiOOH), the first peak occurs between 476 and 489.2 cm^{-1} and the second peak between 553 and 560 cm^{-1} . The ranges within which these peaks appear are larger than those of the as-prepared samples. This is due to the effect of incorporating Fe causing more shifts in the peak positions. In general, the first peak ($\sim 480 \text{ cm}^{-1}$) shifts to slightly higher wavelengths as the electrolytic Fe concentration increases. In addition, when peaks for FeOOH is also present in a spectrum, the second peak (560 cm^{-1}) is not present, or present at lower wavelengths, thereby decreasing the distance between the 480 and 560 cm^{-1} peaks. Again, no specific trend is seen from the values of the peak height ratios. The 480/560 cm^{-1} peak height ratios for all of the samples at 0.6 V are summarised in. From this figure it can clearly be seen that no trend exists for the peak height ratios of the samples at 0.6 V vs Hg/HgO, as reported in previous studies⁶. The most common peak height ratio seen throughout all the samples is 2.

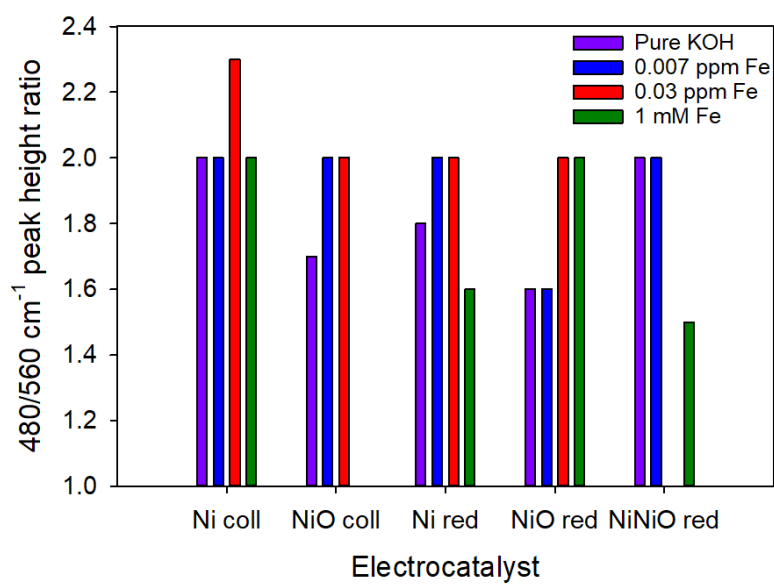


Figure 4-48: The 480/560 cm^{-1} peak height ratio of each of the electrocatalysts at 0.6 V vs Hg/HgO.

5. SPUTTERED THIN FILMS

In this section, electrocatalysts prepared with PVD magnetron sputtering serves as the samples under investigation. The sputtered thin films provide additional information on top of that gathered from the nanoparticle samples, that can be used to elucidate the effect of electrolytic Fe on Ni electrocatalysts. This section is divided into two sections. Section 5.1 is devoted to the experimental methods used to prepare and analyse the sputtered thin films. Section 5.2 discusses the results obtained after applying these methods.

5.1 Experimental

This subsection starts by describing in detail how the sputtered thin films were prepared, before moving on to the physical characterisation methods used to analyse them. Lastly, electrochemical analyses and in-situ Raman spectroscopy is discussed.

5.1.1 Sputtering Ni, NiO and NiNiO thin films

Before sputtering the thin films, GC disks (Sigradur G, HTW Germany) were prepared as substrates. The diameter of the disks are 0.5 mm and the height 0.4 mm. The disks were polished on microfiber cloths in a figure of eight using diamond paste (0.1 μm) and alumina suspension (0.05 μm , Gamma Micropolish II, Beuhler). In between polishing with the two different particle sizes, the disks were rinsed with ultrapure water. Lastly, the disks were consecutively sonicated in milliQ water, 1 M pure KOH and isopropanol for 10 minutes in each solvent.

Pure Ni, NiO and NiNiO films were magnetron sputtered onto polished GC substrates using a custom-made PVD system (PVD products, USA). A pure Ni target (99.99 % from ACI Alloys, Inc.) as well as a NiO target (99.99 % from ACI Alloys, Inc.), was used to deposit these thin films under ultra-high vacuum (UHV) conditions. The films containing Ni were sputtered using Direct Current magnetron sputtering. The NiO target is sputtered with radiofrequency (RF) power. Argon was used as the sputtering gas and at an Ar flow rate of 0.025 L/min and a chamber pressure of 10 mTorr, the flow rate was calibrated. Accordingly, the calibration equation $y = 0.1171x - 0.3756$ was attained, where y represents the sputtering rate (nm/min), and x denotes the power (W). Subsequently, this equation was used to determine the amount of time needed to sputter a 50 nm film.

At 90 W power, a base pressure of 10 mTorr and an Ar flow rate of 0.025 L/min, 5 min and 56 s of sputtering yielded uniform Ni films of 50 nm. NiO films were prepared by reactive sputtering with oxygen. The same conditions were used as described for the Ni films, with the only change being that oxygen was bled into the sputtering chamber at a flow rate of 0.005 L/min. It was found

that reactively sputtered NiO delaminated severely in KOH electrolyte when sputtered directly onto a polished GC electrode surface. To solve this problem, a thin layer (10 nm) of Ni was sputtered onto the GC surface, followed by a 40 nm layer of reactively sputtered NiO. NiNiO was prepared by simultaneously using the Ni and NiO targets. Ni was sputtered at 90 W while NiO was simultaneously sputtered at 50 W, for 5 min and 56 s. Sputtered Ni and NiNiO films had a polished silver appearance whereas the sputtered NiO films had a glossy black colour with a blueish hue.

5.1.2 SEM and EDX

SEM (FEI Quanta FEG 250) with an integrated XMax 20 EDX system (Oxford instruments) was used to determine the compositions of the sputtered thin films semi-quantitatively. Since the sputtered thin films are amorphous and thin, XRD could not be used as a physical characterisation technique to analyse the compositions of these samples as with the nanoparticles (for nanoparticles, powder XRD could be employed). Therefore, EDX is a feasible alternative to evaluate if the desired compositions have been sputtered. Furthermore, the samples were subjected to EDX after cycling in different concentrations of Fe. Three to five different spots on the electrode surfaces were analysed. EDX mapping was also done on the entire electrode surface to visualise the distribution of Ni and O, as well as Fe, after cycling.

5.1.3 XPS

XPS was performed by using an Axis Ultra DLD instrument (Kratos Analytical). The nonmonochromated Mg K α flood source was not available for the XPS analysis of the sputtered thin films. Consequently, a monochromatic Al source was used. CasaXPS (Casa Software, Ltd.) was used to analyse the raw XPS data. The spectra were calibrated according to the C 1s peak at 284.8 eV.

5.1.4 Electrochemical analyses

Glassy carbon disks (Sigradur G, HTW Germany) with sputtered Ni, NiO or NiNiO thin films on their surface were inserted into an interchangeable disk rotating disk electrode, which served as the working electrode for electrochemical analysis. The rest of the electrochemical setup and experiments are the same as described for the nanoparticles in section 4.1.3.

5.1.5 In-situ Raman spectroscopy

The sputtered Ni-based thin films were subjected to in-situ Raman spectroscopy in the same manner as the nanoparticle electrocatalysts. However, no signal could be seen in the Raman spectra of these samples. Even upon increasing the accumulations and integration time, focusing

on different spots on the surface, and increasing the laser power to 10 mW, no peaks for the Ni thin films were seen. Furthermore, no NiOOH peaks were seen at prolonged polarisation of the electrode at 0.6 V vs Hg/HgO. In addition, the spectra were very noisy. Therefore, in-situ Raman spectroscopy could not be used to study the sputtered thin films in this study. These films are amorphous, very thin and have a mirror-like appearance. All of these aspects make them difficult to analyse with in-situ Raman spectroscopy. The mirror-like appearance could cause excessive light-scattering which might be the cause of the noisy spectra.

5.2 Results

Firstly, this section presents the results obtained from SEM-EDX analyses. These results, along with the XPS results discussed in the next subsection, are an indication of the successful preparation of the thin films. In addition, both EDX and XPS results give information about the Fe content and oxidation of the Ni thin films before and after electrochemical cycling. Lastly, the results obtained from electrochemical analyses are presented.

5.2.1 SEM-EDX results of sputtered Ni-based thin films

Since the sputtered thin films are only thin, flat surfaces, useful information is not obtained from SEM images of these samples. As an example of this, SEM images of sputtered Ni at 3 mm and 3 μ m magnification can be seen in Figure 5-1. However, energy dispersive X-ray spectrometry (EDX) was used to semi-quantitatively determine the relative amounts of Ni, O and Fe in the sputtered samples before and after electrochemical cycling.

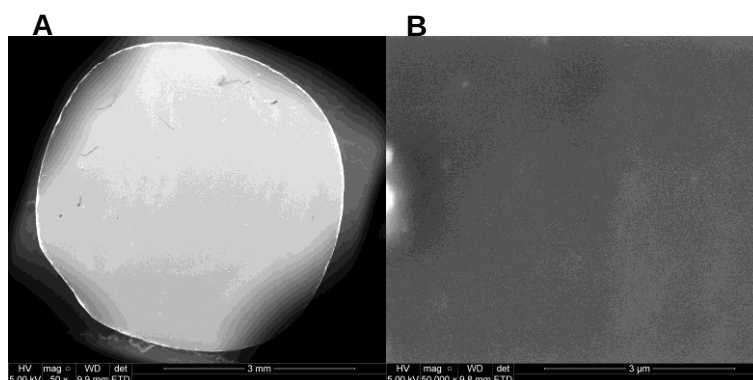


Figure 5-1: SEM images of sputtered Ni at (a) 3 mm and (b) 3 μ m magnification.

In Figure 5-2, the percentage oxygen relative to Ni in each of the samples, obtained through EDX analysis, are summarised. As-prepared samples, as well as samples after 30 CV cycles in each of the Fe concentrations were analysed. Three to five spots on the surfaces of the electrocatalysts were analysed with EDX and the average values are reported.

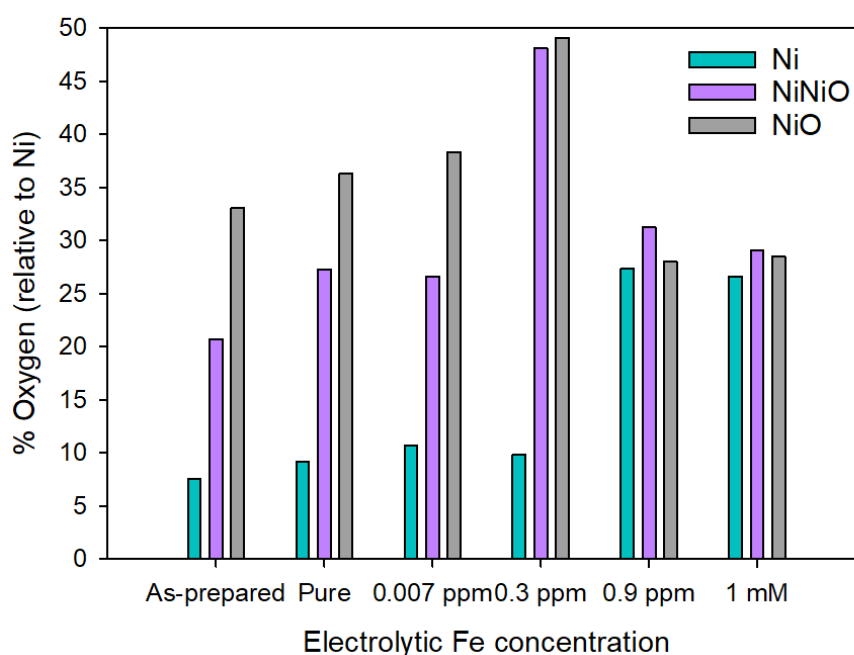


Figure 5-2: The percentage oxygen relative to the percentage Ni in each of the as-prepared sputtered samples, as well as after cycling in each electrolyte.

The EDX results of the as-prepared samples indicate that the thin films have successfully been prepared. This is because NiO clearly contains the highest percentage of oxygen (33.07 %), and Ni the lowest percentage (7.58 %). Oxygen is expected to be present for Ni samples as it is well-known that a thin layer of NiO forms on the surface of a Ni electrode upon exposure to air. The percentage oxygen present for as-prepared NiNiO (20.70 %) is in-between that of Ni and NiO, showing that the intended mixture of Ni and NiO is plausible.

Furthermore, the change in oxygen content of the sputtered thin films after cycling in different concentrations of Fe can be seen in Figure 5-2. The sputtered Ni samples cycled in pure KOH, 0.007 ppm Fe and 0.3 ppm Fe contain almost the same amount of oxygen, which is slightly higher than the as-prepared sample. The Ni samples cycled in 0.9 ppm Fe and 1 mM Fe have similar oxygen contents, which is more than three times that of the as-prepared sample. Therefore, for the sputtered Ni electrocatalyst, cycling in KOH containing higher concentrations of Fe, led to the films being more oxidised. NiNiO films cycled in pure KOH and 0.007 ppm Fe have similar oxygen concentrations, slightly higher than that of the as-prepared sample. The NiNiO film cycled in 0.3 ppm has the largest oxygen concentration, which is more than double that of the as-prepared sample. The NiNiO samples cycled in 0.9 ppm Fe and 1 mM Fe again have similar concentrations of oxygen, which is higher than the samples cycled in pure KOH and 0.007 ppm Fe, but lower than the sample cycled in 0.3 ppm. Lastly, sputtered NiO electrocatalysts cycled in pure KOH and 0.007 ppm Fe again have similar oxygen concentrations, like the other two thin films. The NiNiO

sample cycled in 0.3 ppm Fe also has the highest oxygen concentration, similar to the NiO thin film. Again, the oxygen concentrations of the NiNiO films cycled in 0.9 ppm Fe and 1 mM are similar, but lower than all of the other NiNiO samples. Additionally, something interesting to note is that all samples cycled in 0.9 ppm Fe and 1 mM Fe of each of the electrocatalysts have similar oxygen content, even though the oxygen concentrations of the as-prepared samples differ dramatically.

The Fe concentrations of the sputtered thin films were also analysed with EDX before and after cycling in KOH containing different concentrations of Fe. These results are summarised in Table 5-1. The first thing that is important to note is that the Fe concentrations vary greatly from one point on the surface of the thin films to the next. This shows that during electrochemical cycling in Fe containing electrolytes, Fe does not incorporate into the films homogeneously. Fe seems to incorporate/adsorb as clusters, similar to what was found by a recent study¹¹. After the samples cycled in 0.3 ppm Fe were investigated, it was found that more than three spots on the surface of these thin films need to be analysed to obtain a better average value for the Fe concentration. Therefore, five points were analysed for the samples cycled in 0.9 ppm Fe and 1 mM Fe. The average concentrations of Fe on each surface were calculated and are reported in Table 5-1. For as-prepared samples and samples cycled in pure KOH and 0.007 ppm Fe, the Fe concentration was zero, or below the detection limit of EDX. For Ni, NiNiO and NiO films, the samples cycled in 1 mM Fe contain the highest average Fe concentration. For the sputtered Ni samples, the average Fe concentration in the films increase as the electrolytic Fe concentration increases. For both NiNiO and NiO films, the samples cycled in 0.3 ppm Fe have higher Fe concentrations than the samples cycled in 0.9 ppm Fe. Furthermore, the NiNiO samples seem to have the highest Fe concentrations on average.

Table 5-1: The percentage of Fe relative to the percentage of Ni in each of the as-prepared sputtered samples, as well as after cycling in each electrolyte.

	% Fe relative to Ni		
	Ni	NiNiO	NiO
As-prepared	0	0	0
Pure KOH	0	0	0
0.007 ppm Fe	0	0	0
0.3 ppm Fe	0.07	1.67	1.2
	0.45	2.23	0.14
	0.44	1.65	0.28
	Average:	0.32	0.54
0.9 ppm Fe	0.17	1.15	0.65
	0.50	0.36	0.40
	0.59	0.91	0
	0.37	0.97	0.71
	0.60	0.53	0.014
	Average:	0.45	0.35
1 mM Fe	0.53	1.93	1.14
	0.36	3.03	1.09
	0.74	0.97	1.30
	0.81	2.28	1.32
	0.96	1.92	1.05
	Average:	0.68	1.18

In addition, SEM-EDX mapping was performed on Ni, NiO and NiNiO samples cycled in 0.9 ppm and 1 mM Fe. This was done to observe the distribution of Ni, Fe and O on the surface of the thin films after cycling in electrolytes containing significant amounts of Fe. The mapping images show that Ni and O are homogeneously distributed, whereas Fe is not. This is the case for Ni, NiO and NiNiO cycled in both 0.9 ppm Fe and 1 mM Fe. Therefore, one representative image of the distribution of these elements are shown. To see the elemental mapping for the rest of the samples, the reader is referred to Figure B-1 to Figure B-5 in Appendix B.

In Figure 5-3, the red images indicate the distribution of Ni on the surface, green the distribution of oxygen.

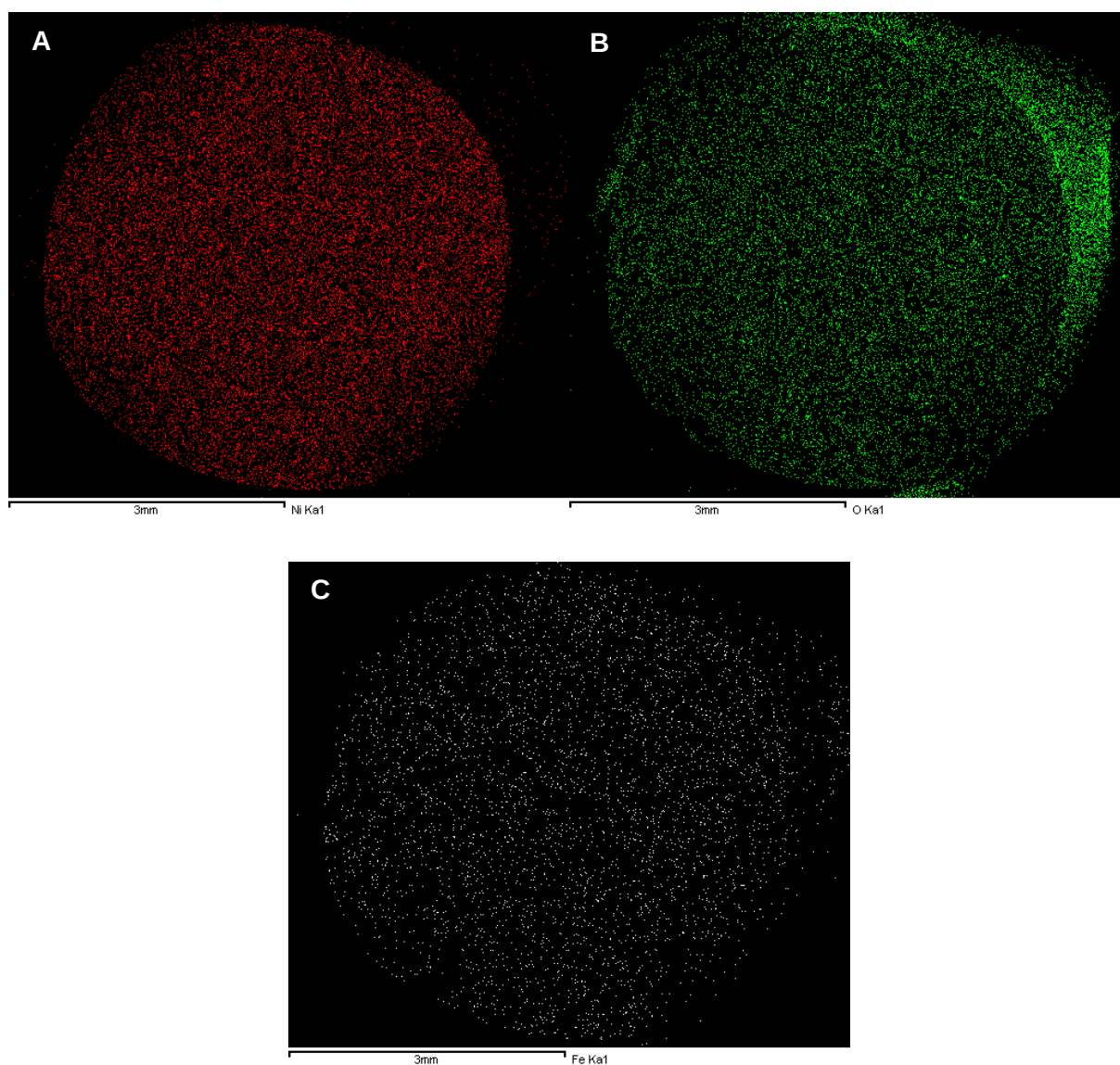


Figure 5-3: SEM-EDX mapping analysis of the entire surface of a sputtered Ni thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.

Figure 5-3 shows that Ni and oxygen are homogeneously distributed on the surfaces on the films. Fe, however, is not and it is clear from these images why different concentrations of Fe are detected at different spots on the surfaces of these samples.

5.2.2 XPS of sputtered Ni-based samples

XPS analysis was performed on all three of the sputtered electrocatalysts samples before and after cycling in pure KOH, and KOH containing 0.007 ppm Fe, 0.3 ppm Fe and 1 mM Fe. For each sample, a survey spectrum was collected first, to see what elements are present in the sample.

An example of a survey spectrum for one of the sputtered samples after cycling can be seen in Figure 5-4.

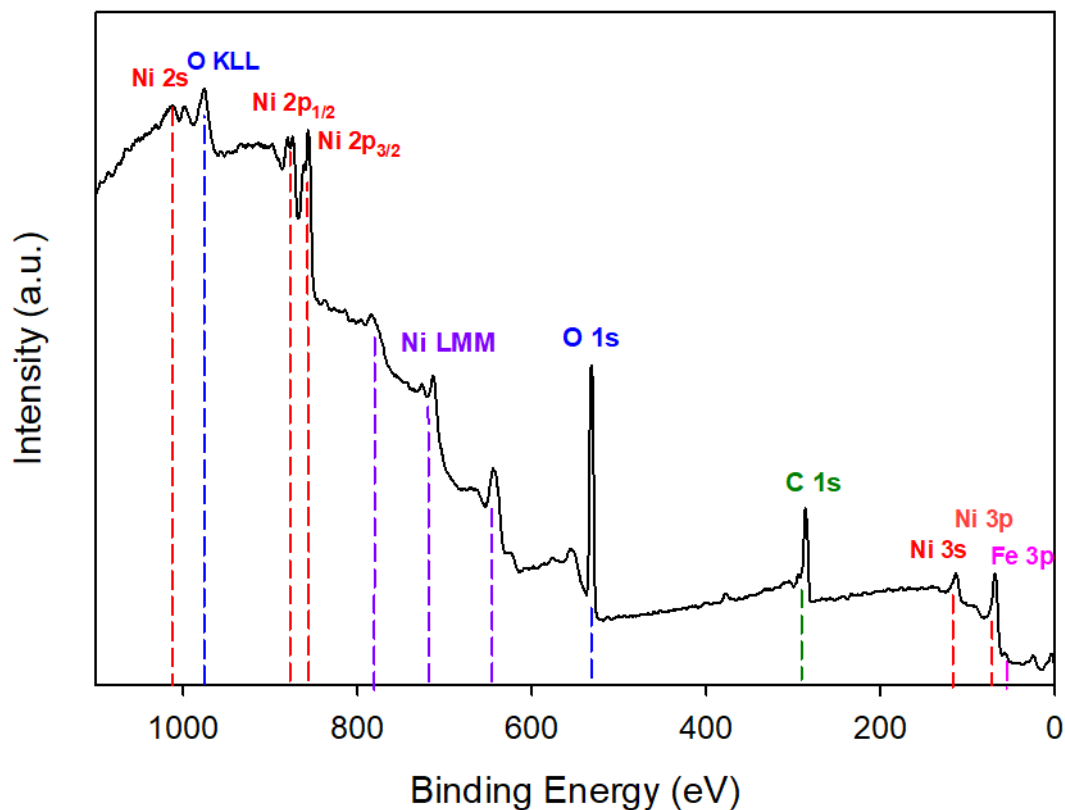


Figure 5-4: XPS survey spectrum for sputtered Ni after cycling in KOH containing 1 mM Fe.

From the survey spectrum it is seen that Ni, Fe, carbon and oxygen are present. After the survey spectra have been collected, high resolution regional scans were performed of the Ni 2p, O 1s, Ni 3p and Fe 3p peaks. Each of these will now be discussed in more detail.

Each Ni 2p XPS spectra consists of Ni 2p_{3/2} (~850 to 860 eV) and Ni 2p_{1/2} (~870 to 875 eV) peaks due to multiplet splitting, as well as satellite peaks (~860 and 880 eV). The Ni 2p_{3/2} and Ni 2p_{1/2} peaks consist of component peaks, which are indicative of the oxidation states of the Ni samples. Ni 2p_{3/2} is the peak that best shows the oxidation states and will consequently be used to discuss the oxidation states of all the sputtered Ni Ni 2p XPS spectra. To see the exact peak positions of the entire Ni 2p XPS spectrum of each sample, the reader is referred to Table B-1 in Appendix B. Figure 5-5 displays the XPS spectra of the as-prepared sputtered electrocatalyst along with the spectra of this electrocatalyst after it has been cycled in KOH containing different concentrations of Fe.

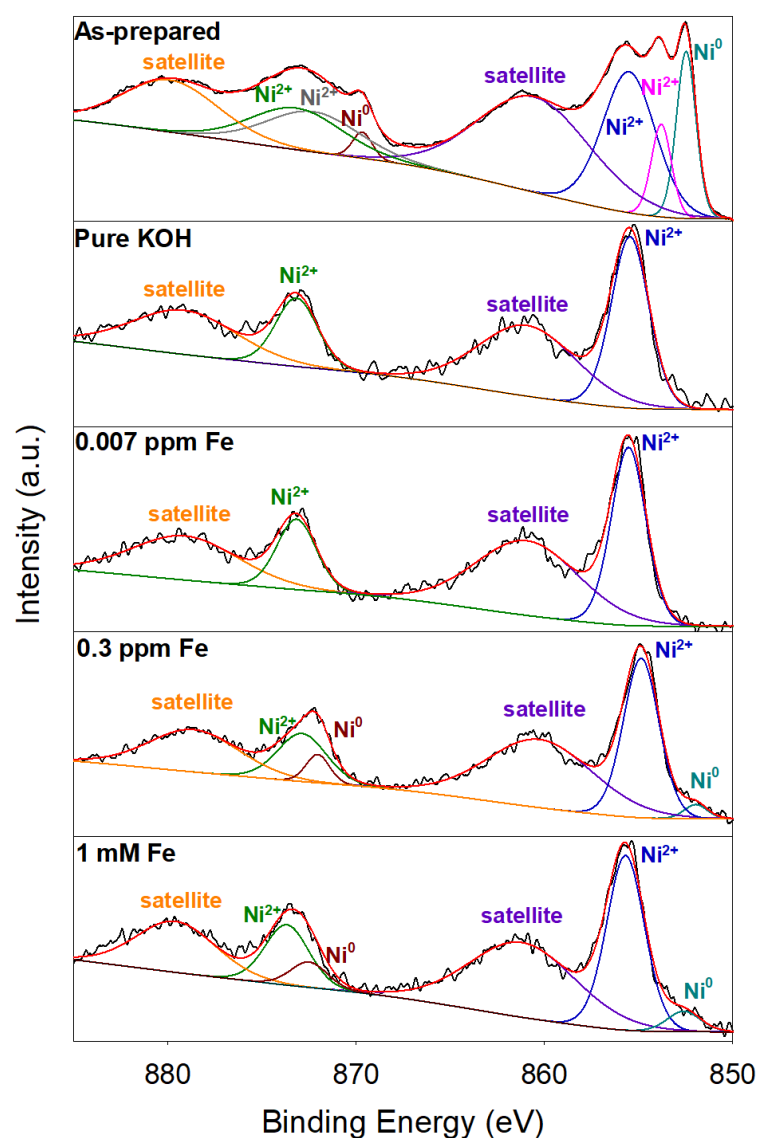


Figure 5-5: Ni 2p XPS spectra of as-prepared sputtered Ni and sputtered Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

Figure 5-5 shows that sputtered Ni consists of two Ni species in the +2 oxidation state and a large portion of metallic Ni. The component peak at 855.5 eV corresponds to $\text{Ni}(\text{OH})_2$ and the one at 853.8 eV corresponds to NiO. $\text{Ni}(\text{OH})_2$ and NiO are present on the surface of sputtered Ni due to spontaneous reactions with the atmosphere. The Ni 2p XPS spectra of sputtered Ni samples cycled in pure KOH and 0.007 ppm Fe both display only one oxidation state evidenced by a component peak at 855.5 eV. Therefore, after cycling in pure KOH and 0.007 ppm Fe, only $\text{Ni}(\text{OH})_2$ is present. Small peaks corresponding to metallic Ni (~ 852 eV) are present for sputtered Ni samples cycled in 0.3 ppm Fe and 1 mM Fe. These peaks are present together with large peaks corresponding to $\text{Ni}(\text{OH})_2$.

Figure 5-6 shows the Ni 2p XPS spectra of the pristine sputtered NiO electrocatalyst, as well as that of sputtered NiO after 30 CV cycles in pure KOH and KOH containing different concentrations of Fe.

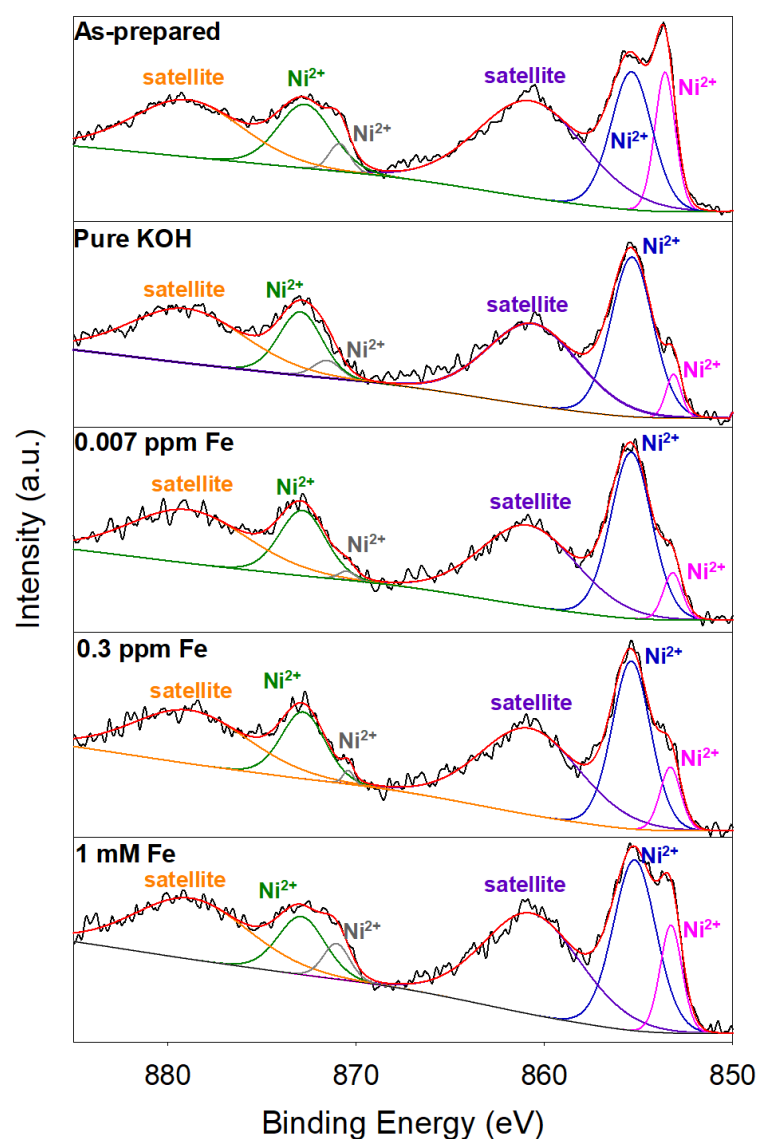


Figure 5-6: Ni 2p XPS spectra of as-prepared sputtered NiO and sputtered NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe

From this figure, it can be seen that as-prepared sputtered NiO consists of two Ni^{2+} oxidation states. The $\text{Ni } 2p_{3/2}$ component peak at 855.4 eV arises due to the presence of $\text{Ni}(\text{OH})_2$ in the sample and the peak at 853.6 eV due to the presence of NiO. The fact that no metallic Ni is present indicates that NiO has been successfully prepared by reactive sputtering. $\text{Ni}(\text{OH})_2$ is present on the surface due to reactions of the NiO surface with the atmosphere. Furthermore, Figure 5-6 shows that the Ni^{2+} peak corresponding to NiO shrinks significantly after 30 CV cycles

in pure KOH, compared to the pristine sample. As previously mentioned, peaks occurring at higher binding energies are more oxidized. Since the Ni^{2+} peak corresponding to NiO occurs at a lower binding energy (853.1 eV) than the peak corresponding to $\text{Ni}(\text{OH})_2$ (855.4 eV), it shows that the sample becomes more oxidized after 30 CV cycles in pure KOH. The NiO peak for the sample cycled in 0.007 ppm Fe is more or less the same size than that of the sample cycled in pure KOH. However, for the sample cycled in 0.3 ppm Fe the peak at ~853 eV is larger, and the largest for the sample cycled in 1 mM Fe. Therefore, The Ni 2p XPS spectra show that sputtered NiO cycled in KOH is less oxidized (contains more NiO with respect to $\text{Ni}(\text{OH})_2$) as the electrolytic Fe concentration increased.

Lastly, sputtered NiNiO was investigated with XPS and the Ni 2p XPS spectra can be seen in Figure 5-7. This figure shows that as-prepared sputtered NiNiO contains metallic Ni (Ni^0 component peak at 852.1 eV) and Ni in the +2 oxidation state as NiO (853.6 eV) and $\text{Ni}(\text{OH})_2$ (855.5 eV). Upon cycling in pure KOH, the NiNiO sample becomes oxidized and only contains $\text{Ni}(\text{OH})_2$, evidenced by a single Ni $2p_{3/2}$ component peak at 855.4 eV. The same is true for the NiNiO sample cycled in KOH containing 0.3 ppm Fe. NiNiO cycled in KOH containing 0.007 ppm Fe and 1 mM Fe both contain small amounts of metallic Ni, evidenced by the small peak present at 852 eV in both of these spectra.

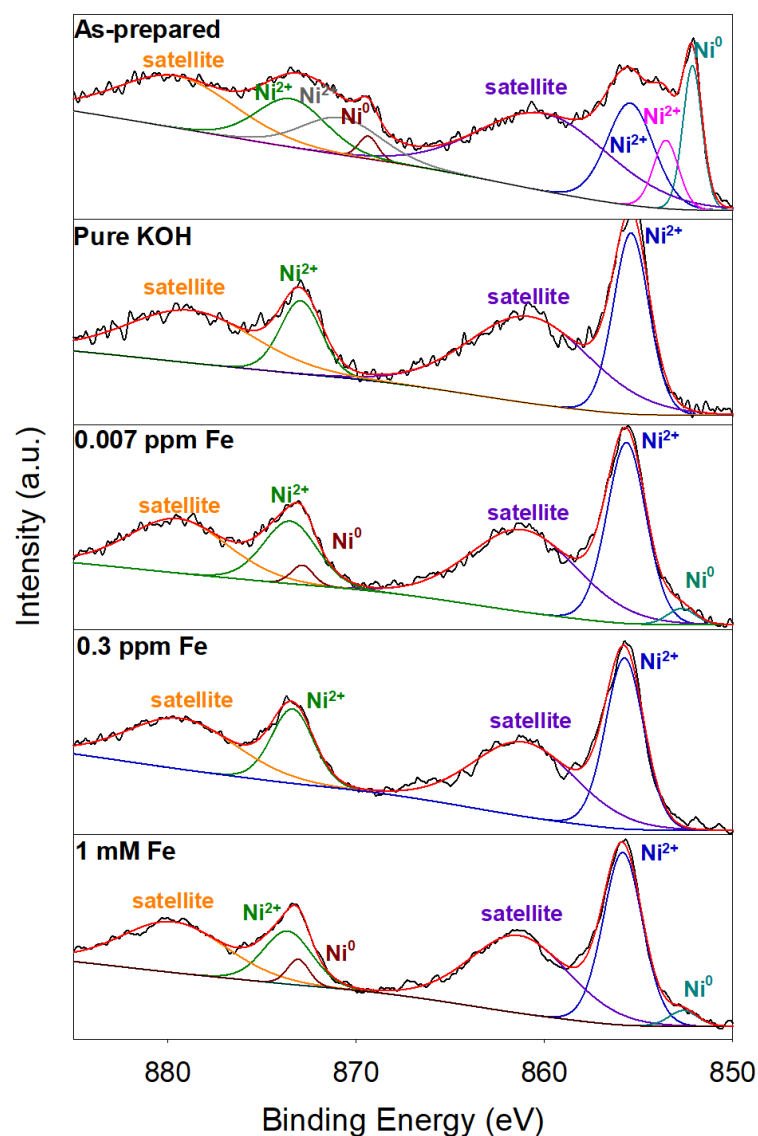


Figure 5-7: Ni 2p XPS spectra of as-prepared sputtered NiNiO and sputtered NiNiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

In addition to Ni 2p, high resolution scans of the O 1s peak was also performed for sputtered Ni-based samples. Since no other oxygen containing components are present in these samples, the O 1s region would be a good reflection of the oxygen present on the surface of these samples.

Three component peaks are seen for each of the sputtered samples. The peak at the highest binding energy (~ 532 eV), likely arises due to the presence of adsorbed water on the surface⁸. However, this peak has previously been ascribed to NiOOH¹²⁵. It is difficult to exactly ascribe each peak to a specific bond, since Fe-O and Ni-O species also have very similar binding energies. However, previous studies of Ni electrocatalysts in Fe containing electrolyte described the peak

at 531 eV as Ni-OH ($\text{Ni}(\text{OH})_2$) and the peak at 529 eV to Ni-O (NiO). Since it is also known that species occurring at higher binding energies are more oxidized, these spectra can show if the surfaces become more or less oxidised upon cycling in electrolytes containing different concentrations of Fe. The O 1s XPS spectra for sputtered Ni samples can be seen in Figure 5-8.

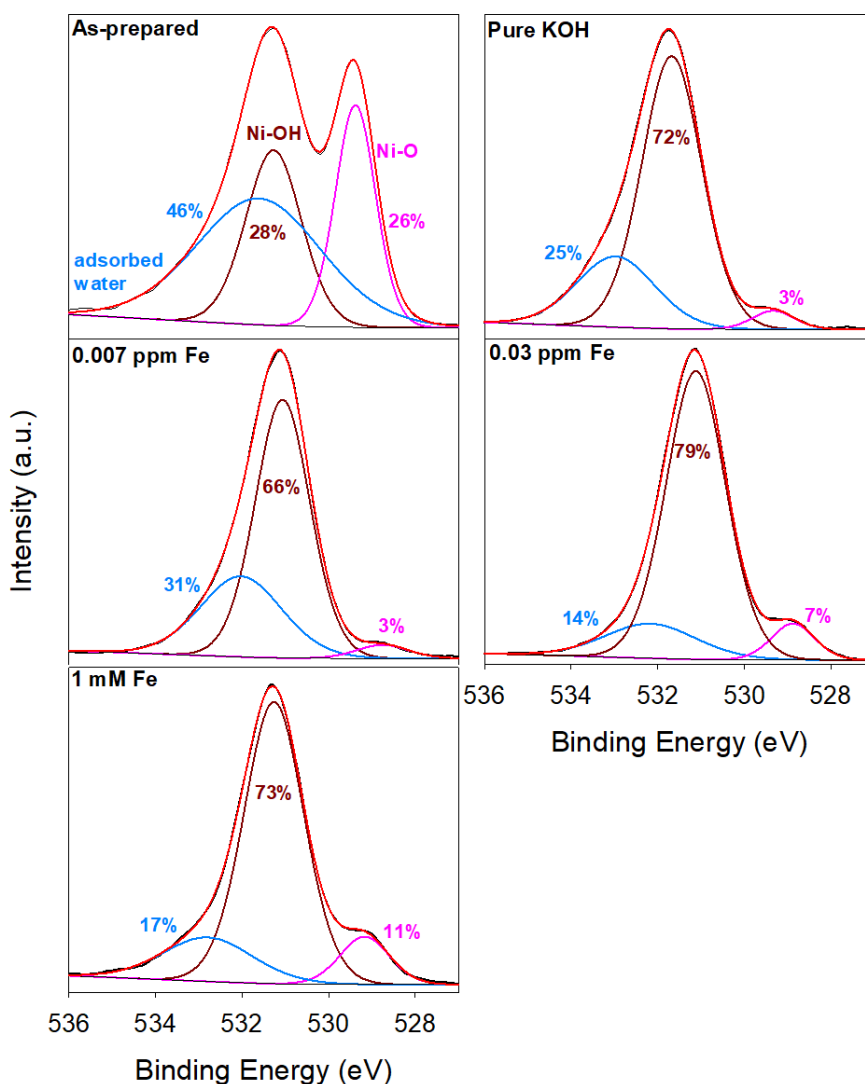


Figure 5-8: O 1s XPS spectra of as-prepared sputtered Ni and sputtered Ni after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

Figure 5-8 shows that the pristine sputtered Ni sample and the sample cycled in 1 mM Fe have the highest concentrations of NiO, which is the least oxidized species. The concentrations of NiO in the samples cycled in pure KOH and 0.007 ppm Fe are the same, and that of the sample cycled in 0.3 ppm Fe slightly higher. These results are in good agreement with a previous study that found that cycling Ni electrocatalysts in electrolyte containing concentrated amounts of Fe

resulted in the films being less oxidized, whereas cycling in lower Fe concentrations left the films more oxidised⁸.

Figure 5-9 shows the O 1s XPS spectra of as-prepared sputtered NiO and NiO cycled in KOH containing different concentrations of Fe.

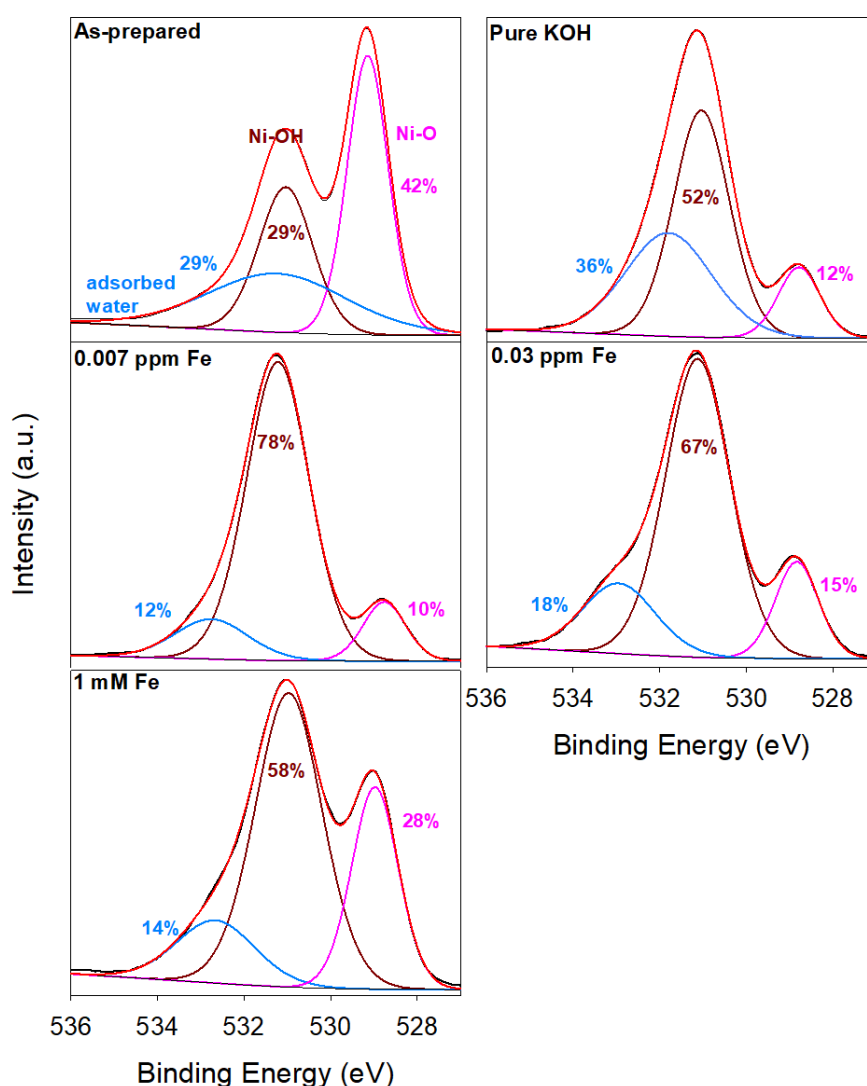


Figure 5-9: O 1s XPS spectra of as-prepared sputtered NiO and sputtered NiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe.

From Figure 5-9, the same trend is seen as in Figure 5-8. The as-prepared sputtered NiO sample and the sample cycled in 1 mM Fe are the least oxidized. The sample cycled in 0.3 ppm Fe is slightly less oxidized than the samples cycled in pure KOH and 0.007 ppm Fe, which are all more oxidized than the sample cycled in concentrated Fe.

Lastly, Figure 5-10 shows the O 1s spectra of NiNiO.

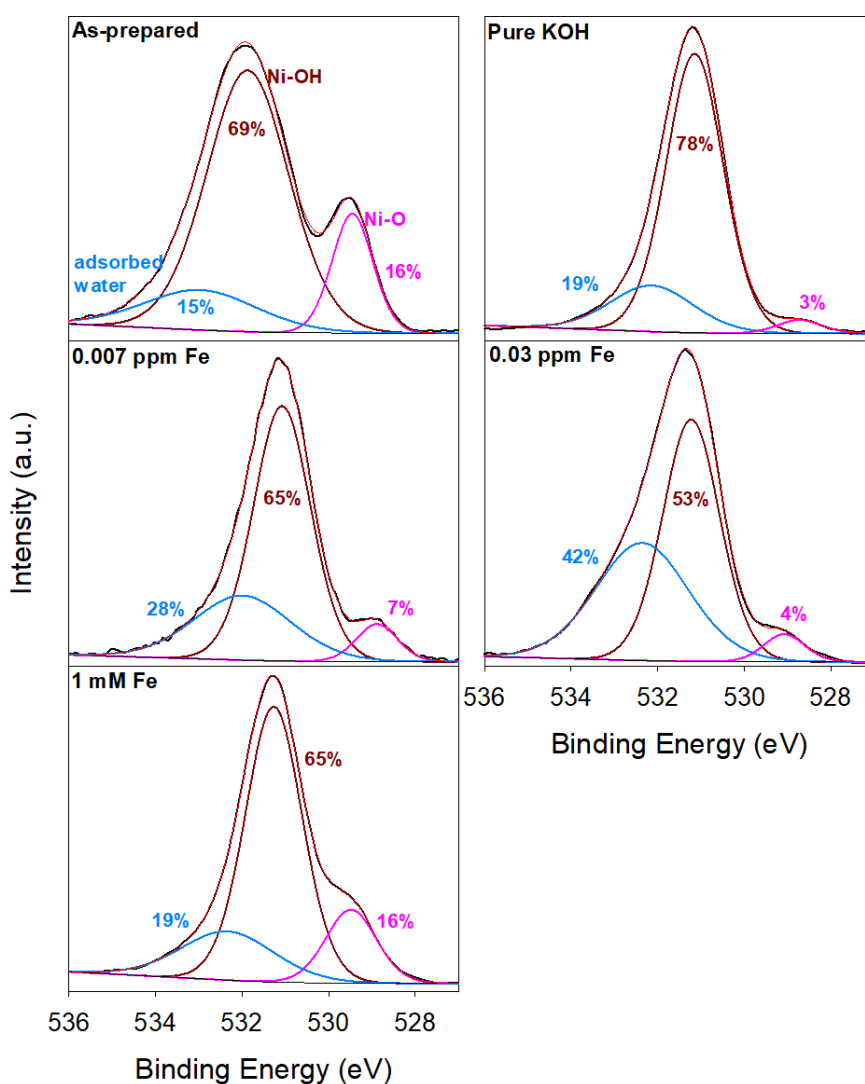


Figure 5-10: O 1s XPS spectra of as-prepared sputtered NiNiO and sputtered NiNiO after 30 CV cycles in pure KOH and KOH containing 0.007 ppm, 0.3 ppm and 1 mM Fe

Figure 5-10 shows again that the pristine NiNiO sample and the sample cycled in 1 mM Fe are the least oxidized.

XPS was also used to quantify the amount of Fe present in the sputtered samples before and after cycling. Since achromatic Mg K α radiation was not available, a monochromated Al K α X-ray source had to be used. Therefore, Ni auger peaks rendered the Fe 2p peak impractical for quantification or other analyses. Thus, high resolution scans of Ni 3p and Fe 3p peaks were used to quantify the XPS spectra of the sputtered Ni samples. As an example, Figure 5-11 shows the Ni 3p and Fe 3p peaks for the spot at the center on the surface of each sputtered Ni sample cycled in different concentrations of Fe, as well as the pristine sample.

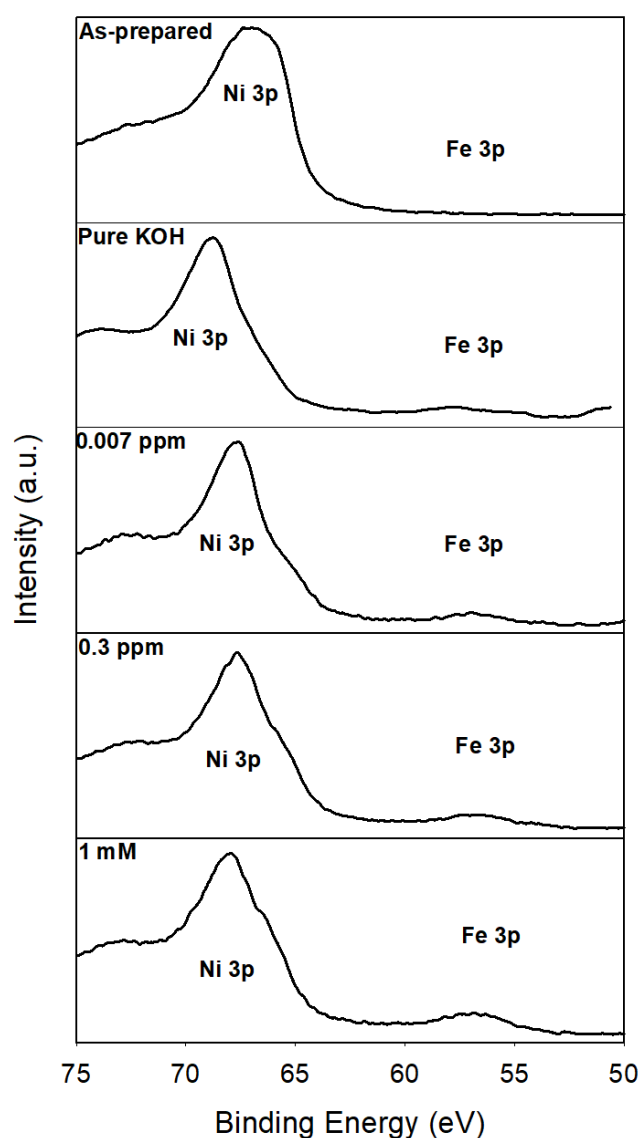


Figure 5-11: Ni 3p and Fe 3p XPS peaks of sputtered Ni as-prepared and cycled in KOH containing different concentrations of Fe.

From Figure 5-11 it can be seen that the Fe 3p peak grows bigger as more Fe is present in the electrolyte. Three spots on the surface of each sample were quantified to obtain an indication of the homogeneity of the Fe on the surface. Therefore, three concentrations will be reported for each sample in the bar charts in Figure 5-12, Figure 5-13 and Figure 5-14. The first spot is approximately at the center of the sample, where the other two are each 1 mm away, so that the three points form a 90° angle. The bar chart representing the Fe concentrations on the surface of the sputtered Ni sample can be seen in Figure 5-12.

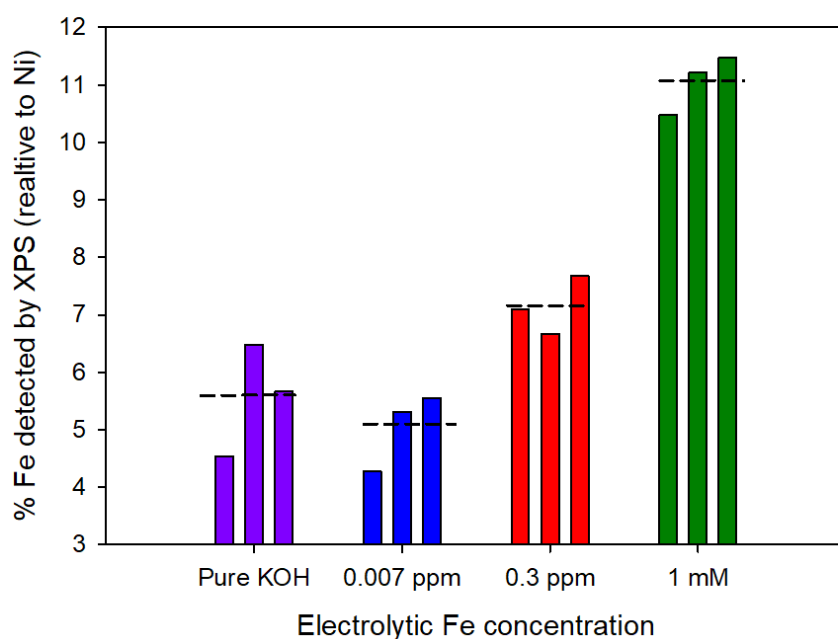


Figure 5-12: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered Ni electrocatalysts cycled in KOH containing different concentrations of Fe.

The pristine sample is not included in this bar chart, as no Fe is detected on its surface. In Figure 5-12, it can be seen that different Fe concentrations are found at different spots on the surface of the sputtered Ni electrocatalyst after cycling in pure KOH as well as KOH containing different concentrations of added Fe. This means that Fe is not homogeneously distributed on the surface of the samples after cycling. The black dashed lines indicate the averages of the Fe concentrations. The sample cycled in pure KOH has an average Fe concentration of 5.56% relative to Ni. This is similar to that of the sample cycled in KOH containing 0.007 ppm Fe, which is 5.04%. The sample cycled in 0.3 ppm Fe has a slightly higher average Fe concentration of 7.15%, whereas the sample cycled in 1 mM Fe has the largest Fe concentration of 11.15%.

Figure 5-13 represents the Fe concentrations at three points on the surface of a NiO electrocatalyst that has been cycled in KOH containing different concentrations of Fe. This figure shows again that Fe is not homogeneously distributed on the surface of the sputtered NiO electrocatalyst, as evidenced by different Fe concentrations at three spots on the same surface after cycling. The concentration of Fe on the surface of the sputtered NiO sample cycled in KOH containing 1 mM Fe is much higher than that of the other three samples. The average Fe concentration (indicated by the black dashed lines) on the surface of the NiO samples cycled in pure KOH and 0.007 ppm Fe are again relatively similar, with values of 2.13% and 2.21%, respectively. The sample cycled in 0.3 ppm Fe has an average Fe concentration of 4.27%. The

sample cycled in 1 mM Fe has an average Fe concentration four times larger than the sample cycled in 0.3 ppm Fe, with an average value of 17.76%.

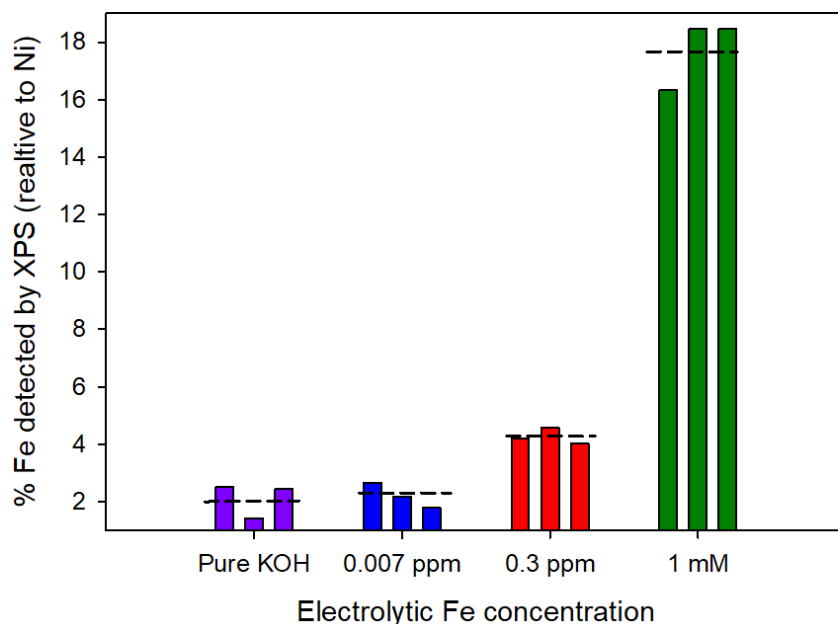


Figure 5-13: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered NiO electrocatalysts cycled in KOH containing different concentrations of Fe.

Lastly, The Fe concentrations at different spots on the surface of sputtered NiNiO is summarized in Figure 4-14. This figure shows that Fe is also unevenly distributed on the surface of sputtered NiNiO after cycling. The average Fe concentrations of the samples cycled in pure KOH, 0.007 ppm Fe and 0.3 ppm Fe are similar and have values of 3.83%, 4.13% and 4.19%, respectively. The average Fe concentration on the surface of the sample cycled in 1 mM Fe is six times larger, with an average of 26.85%. The NiNiO sample also has the largest Fe concentration on its surface after cycling in 1 mM Fe, compared to sputtered Ni and NiO.

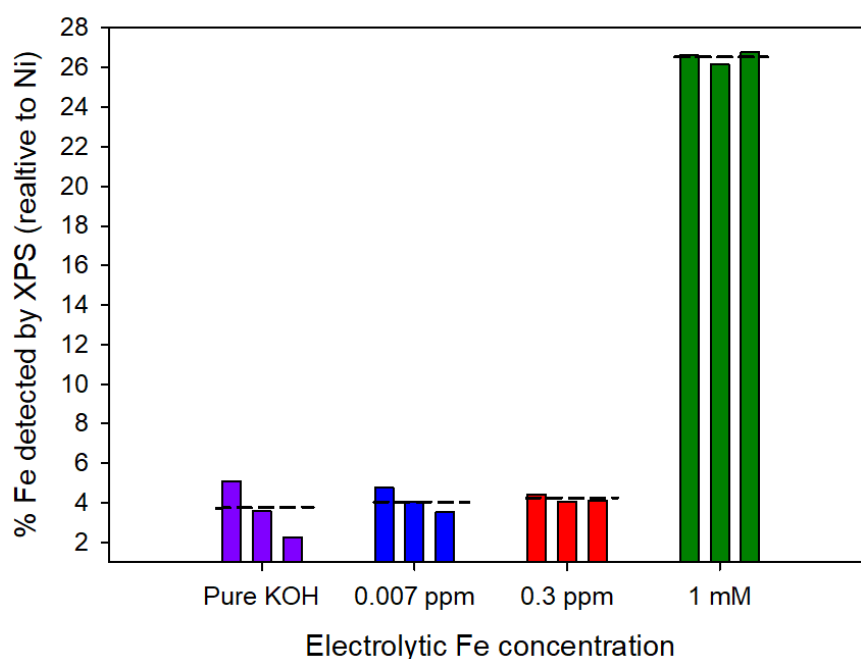


Figure 5-14: A bar chart illustrating the Fe concentrations at 3 spots on the surface of sputtered NiNiO electrocatalysts cycled in KOH containing different concentrations of Fe.

5.2.3 Electrochemical analysis of sputtered Ni-based samples

50 nm thick films of Ni, NiO and NiNiO were sputtered onto GC supports in order to perform more in-depth electrochemical analyses to study the effect of electrolytic Fe on Ni. Sputtering thin films are a fast and effective way to produce many reproducible samples in a short time, making them ideal for investigating numerous films in various electrolytic Fe concentrations. Seven electrolytic Fe concentrations were investigated for sputtered samples, i.e., pure KOH, 0.003 ppm, 0.007 ppm, 0.09 ppm, 0.9 ppm and 1 mM. These experiments provide a means to investigate and identify certain trends, such as the relationship between electrolytic Fe concentration and the overpotential at 10 mA cm^{-2} .

5.2.3.1 CVs of sputtered Ni-based samples

In Figure 5-15, the 30th CV cycles of sputtered Ni cycled in pure KOH, and KOH containing 5 different electrolytic Fe concentrations are displayed.

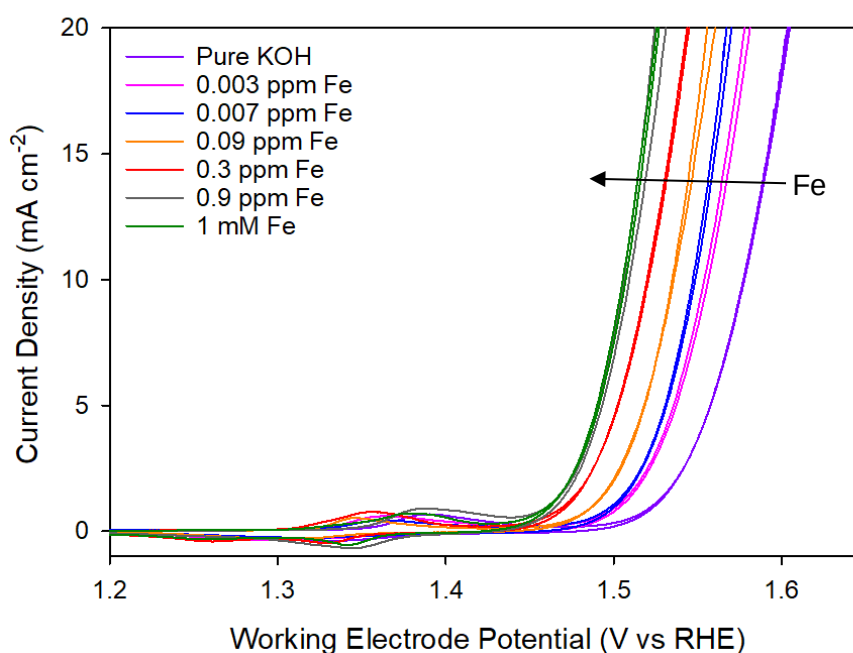


Figure 5-15: 30th CV cycle at 20 mV s⁻¹ of sputtered Ni in pure KOH (purple) and KOH containing six different concentrations of Fe.

From Figure 5-15, it can be seen that the current response at the applied potentials keeps increasing as the electrolytic Fe concentration is increased and stabilises at 0.9 ppm Fe. The overpotential at 10 mA cm⁻² for the sample cycled in pure KOH is 347 mV. This value decreases to 321 mV upon addition of 0.003 ppm Fe. When the Fe concentration is further increased to 0.007 ppm, the overpotential decreases to 316 mV. This relationship between electrolytic Fe concentration and overpotential also holds true for the other Fe concentrations. Samples cycled in KOH containing 0.09 ppm, 0.3 ppm and 0.9 ppm Fe, exhibit overpotentials of 305 mV, 290 mV and 276 mV, respectively. The Ni sample cycled in 1 mM Fe exhibits the same overpotential at 10 mA cm⁻² as the sample cycled in 0.9 ppm Fe. Because of the large currents, the redox features of the samples are diminished in Figure 5-15. Therefore, the scale is adjusted in Figure 5-16 to better observe these features.

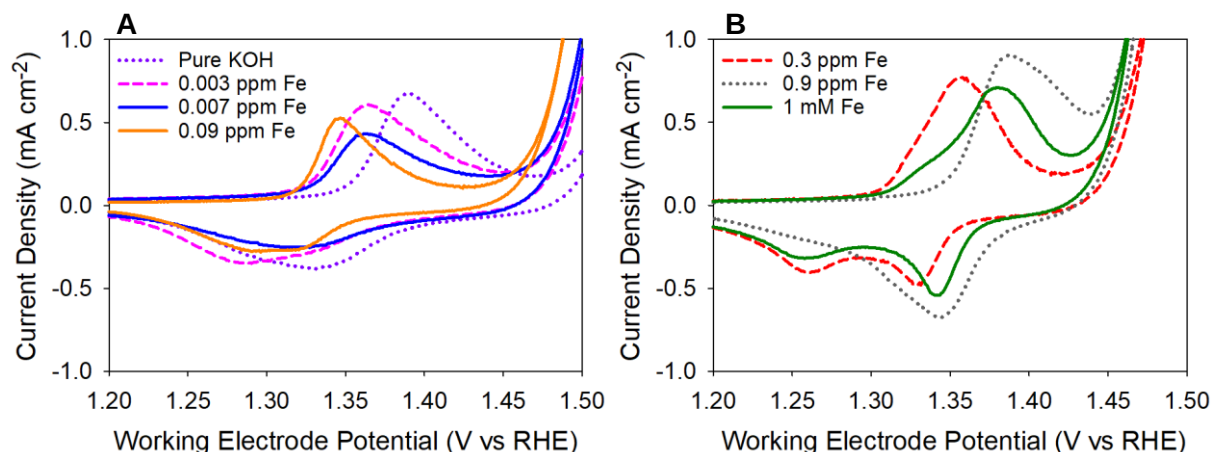


Figure 5-16: Redox features of the 30th CV cycles at 20 mV s⁻¹ of sputtered Ni in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink) and 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange) 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).

Sputtered Ni cycled in pure KOH has an oxidation wave at 1.39 V vs RHE and a reduction wave at 1.33 V vs RHE. The sample cycled in 0.003 ppm Fe has an oxidation wave at 1.36 V vs RHE and a broad reduction wave at about 1.29 V vs RHE with a shoulder to the right. The sample cycled in 0.007 ppm Fe has redox features at the same positions as the sample cycled in 0.003 ppm Fe. However, the redox waves of the sample cycled in 0.007 ppm Fe are smaller than that of the sample cycled in 0.003 ppm Fe. Lastly, the sample cycled in 0.09 ppm Fe has an oxidation wave at 1.345 V and a reduction feature that seems to consist of two peaks that are not well split at 1.30 V vs RHE. For these samples, the oxidation peak shifts cathodically (to the left) as the Fe concentration increases from zero to 0.09 ppm Fe.

The sputtered Ni sample cycled in KOH containing 0.3 ppm Fe has an oxidation wave at 1.356 V vs RHE and a cathodic peak doublet at 1.26 V vs RHE and 1.33 V vs RHE. The samples cycled in 0.9 ppm Fe and 1 mM Fe have oxidation waves that are shifted anodically with respect to that of the sample cycled in 0.3 ppm. The oxidation wave of the sample cycled in 0.9 ppm is the largest of these three samples and located at 1.39 V vs RHE. The oxidation feature of the sample cycled in 1 mM is located at 1.38 V vs RHE and has a shoulder to the left. The sample cycled in 0.9 ppm Fe has a reduction wave at 1.345 V vs RHE. The sample cycled in 1 mM has a cathodic peak doublet at 1.26 V vs RHE and 1.34 v vs RHE.

The thirtieth CV of sputtered NiO after electrochemical cycling in KOH containing various concentrations of Fe can be observed in Figure 5-17.

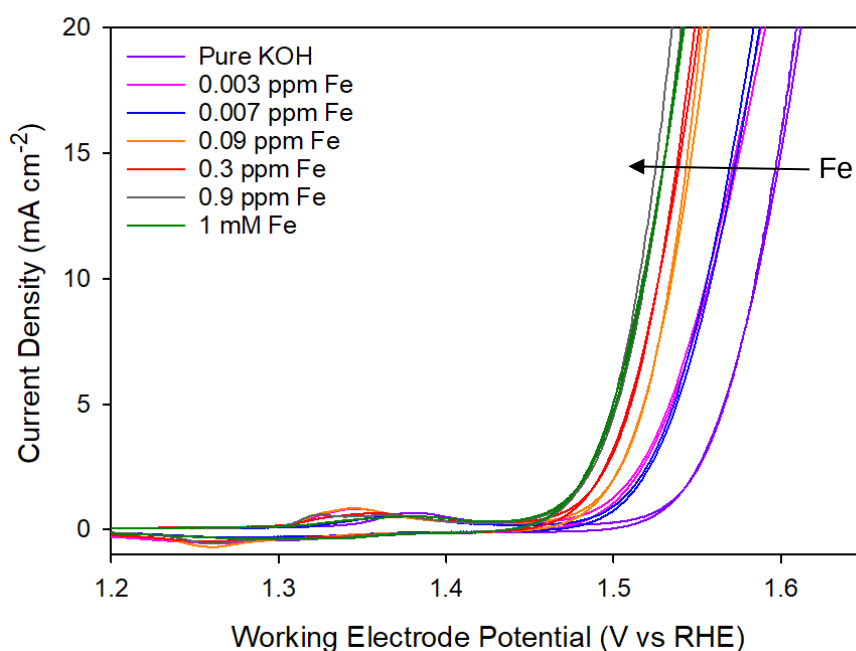


Figure 5-17: 30th CV cycle at 20 mV s⁻¹ of sputtered NiO in pure KOH (purple) and KOH containing six different concentrations of Fe.

From Figure 5-17 it can be seen that higher current densities are reached at lower potentials as the electrolytic Fe concentration is increased. This means that the OER activity increases as the Fe concentration does. The OER activity stops increasing at a Fe concentration of 0.9 ppm Fe. Furthermore, it can be seen that the samples cycled in 0.003 ppm Fe and 0.007 ppm Fe have similar activities, as does the samples cycled in 0.9 ppm Fe and 1 mM Fe. The overpotentials obtained at 10 mA cm⁻² are 355 mV, 323 mV, 325 mV, 304 mV, 297 mV, 289 mV, 289 mV in order of increasing Fe concentration.

To see the redox features, the scale has been adjusted in Figure 5-18. The sputtered NiO electrocatalyst cycled in pure KOH has an oxidation feature at 1.38 V vs RHE and a reduction feature at 1.30 V vs RHE. The samples cycled in 0.003 ppm Fe and 0.09 ppm Fe have redox features at similar positions. These two samples both have an oxidation feature at 1.34 V vs RHE and a reduction feature at 1.26 V vs RHE. The sample cycled in 0.007 ppm Fe has an oxidation feature at 1.37 V vs RHE and a broad reduction feature at 1.28 V vs RHE.

For the NiO sample cycled in 0.3 ppm Fe, an oxidation peak is found at 1.36 V vs RHE. Two reduction features can be seen that are not well-defined; one at 1.256 V vs RHE and one at 1.33 V vs RHE. The sample cycled in 0.9 ppm Fe, has two well-defined oxidation features, therefore an anodic peak doublet (1.32 V and 1.36 V vs RHE). It also has a cathodic peak doublet at 1.32 V and 1.26 V vs RHE. Lastly, the sample cycled in 1 mM have broad redox features, which appear

to be two features that did not split well. The broad oxidation feature is centered at 1.37 V vs RHE and the broad reduction feature at 1.32 V vs RHE.

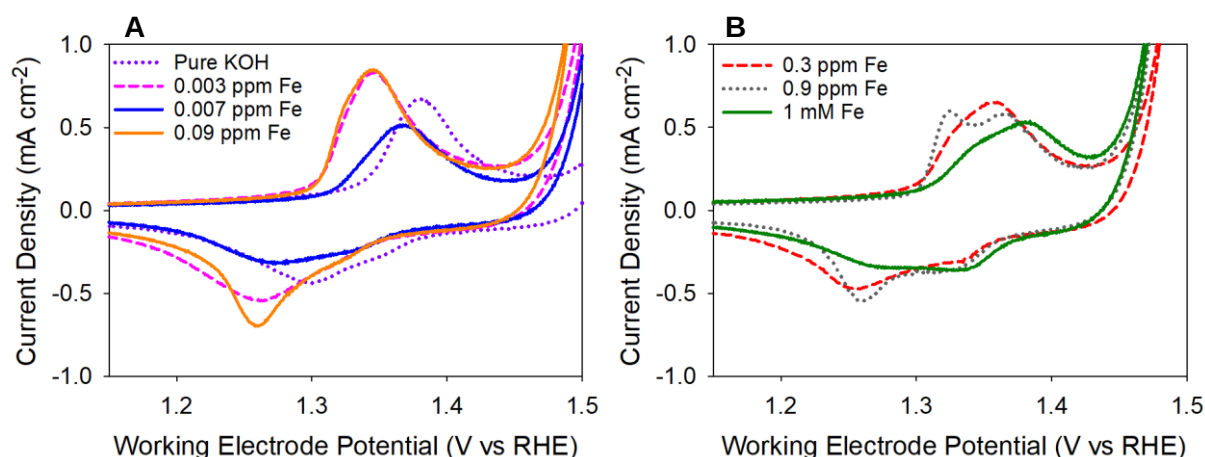


Figure 5-18: Redox features of the 30th CV cycles at 20 mV s⁻¹ of sputtered NiO in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink) and 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange), 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).

In Figure 5-19, the 30th CV cycle of NiNiO samples cycled in pure KOH and KOH containing 5 different concentrations of Fe can be seen.

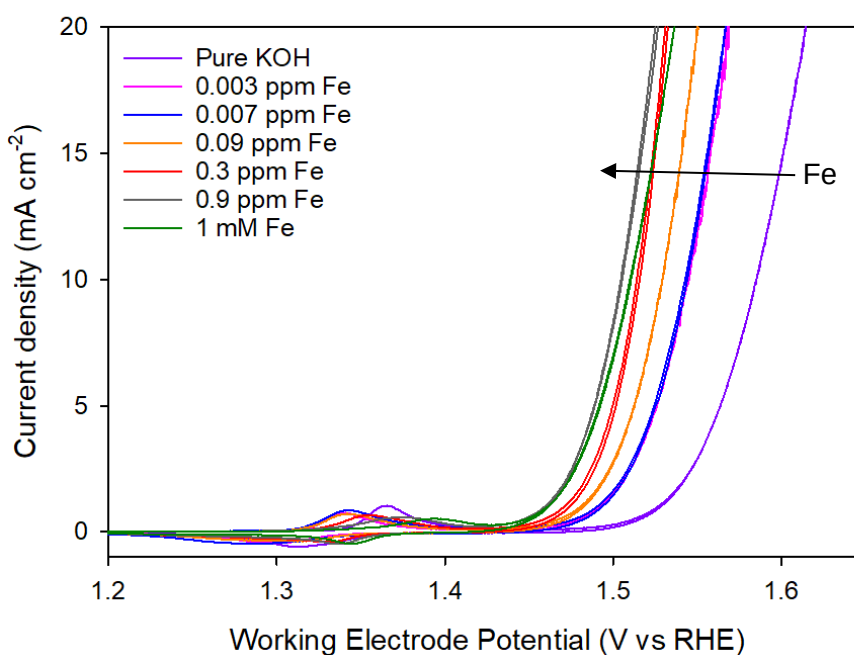


Figure 5-19: 30th CV cycle at 20 mV s⁻¹ of sputtered NiNiO in pure KOH (purple) and KOH containing six different concentrations of Fe.

From Figure 5-19, it is clear that there is a large increase in OER activity (evident by larger current responses at lower potentials) when only 0.003 ppm Fe is present in the electrolyte. NiNiO samples cycled in 0.003 ppm Fe and 0.007 ppm Fe have similar OER activities. The overpotentials of the NiNiO films at 10 mA cm⁻² are 355 mV, 314 mV, 313 mV, 299 mV, 284 mV, 275 mV and 281 mV, in order of increasing electrolytic Fe concentration. From the overpotential values, it seems that an optimum OER activity is reached when 0.9 ppm Fe is present in the electrolyte, after which the overpotential is not reduced any further. The scale is adjusted in Figure 5-20 to show the redox features of the sputtered NiNiO samples cycled in KOH containing different concentrations of Fe,

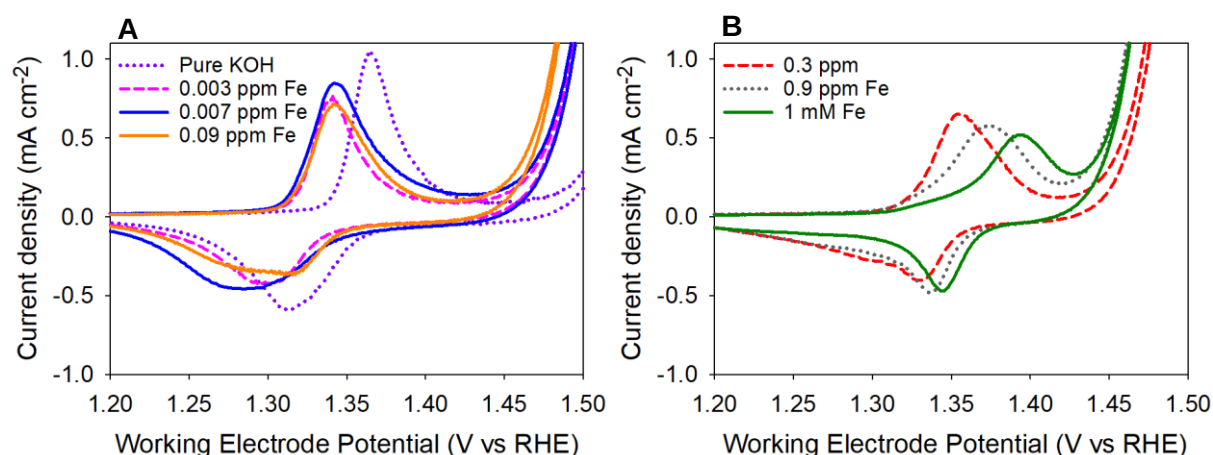


Figure 5-20: Redox features of the 30th CV cycles at 20 mV s⁻¹ of sputtered NiNiO in (a) pure KOH (purple) and KOH containing 0.003 ppm Fe (pink), 0.007 ppm Fe (blue) and (b) 0.09 ppm Fe (orange) 0.3 ppm Fe (red), 0.9 ppm Fe (grey) and 1 mM Fe (green).

The sputtered NiNiO sample cycled in pure KOH has a sharp oxidation feature at 1.36 V vs RHE and a sharp reduction feature at 1.31 V vs RHE. The oxidation features of the samples cycled in 0.003 ppm Fe, 0.007 ppm Fe and 0.09 ppm Fe are shifted cathodically with regards to the sample cycled in pure KOH. The all have one sharp oxidation feature around 1.34 V vs RHE. All three of these samples have broad reduction features between 1.28 V and 1.30 V vs RHE.

The NiNiO samples cycled in 0.3 ppm Fe, 0.9 ppm Fe and 1 mM Fe have oxidation features at 1.36 V, 1.38 V and 1.40 V vs RHE, respectively. The corresponding reduction features are sharp and located at 1.33 V 1.34 V and 1.35 V vs RHE.

5.2.3.2 LSVs and Tafel analysis of sputtered Ni-based samples

LSVs of sputtered Ni, NiO and NiNiO after 30 CV cycles in each electrolyte composition can be observed in Figure 5-21.

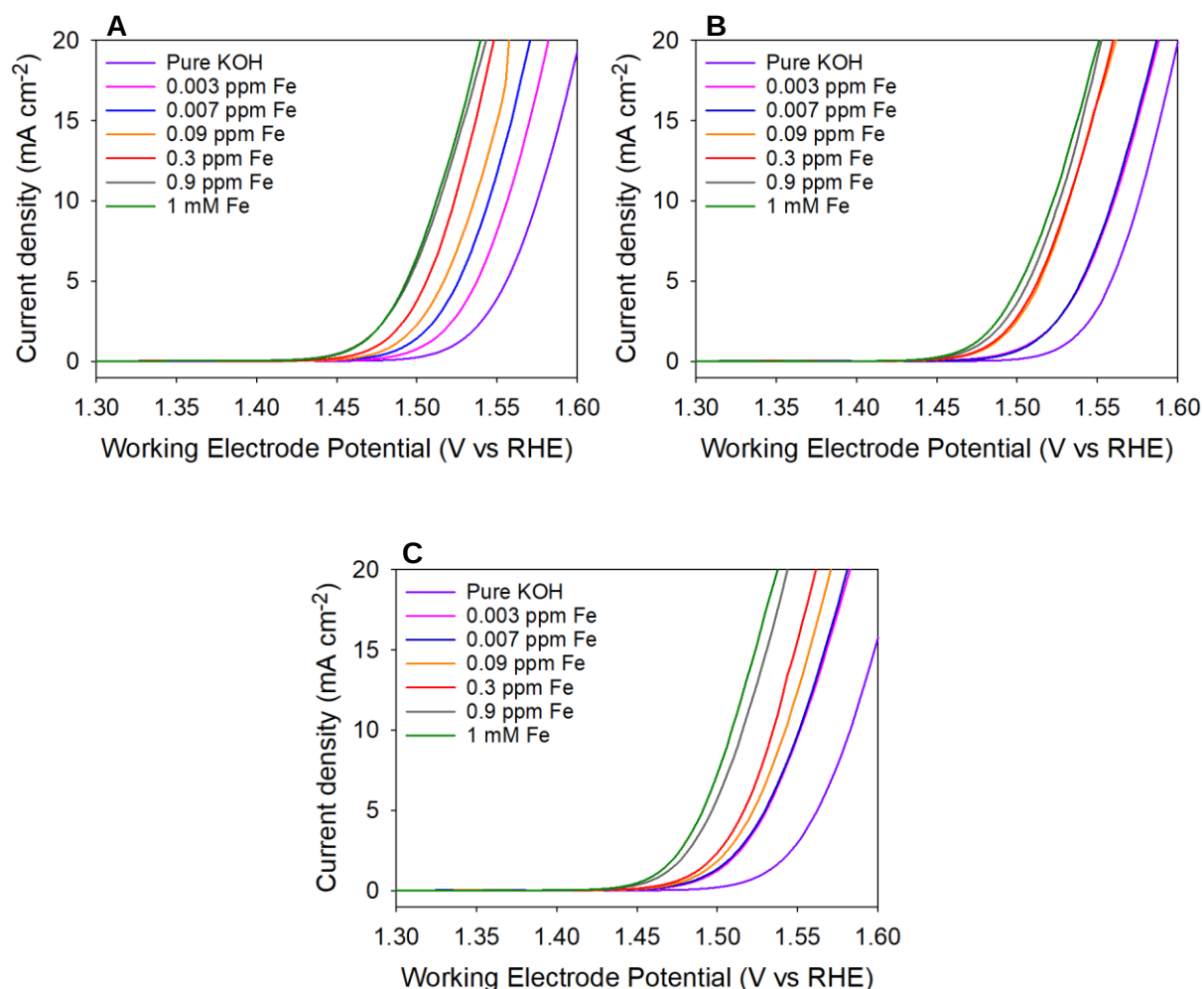


Figure 5-21: LSVs at 1 mV s^{-1} of sputtered (a) Ni (b) NiO and (c) NiNiO after 30 CVs in pure KOH (purple), and KOH containing six different concentrations of Fe.

From Figure 5-21 it can be seen that the current densities of the electrocatalysts increase as the electrolytic Fe concentration increases. This implies that as the concentration of Fe in the electrolyte increases, so does the OER activity. The overpotential at 10 mA cm^{-2} can be obtained from the LSVs in Figure 5-21 and these values are summarised in the form of a bar chart in Figure 5-22. The overpotentials of sputtered Ni at 10 mA cm^{-2} are 346 mV, 326 mV, 315 mV, 305 mV, 293 mV, 284 mV and 282 mV in the order of increasing electrolytic Fe concentration. These values are in good agreement with those obtained from the CVs. According to the figure of merit proposed by Tahir *et al.*⁴, sputtered Ni electrocatalysts cycled in KOH containing Fe concentrations of 0.09 ppm or less, are “excellent” OER electrocatalysts. Sputtered Ni electrocatalysts cycled in concentrations between 0.3 ppm and 1 mM are considered as “ideal” by this figure of merit.

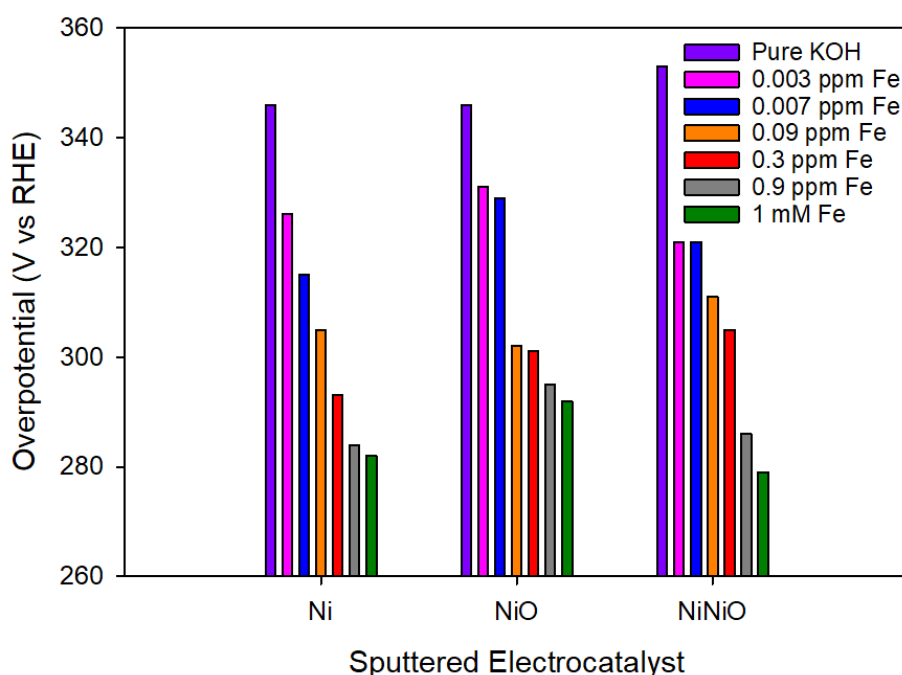


Figure 5-22: A bar chart summarising the overpotential values of sputtered Ni, NiO and NiNiO after 30 CV cycles in KOH containing different concentrations of Fe.

The overpotentials at 10 mA cm^{-2} of sputtered NiO samples are 346 mV, 331 mV, 329 mV, 302 mV, 301 mV, 295 mV and 292 mV, in the order of increasing Fe concentration. From Figure 5-21 and Figure 5-22 it can also be seen that the samples cycled in 0.003 ppm Fe and 0.007 ppm Fe have the same OER activity. The two samples cycled in 0.09 ppm and 0.3 ppm also have the same activity, as does the samples cycled in 0.9 ppm Fe and 1 mM Fe. All sputtered NiO samples cycled in KOH containing 0.3 ppm Fe or less are considered “excellent”. The two samples cycled in 0.9 ppm Fe and 1 mM Fe are considered as “ideal” OER electrocatalysts.

Lastly, the overpotentials at 10 mA cm^{-2} of sputtered NiNiO samples, cycled in electrolytes containing different Fe concentrations, can be seen in Figure 5-22. The overpotentials are 353 mV, 321 mV, 321 mV, 311 mV, 305 mV, 286 mV and 279 mV, starting from pure KOH and in the order of increasing electrolytic Fe concentration. NiNiO samples cycled in KOH containing 0.3 ppm Fe or less are considered as “excellent” electrocatalysts, whereas the samples cycled in 0.9 ppm Fe and 1 mM are “ideal” electrocatalysts.

As with the nanoparticle electrocatalysts, CA was used for Tafel analysis. Current versus voltage curves were constructed from the CA data and can be observed in Figure 5-23, Figure 5-24 and Figure 5-25 for sputtered Ni, NiO and NiNiO, respectively.

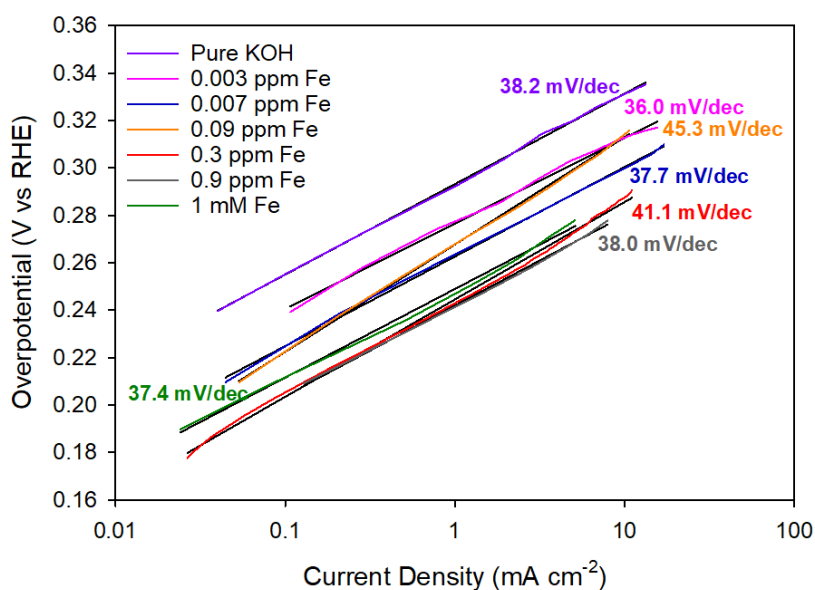


Figure 5-23: Tafel plots for sputtered Ni after cycling in pure KOH and KOH containing six different Fe concentrations.

The Tafel slopes are determined from the slopes of the straight-line plots of the overpotential versus the absolute value of the logarithm of the current density. The Tafel slopes for the sputtered Ni electrocatalysts are all between 36 mV/dec and 45.3 mV/dec. According to the literature summarised in Table 2-5, these values all correspond with Ni that has been cycled in KOH containing Fe^{139,6}, or NiFe electrocatalysts^{71,12,11,84}.

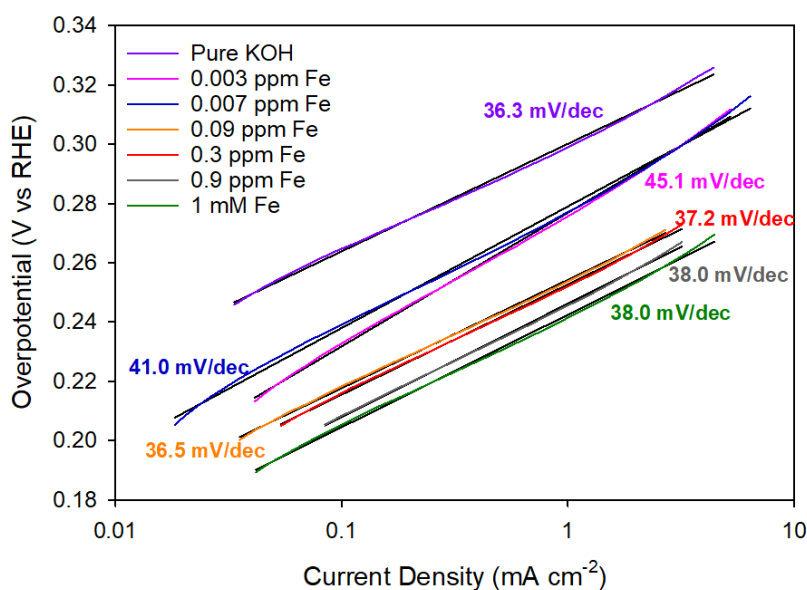


Figure 5-24: Tafel plots for sputtered NiO after cycling in pure KOH and KOH containing six different Fe concentrations.

For sputtered NiO, all samples have Tafel slopes between 36.3 mV/dec and 45.1 mV/dec. Again, these values correspond to the Tafel slopes of Ni-based electrocatalysts that has been cycled in KOH containing Fe^{139,6}, or NiFe electrocatalysts^{71,12,11,84}.

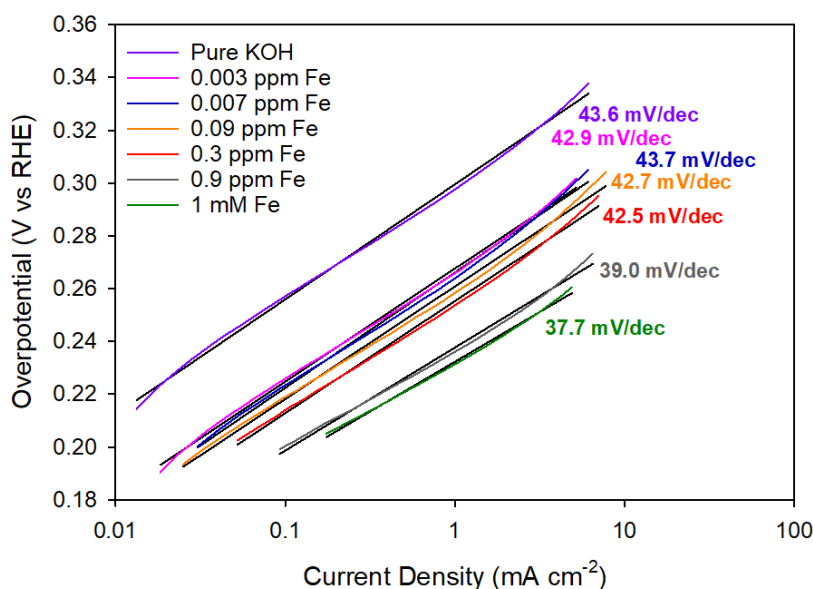


Figure 5-25: Tafel plots for sputtered NiNiO after cycling in pure KOH and KOH containing six different Fe concentrations.

Lastly, the Tafel slopes of sputtered NiNiO obtained from Figure 5-25 are between 37.7 mV/dec and 43.7 mV/dec. This is a narrow range and the values correspond once again with that of previous studies where Ni electrocatalysts are present with Fe^{71,12,11,84}.

5.2.3.3 LSVs after re-cycling activated samples in pure KOH

Sputtered samples cycled 30 times in KOH containing 0.007 ppm, 0.9 ppm and 1 mM Fe, were removed from the Fe-containing electrolyte and cycled 30 times in pure KOH. This was done to determine if samples activated in Fe-containing electrolyte undergoes an increase or decrease in activity when the same Fe concentration is no longer present. In other words, this determines if the samples stay activated after activation in Fe containing electrolytes.

In Figure 5-26, LSVs of sputtered Ni samples cycled in 0.007 ppm Fe, 0.9 ppm Fe and 1 mM Fe can be seen in the orange curves. The blue curves represent the LSVs of each of these samples that were removed from Fe-containing KOH after cycling and cycled 30 times in pure KOH.

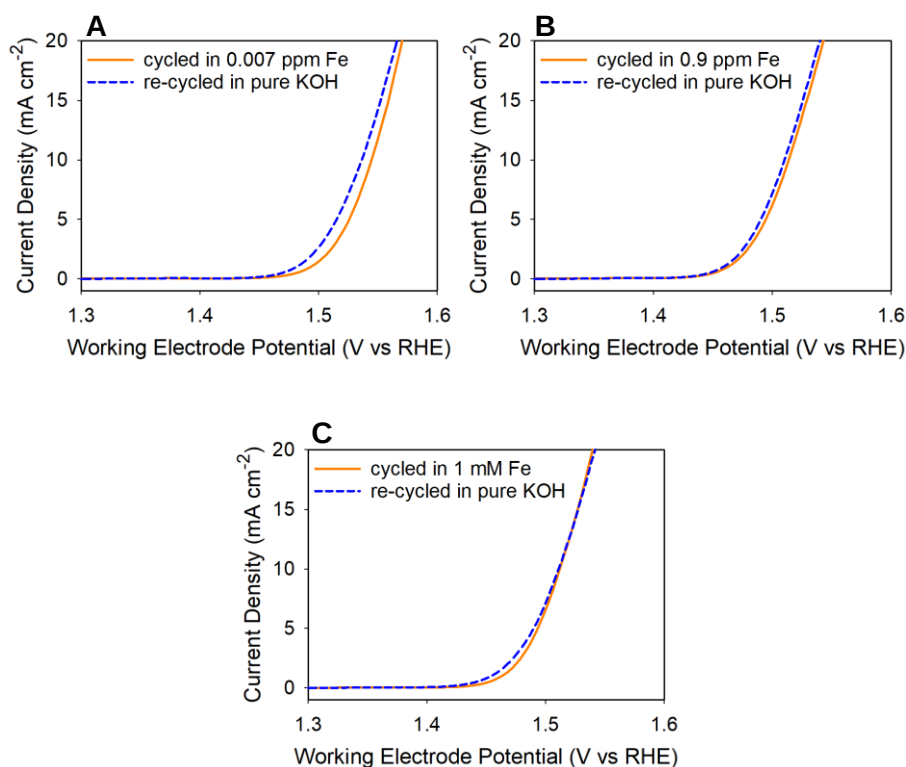


Figure 5-26: LSVs of sputtered Ni after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).

From all three samples that can be seen in Figure 5-26, it is clear that the OER activity does not change after 30 cycles in pure KOH. Therefore, once the sputtered Ni electrocatalysts are activated, the activity stays the same.

In Figure 5-27 sputtered NiO samples that have been re-cycled in pure KOH can be observed. Sputtered NiO samples cycled in KOH containing Fe also stays activated after 30 CV cycles in pure KOH and does not decrease or increase in OER activity. The same holds true for sputtered NiNiO samples, which can be observed in Figure 5-28.

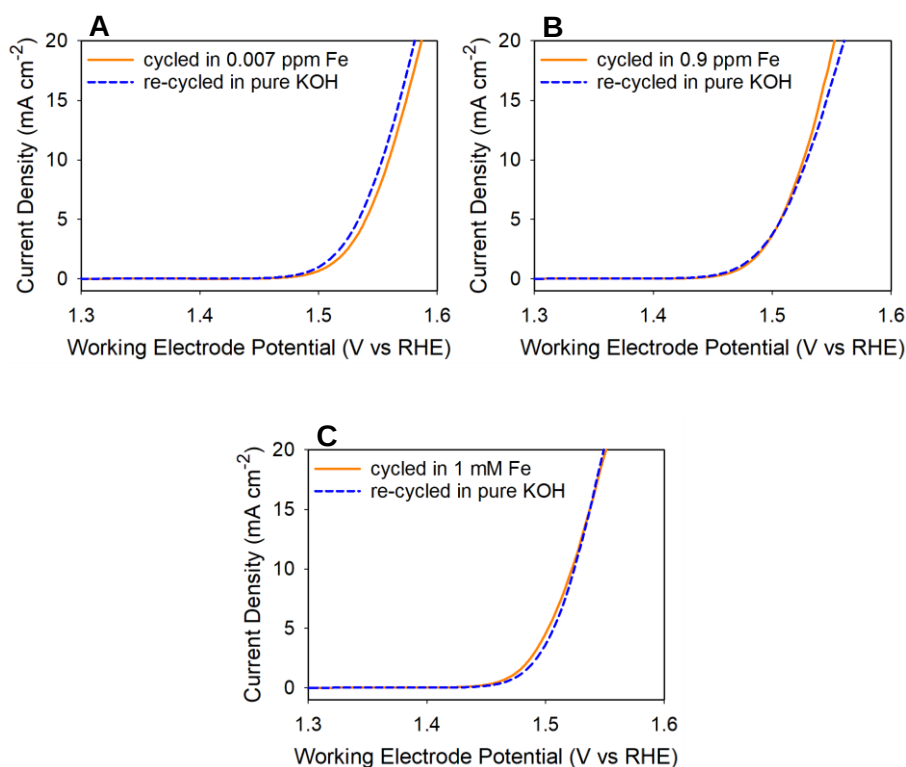


Figure 5-27: LSVs of sputtered NiO after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).

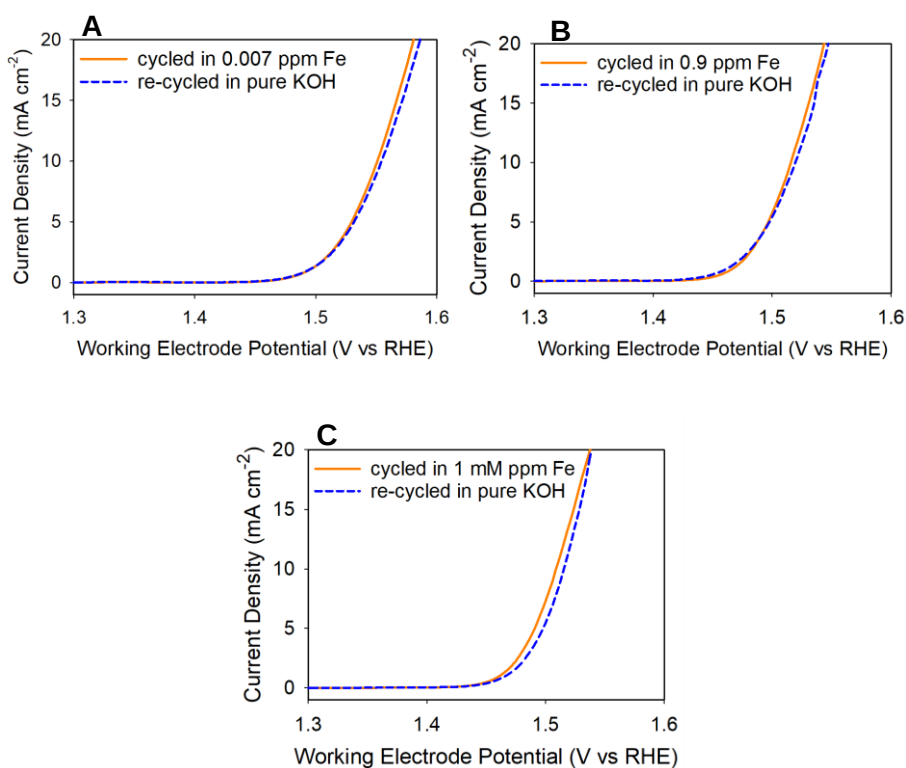


Figure 5-28: LSVs of sputtered NiNiO after cycling in (a) 0.007 ppm Fe, (b) 0.9 ppm Fe and (c) 1 mM Fe (orange) and after re-cycling each sample in pure KOH (blue).

5.2.3.4 EDL capacitance of sputtered Ni-based samples

Cyclic voltammetry in the non-Faradaic region between 0 and 0.1 V Vs Hg/HgO was used towards the determination of the double layer capacitance of the sputtered electrocatalysts. Different scan rates between 5 mV/s and 300 mV/s was used, so that a plot of current versus scan rate could be obtained. An example of the CV experiment used can be seen in Figure 5-29. This figure serves as representative and all of the CVs toward the double layer capacitance measurements of sputtered samples can be seen in Appendix B, Figure B-6, Figure B-7 and Figure B-8.

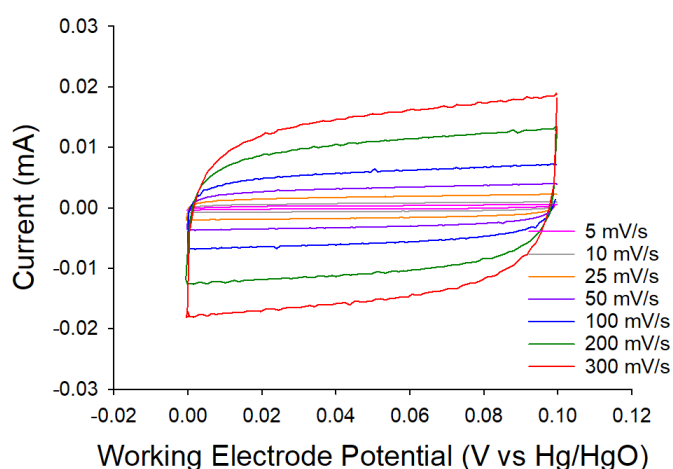


Figure 5-29: CVs of sputtered Ni in KOH containing 0.003 ppm Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

From the abovementioned CVs, two straight line plots are obtained for each sputtered sample in KOH containing each of the investigated Fe concentrations. The two straight lines have the same slope but opposite sign. The straight line plots obtained from the CVs sputtered Ni, NiO and NiNiO can be seen in Figure 5-30.

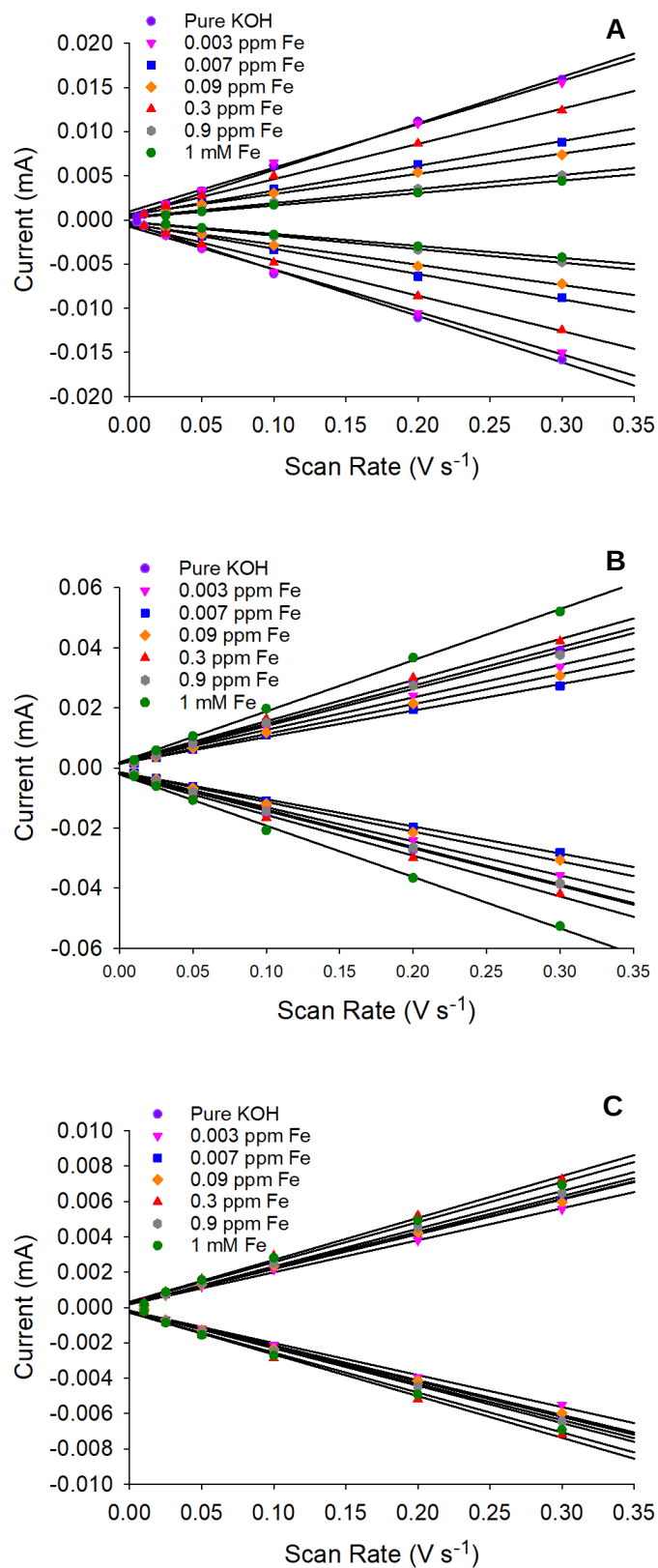


Figure 5-30: A plot of scan rate against the current response at 0.05 V vs Hg/HgO for sputtered (a) Ni, (b) NiO and (c) NiNiO in different Fe concentrations.

From the average of the positive and negative slope of each sample, the double layer capacitance can be obtained. These values for the sputtered samples cycled in different Fe concentrations are summarised in the bar chart in Figure 5-31.

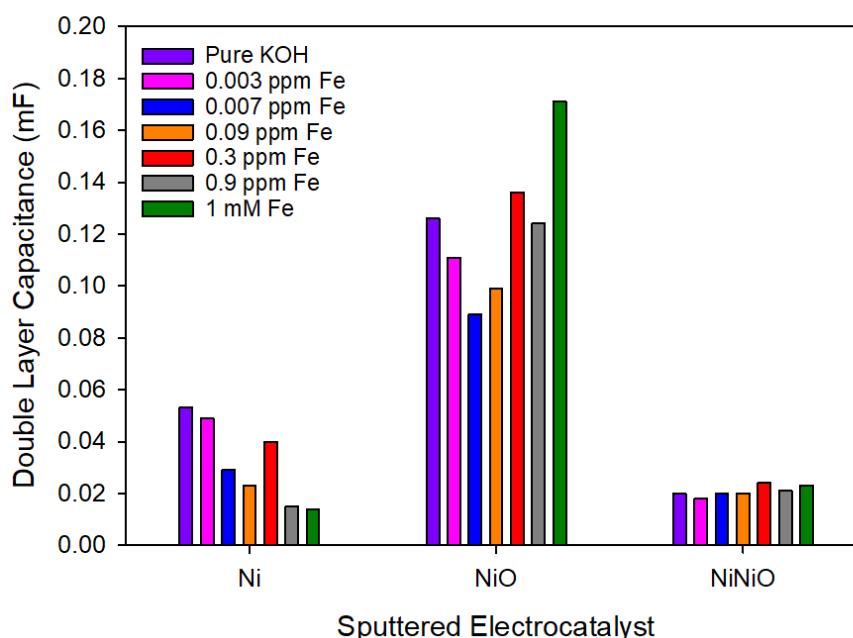


Figure 5-31: A bar chart summarising the electrochemical double layer capacitance values of sputtered Ni, NiO and NiNiO (50 nm films) after 30 CVs in KOH containing different concentrations of Fe.

Firstly, the electrochemical double layer capacitance of the sputtered Ni sample cycled in pure KOH has the largest value (0.053 mF) and the sample cycled in 1 mM Fe the smallest (0.014 mF). The general trend for sputtered Ni samples is that the double layer capacitance decreases as the electrolytic Fe concentration increases. This holds true for all samples, except the sample cycled in 0.3 ppm Fe. Sputtered NiO has the largest overall double layer capacitance of all the sputtered electrocatalysts. The double layer capacitance of sputtered NiO decreases as the Fe concentration is increased from zero to 0.007 ppm. The double layer capacitance then increases again until the sample cycled in 1 mM Fe, which has the largest double layer capacitance. Interestingly, the double layer capacitance of all of the sputtered NiNiO samples are almost the same (~ 0.02 mF), regardless of the electrolytic Fe concentration.

5.2.3.5 Electrochemical impedance spectroscopy toward the determination of charge transfer resistance of sputtered Ni-based thin films

Potentiometric electrochemical impedance spectroscopy was used to further investigate the inherent electrochemical properties of each sputtered sample. With this technique, the effect of electrolytic Fe concentration on the charge transfer resistance (R_{ct}) of each sputtered Ni electrocatalyst could be determined. EIS measurements were carried out at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO. The AC perturbation potential amplitude used was 10 mV. The frequency range was 30 kHz to 0.1 Hz.

In Figure 5-32, the Nyquist plots for sputtered Ni is displayed. It can be seen that one single semi-circle is present for each sample at each potential. This means that the entire GC substrate is covered with the sputtered thin film and that we are solely observing the kinetics of the Ni thin film¹⁴². Furthermore, a simple Randle's cell (Figure 2-9) was used to circuit-fit the impedance data in Figure 5-32. The total impedance of the Ni thin film can therefore be obtained from the sum of the high and low frequency intercepts of the real component (x-axis)¹⁴². The uncompensated resistance (obtained from the x-axis intercept on the left), can be subtracted from the total impedance to obtain R_{ct} .

The scaling of the plots in Figure 5-32 could not be kept the same throughout all the samples, or the plots would be completely diminished. By observing the scales closely, it can be seen that the semi-circles are smaller the higher the electrolytic Fe concentration. In addition, the semi-circles are smaller with higher applied potential.

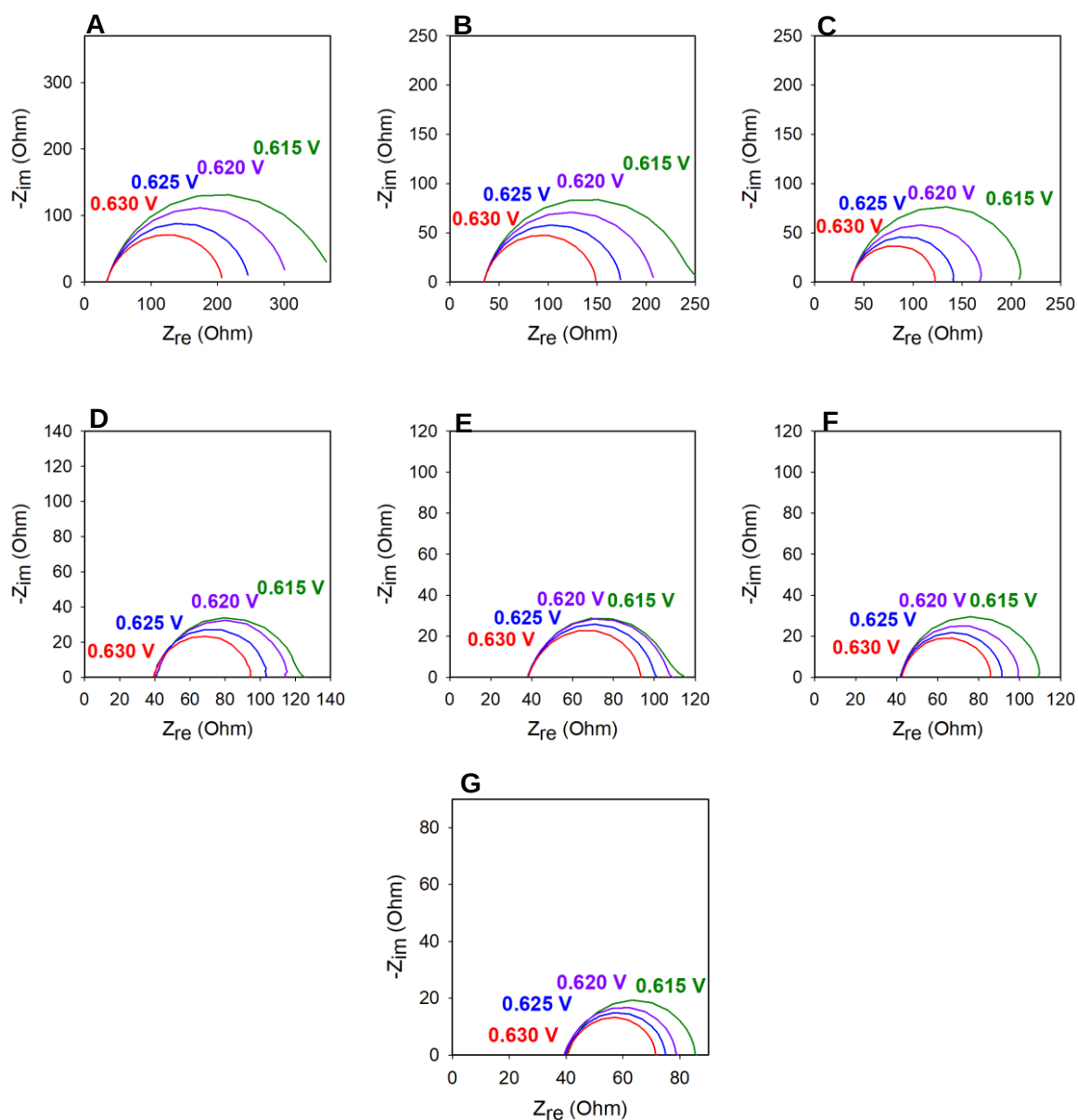


Figure 5-32: Nyquist plots obtained from the EIS measurements of sputtered Ni performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.

By fitting the Nyquist plots in Figure 5-32 to an equivalent circuit (Randle's cell), the R_{ct} values of the sputtered Ni samples were obtained and are summarised in Table 5-2.

Table 5-2: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered Ni in KOH containing different concentrations of Fe.

	R_{ct} at 0.615 V (Ohm)	R_{ct} at 0.62 V (Ohm)	R_{ct} at 0.625 V (Ohm)	R_{ct} at 0.63 V (Ohm)
Pure KOH	338.7	277.7	219.1	178.1
0.003 ppm Fe	212	174.1	140.7	115.4
0.007 ppm Fe	175.9	134	105.6	86.13
0.09 ppm Fe	82.2	75.01	64.71	55.41
0.3 ppm Fe	71.83	67.43	60.83	54.32
6.5 ppm Fe	68.34	58.03	49.79	43.54
1 mM Fe	45.19	39.78	35.29	31.42

From Table 5-2, it is clear that the R_{ct} at each potential value decreases as the electrolytic Fe concentration increases. Upon inspection of the R_{ct} values at 0.63 V (where the most appreciable OER activity is observed), it can be seen that the R_{ct} is 178.1 ohm after sputtered Ni was cycled in pure KOH. This value decreases all the way to 31.42 ohm when Ni is cycled in KOH containing 1 mM Fe. From this table, it is clear that the addition of Fe to KOH decreases the R_{ct} of sputtered Ni electrocatalysts.

In Figure 5-33, the Nyquist plots obtained from the EIS measurements of sputtered NiO can be observed. In this figure, single semi-circles can again be observed for all of the sputtered NiO samples. Note again that the scaling had to be adapted to prevent diminishing the plots. It can be seen that the semi-circles become smaller as the Fe concentration of the electrolyte is increased. The Nyquist plots were used to obtain the R_{ct} values for NiO samples cycled in pure KOH and six different Fe concentrations. A summary of the R_{ct} values can be seen in Table 5-3.

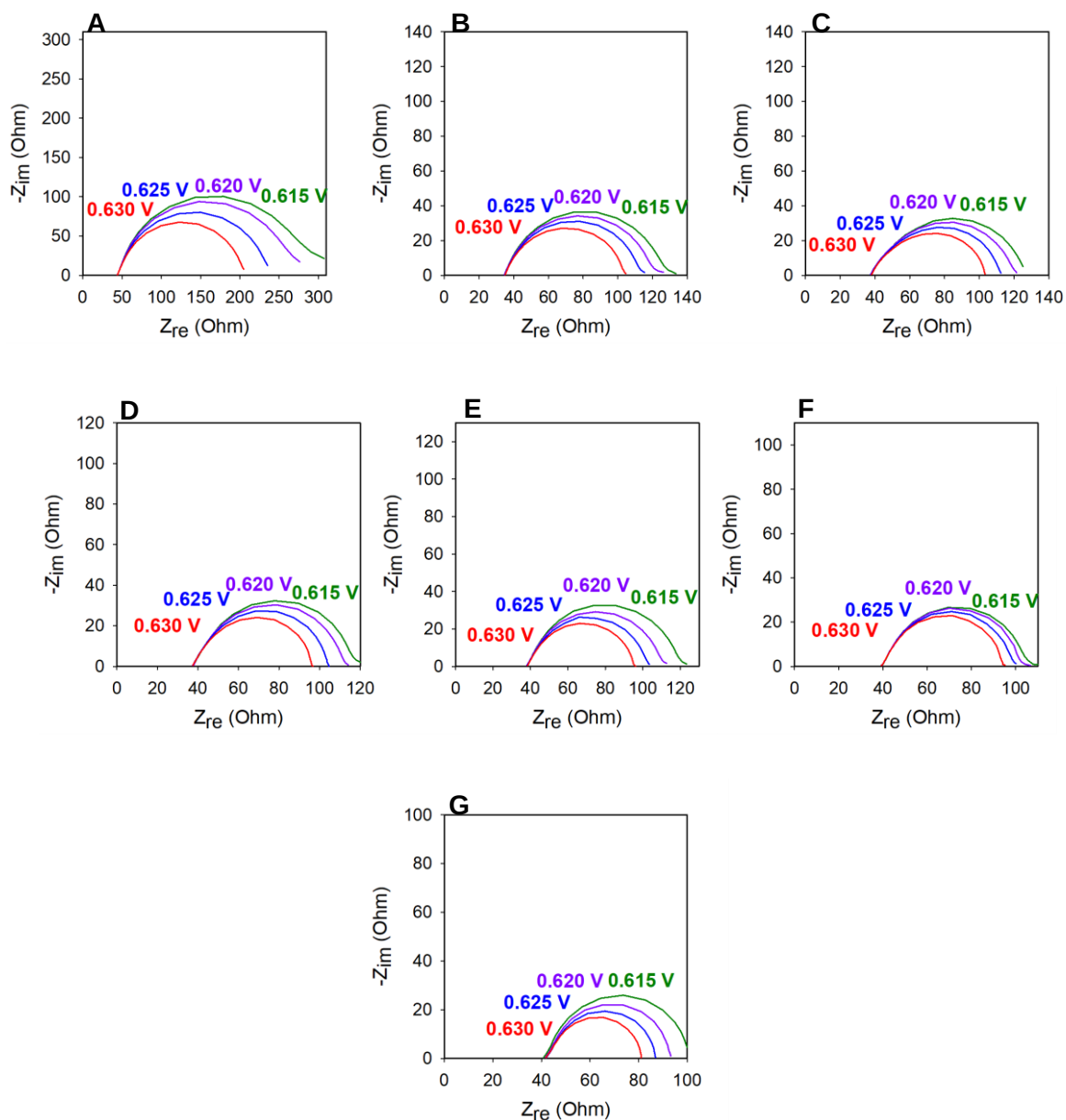


Figure 5-33: Nyquist plots obtained from the EIS measurements of sputtered NiO performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.

Table 5-3: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered NiO in KOH containing different concentrations of Fe.

	R_{ct} at 0.615 V (Ohm)	R_{ct} at 0.62 V (Ohm)	R_{ct} at 0.625 V (Ohm)	R_{ct} at 0.63 V (Ohm)
Pure KOH	253.3	230.7	194.9	163.4
0.003 ppm Fe	94.45	88.08	79.59	69.61
0.007 ppm Fe	92.21	85.25	76.59	67.18
0.09 ppm Fe	82.37	75.8	67.87	59.76
0.3 ppm Fe	83.43	73.81	65.32	57.72
6.5 ppm Fe	67.39	64.33	60.28	55.41
1 mM Fe	60.6	52	45.32	39.71

From Table 5-3, it can be seen that the R_{ct} of sputtered NiO at each potential decreases as the electrolytic Fe concentration increases. In addition, it is interesting to note that the R_{ct} of NiO samples cycled in 0.003 ppm Fe and 0.007 ppm Fe are similar. The NiO samples cycled in 0.09 ppm Fe, 0.3 ppm Fe and 0.9 ppm Fe also have similar R_{ct} values. At 0.63 V, the R_{ct} of NiO decreases from 163.40 ohm for the sample cycled in pure KOH to 39.71 ohm for the sample cycled in KOH containing 1 mM Fe.

Lastly, the Nyquist plots obtained from the EIS experiments of sputtered NiNiO samples can be observed in Figure 5-34. The GC supports are again completely covered by the sputtered NiNiO thin films, as seen from the single semi-circles observed in this figure. The scale could be kept the same for the samples cycled in pure KOH, and KOH containing 0.003 ppm, 0.007 ppm, 0.09 ppm and 0.3 ppm Fe. For the samples cycled in 0.9 ppm Fe and 1 mM Fe, the scale had to be adjusted. The R_{ct} values were obtained from fits of the plots in Figure 5-34, and are summarised in Table 5-4. In this table, it can be seen that the R_{ct} at 0.63 V decreases from 105.30 ohm when NiNiO is cycled in pure KOH to 26.29 ohm when NiNiO is cycled in 1mM Fe. The NiNiO samples cycled in 0.003 ppm Fe and 0.007 ppm Fe have almost the same R_{ct} , similar to Ni and NiO.

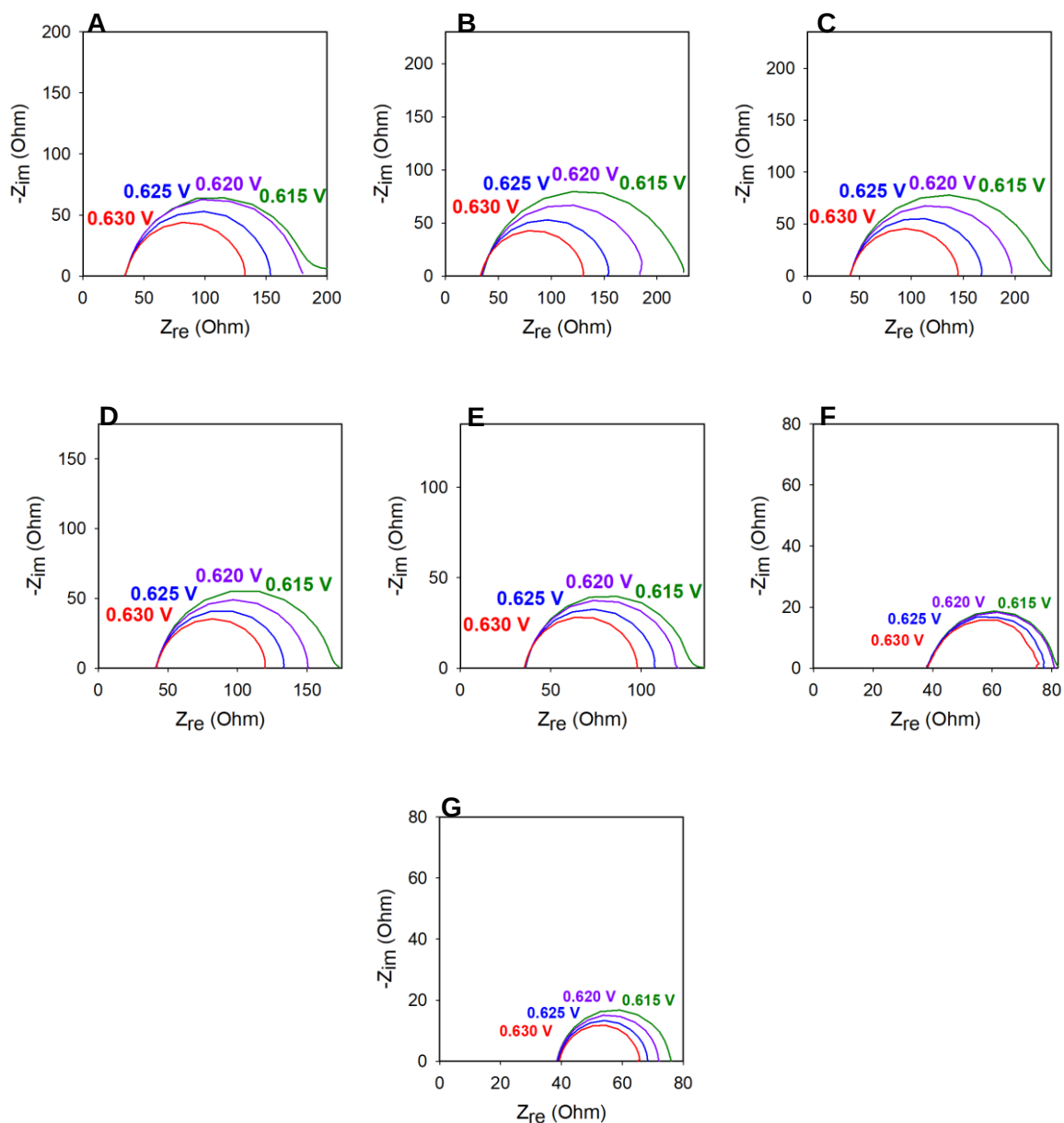


Figure 5-34: Nyquist plots obtained from the EIS measurements of sputtered NiNiO performed in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe at 0.615 V, 0.620 V, 0.625 V and 0.630 V vs Hg/HgO.

Table 5-4: A summary of the charge transfer resistance (R_{ct}) values obtained from EIS measurements of sputtered NiNiO in KOH containing different concentrations of Fe.

	R_{ct} at 0.615 V (Ohm)	R_{ct} at 0.62 V (Ohm)	R_{ct} at 0.625 V (Ohm)	R_{ct} at 0.63 V (Ohm)
Pure KOH	188.00	158.10	128.90	105.30
0.003 ppm Fe	190.10	154.00	122.00	98.32
0.007 ppm Fe	175.00	145.00	120.60	99.30
0.09 ppm Fe	128.50	110.20	92.72	78.85
0.3 ppm Fe	93.16	84.03	72.23	62.64
6.5 ppm Fe	44.04	42.89	39.79	37.17
1 mM Fe	37.42	33.45	29.52	26.29

At 0.63 V vs Hg/HgO, the potential is in the OER region. Therefore, by comparing the R_{ct} values of the different electrocatalysts at this potential, one can get some insight into the electrocatalyst operation. The R_{ct} values of all three sputtered electrocatalysts in the different electrolytes at 0.63 V vs Hg/HgO is summarised in a bar chart in Figure 5-35.

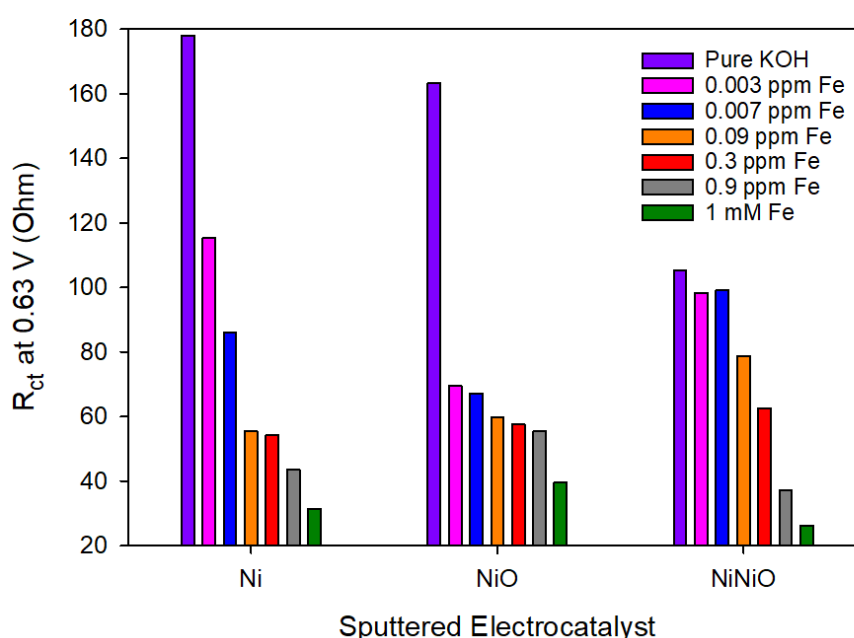


Figure 5-35: A bar chart of the charge transfer resistance at 0.63 V for sputtered Ni, NiO and NiNiO in KOH containing different concentrations of Fe.

6. DISCUSSION

The results from this study led to a few important findings that will be discussed according to the following statements:

1. Increasing electrolytic Fe concentration increases the OER activity of all Ni-based electrocatalysts. However, at a certain Fe concentration, which is unique for each morphology, no further increase in OER activity is observed. This is evidenced by CVs and LSVs.
2. The OER activity is increased by the presence of α -FeOOH on the surface of Ni electrocatalysts. This statement is supported by in-situ Raman spectroscopy, XPS and EDX results. Fe was found to be present only on the surface and not incorporated into the bulk structure, as suggested by previous literature.
3. It was found that the as-prepared oxidation state of the Ni electrocatalysts (before contact with electrolyte) has minimal effect on Fe uptake or electrocatalytic activity. However, the morphology of Ni electrocatalysts has a large influence on the Fe uptake and subsequently the OER activity.

Each of these main findings will be discussed in more detail below, along with the results that support each statement.

1. Increasing the electrolytic Fe concentration decreases OER overpotentials, with different optimum values for each electrocatalyst.

A widely accepted benchmark for the activity of OER electrocatalysts is the value of the overpotential at 10 mA cm^{-2} . Therefore, this benchmark is also used in this study to evaluate and compare the OER activities of different Ni-based electrocatalysts in KOH containing different concentrations of Fe. The bar chart in Figure 6-1 concisely summarises the overpotential at 10 mA cm^{-2} for each of the electrocatalysts after 30 CV cycles in pure KOH, and KOH containing 0.3 ppm Fe and 1 mM Fe. The orange stars in the figure indicate which samples had peaks corresponding to FeOOH in their in-situ Raman spectra, and will be discussed in the next point.

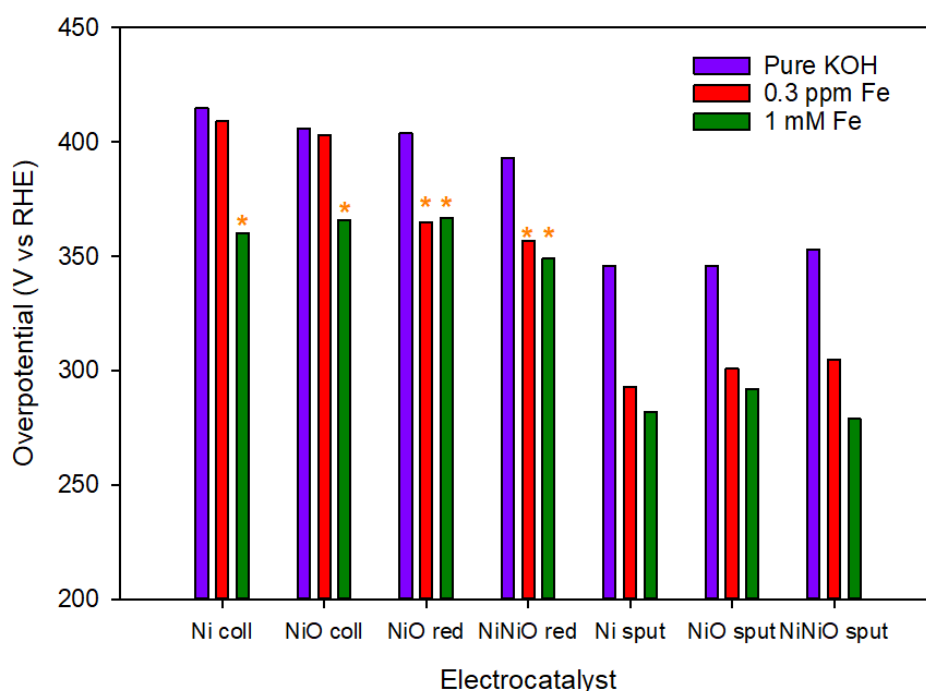


Figure 6-1: A bar chart summarizing the OER overpotentials of each of the Ni-based electrocatalysts after 30 CV cycles in pure KOH, 0.3 ppm Fe and 1 mM Fe.

Firstly, colloidal Ni and NiO nanoparticles prepared by a tailored synthesis method exhibit a decrease in overpotential when the samples are cycled in KOH containing 1 mM Fe. The overpotential decreases with 55 mV for colloidal Ni and 40 mV for colloidal NiO, when 1 mM Fe is added to 0.1 M KOH. Secondly, the OER activities of the nanoparticles prepared by chemical reduction significantly decreases after the addition of only 0.3 ppm Fe. The overpotential of NiO at 10 mA cm^{-2} decreases with 39 mV when 0.3 ppm Fe is present in the electrolyte, and that of NiNiO with 36 mV.

Sputtered Ni, NiO and NiNiO thin films were also investigated. A larger array of Fe concentrations was investigated for these samples. The overpotentials decrease as the electrolytic Fe concentration increases, until it is minimized when the sample is cycled in 0.9 ppm. For sputtered Ni, a 64 mV decrease in overpotential is observed when the sample is cycled in 1 mM Fe versus pure KOH. For NiO, this decrease is 54 mV and for NiNiO 74 mV. The sputtered samples already show a significant decrease in overpotential (between 15 and 32 mV) when only 0.003 ppm Fe is added to the electrolyte. This is interesting, since it is reported that 1 M TraceSelect KOH contains $<36 \text{ ppb Fe}^5$. Therefore, these results indicate how important it is to report the amount of Fe present in electrolytes when presenting and comparing the overpotentials of new Ni electrocatalysts. In addition, reagent-grade KOH in pellet form is reported to contain $\leq 0.66 \text{ ppm Fe}$. From Figure 6-1 it is clear that 0.3 ppm Fe dramatically increases the OER activity. The results

of this study is also in good agreement of that reported by Corrigan, indicating that an Fe concentration of 1 ppm Fe significantly enhances the OER activity of Ni electrocatalysts². Therefore, studies reporting Ni activities in reagent grade KOH will have to be repeated in pure KOH to get a true indication of the inherent OER activity of the Ni electrocatalysts. Furthermore, it is clear that future studies of pure Ni electrocatalysts cannot be executed in reagent-grade KOH.

It is important to take into account that no traces of Fe are expected to be present for the as-prepared sputtered samples. There is a significantly higher chance that the as-prepared nanoparticle films already contain trace amounts of Fe. This Fe can originate from the Ni precursors used to prepare the electrocatalysts, or the different reagents used in the nanoparticle preparation as well as ink preparation. This could be the reason why no significant increase in OER activity is observed for the nanoparticle OER electrocatalysts when Fe concentrations under 0.3 ppm is present in the electrolyte.

Figure 6-1 shows that each unique synthesis method leads to a unique Fe saturation concentration for each electrocatalyst. This is the point where increasing the electrolytic Fe concentration further has no influence on the OER activity. This concentration is the lowest for Ni samples prepared by chemical reduction (0.3 ppm), and the highest for colloidal nanoparticles (1 mM). The morphologies of the electrocatalysts might explain the different saturations. The morphology of the particles prepared by chemical reduction are nanosheets. Nanosheets likely have more defect and edge sites for Fe to adsorb, leading to saturation at a lower concentration. Thinner samples were reported to incorporate Fe more readily⁵. This could explain why the OER activity of the sputtered samples start to increase when very low amounts of Fe is present and keeps increasing until 0.9 ppm Fe.

The overpotentials of the sputtered electrocatalysts are overall the lowest. All of the nanoparticles have more or less the same overpotentials, where NiNiO prepared by the reduction synthesis method has the lowest overpotentials. The overpotentials of the nanoparticles after cycling in pure KOH are between 393 mV and 415 mV. After cycling in 1 mM Fe, their overpotentials are between 349 mV and 367 mV. Sputtered samples have overpotentials between 346 mV and 353 mV after cycling in pure KOH and between 279 and 292 after cycling in 1 mM Fe.

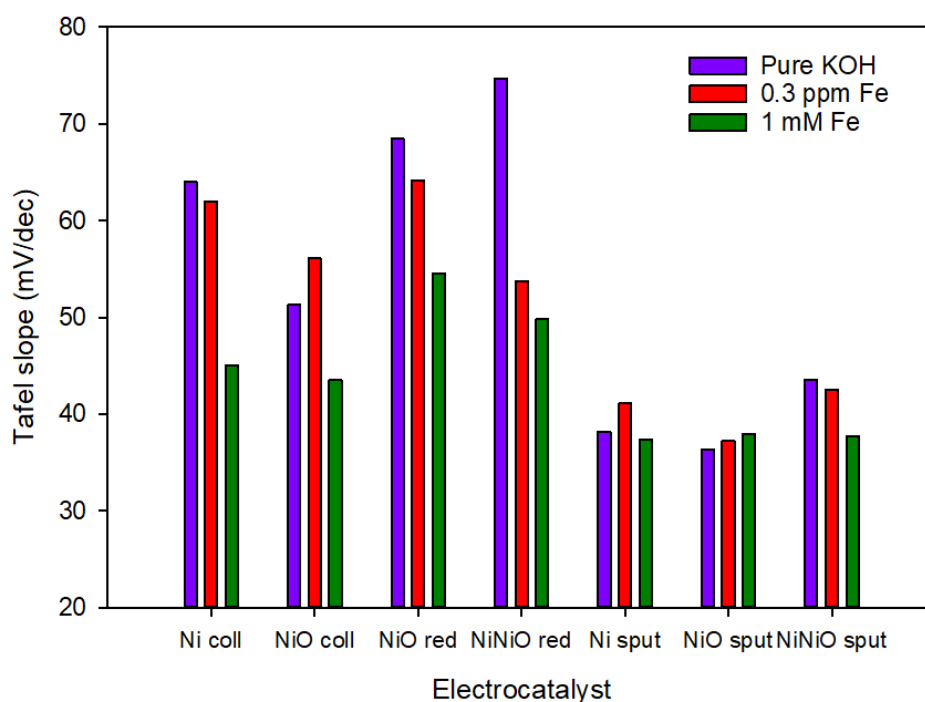


Figure 6-2: A bar chart summarizing the OER overpotentials of each of the Ni-based electrocatalysts after 30 CV cycles in pure KOH, 0.3 ppm Fe and 1 mM Fe.

Furthermore, electrocatalysts with overpotentials below 365 mV have Tafel slopes below 50 mV/dec, with a few single exceptions. The Tafel slopes of the nanoparticles cycled in different Fe concentrations vary, with values ranging between 75 mV/dec and 43 mV/dec. Therefore, the morphologies of the nanoparticles as well as the exact electrolytic Fe concentration influences the rate-determining step of the OER mechanism. All sputtered electrocatalysts cycled in different Fe concentrations have a Tafel slope of ~40 mV/dec, with values ranging between 36 mV/dec and 45.3 mV/dec. Therefore, all sputtered electrocatalysts could have the same OER mechanism or rate-determining step. The bifunctional OER mechanism with both Fe and Ni as active sites has been reported to have a rate-determining step corresponding to a Tafel slope of 40 mV/dec¹¹. However, several other OER mechanisms have been reported to have rate determining steps corresponding to Tafel slopes of 40 mV/dec. Therefore, a conclusive statement on the OER mechanism and rate-determining step cannot solely be based on the value of the Tafel slopes. Additional experiments where the KOH concentration is varied are needed, since the Tafel slope of electrocatalysts evolving oxygen with the bifunctional mechanism is independent of the OH⁻ concentration¹¹. However, the Tafel slope of electrocatalysts following the traditional method following four successive proton-coupled electron transfers is dependent on the concentration of OH⁻.

In addition to CVs and LSVs, the charge transfer resistance also serves as an indication of the OER activity. The charge transfer resistance has been determined for all of the sputtered samples, as these samples cover the surface of the substrate completely. The charge transfer resistance decreases for all sputtered samples as the electrolytic Fe concentration increases. This is in good agreement with the decrease in overpotentials.

2. After electrochemical cycling, iron is present on the surface of Ni-based electrocatalysts.

The results of analyses of both the nanoparticle and sputtered electrocatalysts support this statement. In-situ Raman spectroscopy results are primarily used to prove this statement, with XPS, EDX and CV results strengthening this argument. These results show that Fe is located in the surface of nanoparticle and sputtered Ni electrocatalysts and does not incorporate into the bulk structure.

Previous studies state that Fe from the electrolyte will incorporate into the bulk of Ni electrocatalysts to form a NiFe-LDH structure⁶. When Fe is incorporated into Ni electrocatalysts, it replaces some of the lattice Ni in NiOOH, resulting in an NiFe LDH structure. This structure can be identified in Raman spectra by examining the two peaks at ~ 480 and 560 cm^{-1} , ascribed to the Ni-O vibrations of NiOOH^{56,62}. When an NiFe LDH structure is present, the 560 cm^{-1} peak increases in intensity relative to the 480 cm^{-1} peak and these peaks appear noticeably broader⁶. In addition, no peaks corresponding to a separate Fe phase are present when Fe is present in the bulk of Ni electrocatalysts.

It is important to take into account that a lot of factors can influence Fe incorporation. This includes the time that the Ni electrocatalyst is in contact with Fe containing electrolyte and the concentration of this electrolyte. It has previously been reported that Fe first incorporates into the structure of Ni electrocatalysts at the surface, edge or defect sites and incorporates into the bulk over time⁹. Previous studies reporting the presence of a NiFe LDH structure aged the Ni electrocatalysts for several days in 1 M KOH containing Fe⁶. The higher KOH concentration and longer exposure times could contribute to Fe incorporating into the bulk of these electrocatalysts.

Figure 4-38 to Figure 4-47 show the Raman spectra of Ni electrocatalysts before and after cycling in pure KOH and KOH containing different concentrations of Fe. Furthermore, Table 4-3 and Table 4-4 summarise the peak positions and $480/560\text{ cm}^{-1}$ peak height ratios of the peaks in these Raman spectra. There are two main findings in the Raman spectra for Ni nanoparticles that serve as evidence that Fe is present on the surface of Ni catalysts and not in the bulk. In addition, these findings are supported by XPS, EDX and CV results for both Ni nanoparticles and sputtered Ni and will consequently be discussed.

Firstly, from the Raman investigation, it is evident that the 480/560 cm^{-1} peak height ratio does not decrease with increasing Fe concentration. The peaks also do not appear broader after Fe addition. This means that the presence of a NiFe-LDH structure is not detected. The observation that Fe is not incorporated into the bulk structure is strengthened by the CV results for nanoparticles in section 4.2.4. As indicated in literature, Fe incorporation into the bulk results in an anodic shift and decreased intensity of the oxidation peak as the Fe concentration increases⁹. The CVs in this study do not exhibit these changes and therefore Fe did not incorporate into the bulk electrocatalyst structures. Similar behaviour was observed for the sputtered Ni electrocatalysts, indicating that, regardless of the different nature of films, a similar process occurs on the surface. In addition, the broad redox peaks and occasional presence of a second oxidation an/or reduction peak indicate that Fe is not homogeneously distributed throughout the electrocatalysts in this study⁹.

Furthermore, Table 4-4 shows that there is inconsistency in the 480/560 cm^{-1} peak height ratios and exact peak positions. This is in accordance with a recent study that reported in-situ Raman spectra of a FeOOH-NiOOH electrocatalyst (a NiOOH electrocatalyst with FeOOH covalently bonded to the surface)¹¹. This study reported that surface FeOOH results in a heterogeneous structure and that three points on the same electrocatalyst surface can yield Raman spectra with varying peak positions and intensities¹¹. This is because the FeOOH occurs as clusters, that are covalently bonded to the surface¹¹.

XPS results of sputtered films and nanoparticles and EDX results of sputtered films also support the non-homogeneous presence of FeOOH on the surface, since the Fe concentrations at various points on the surface is different. XPS was used to quantify the Fe concentration at three different points on the surface of nanoparticle and sputtered electrocatalysts after they were cycled in KOH containing different concentrations of Fe. The XPS quantification results of the nanoparticles showed that the Fe concentrations differ quite dramatically from one point on the surface to the next, indicating that the Fe on the surface is not homogeneously distributed. The XPS results of sputtered thin films showed less dramatic differences in Fe concentrations for the three spots on the surface, especially for higher electrolytic Fe concentrations. Although the concentration differences are less dramatic, it can still clearly be seen that Fe is not homogeneously distributed on the surfaces of these electrocatalysts after cycling. In addition, EDX was also performed on sputtered samples after cycling. Three to five points on the surfaces of the sputtered films were analysed by EDX after the samples were cycled. These points also showed variations in Fe concentrations for the same samples.

EDX and XPS results for sputtered thin films show strong evidence that Fe is present mainly or only in the surface. The penetration depth of EDX (a few microns) is much deeper than that of

XPS (roughly 5-10 nm). Therefore, EDX gives a semi-quantitative indication of the concentration of Fe in the bulk of the sample, whereas XPS reflects the surface composition. Figure 6-3 visually represents the amounts of Fe detected by XPS and EDX for sputtered samples cycled in different Fe concentrations.

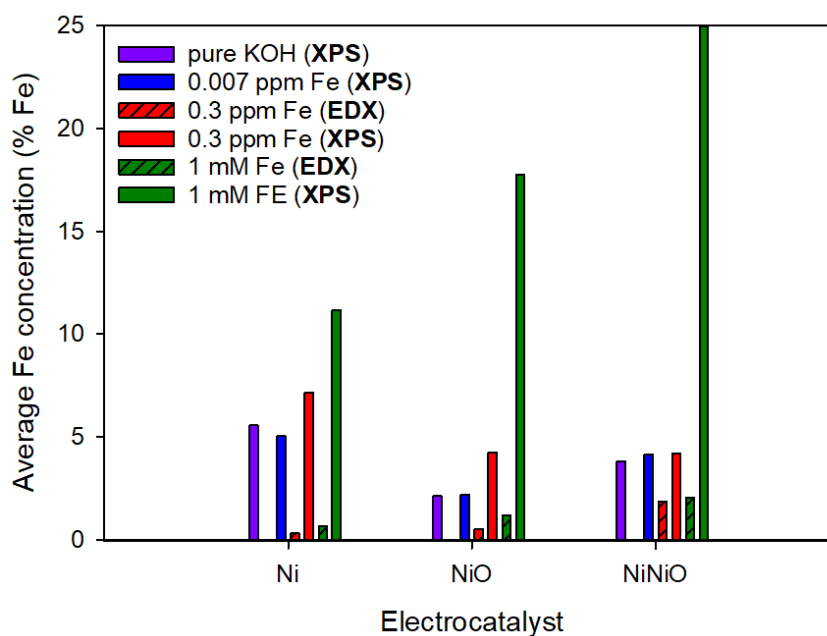


Figure 6-3: Fe concentrations in the bulk (EDX) and on the surface (XPS) of sputtered Ni electrocatalysts after cycling in KOH containing Fe.

For sputtered samples, the concentration of Fe detected by XPS is orders of magnitude larger than that detected by EDX. The average Fe concentration found on the surfaces of sputtered Ni, NiO and NiNiO cycled in 0.3 ppm by XPS were 7.15%, 4.27% and 4.19%, respectively. These concentrations were found to be 0.32%, 0.54% and 1.85% by EDX. For Ni, NiO and NiNiO cycled in 1 mM, XPS results showed an average of 11.15%, 17.76% and 26.85% Fe, respectively. The EDX results indicated average values of 0.68%, 1.18% and 2.03%. This clearly shows that the largest portion of Fe found in these samples are in the surface.

The amounts of Fe from XPS are in good agreement with what was previously reported for similar studies. Klaus *et al.* reported that 5% Fe was present in Ni samples after 12 CV cycles in 1 M reagent-grade KOH (≤ 0.66 ppm Fe). This study reports similar Fe concentrations for sputtered Ni, NiO and NiNiO cycled in SC-grade KOH as well as 0.3 ppm Fe. Another study reported that between 10 and 15% Fe was present in NiO samples that were cycled in Fe saturated KOH⁸. This is in agreement with sputtered Ni and NiO. Lastly, it has been reported that Ni samples cycled 100 times in 1 mM Fe contained 25 % Fe⁹, which is similar to what was found for sputtered NiNiO.

In addition, Figure 6-3 shows that the amount of Fe found in the surface of sputtered NiNiO is the largest for all of the sputtered samples. Furthermore, this value is close to what is reported to be the amount of Fe soluble in NiOOH⁹. It has also been reported that Ni electrocatalysts become saturated with Fe at close to 20% Fe⁶. Furthermore, it has been shown that co-deposited NiFe electrocatalysts containing 5% and 25% Fe have similar activities⁵. The results of this study are in accordance with this. For example, NiNiO cycled in 0.3 ppm Fe contains 4.19% Fe and NiNiO cycled in 1 mM contain 26.85% Fe. Even though this is a large difference in Fe content, the overpotentials of these two samples are similar, as evidenced from Figure 6-1. The same hold true for sputtered Ni and NiO.

SEM-EDX mapping (fig) of the sputtered films also indicate that Fe is not homogeneously distributed across the surface of the electrocatalysts. The fact that the FeOOH is irreversibly bonded to the surface is strengthened by the LSVs obtained for the sputtered films that was recycled in pure KOH and shown in section 5.2.3.3. It was shown that the activity-enhancing effect of Fe remains prominent after the Ni electrocatalyst is removed from Fe-containing electrolyte and cycled again in pure KOH. Therefore, the Fe has to be bonded to the Ni surface non-reversibly resulting in a stable electrocatalyst consisting of a Ni(OH)₂/NiOOH with clusters of FeOOH on the surface.

What is also important to note, is that the the 480/560 cm⁻¹ peak height ratio for NiFe LDH is reported as 1.18, where that of FeOOH-NiOOH is 1.78 and that of NiOOH is 2.2 (importantly, all of these values refer to peak height ratios measured at 0.6 V vs Hg/HgO)¹¹. Table 4-4 indicates that the peak height ratios at 0.6 V vs Hg/HgO of the electrocatalysts in this study, are between 1.5 and 2. This is a further indication that the samples in this study are either Ni (in various oxidation states) or FeOOH surface-bound to Ni electrocatalysts and not NiFe LDH.

The second important observation from the Raman spectra, is that peaks corresponding to α -FeOOH are present for colloidal catalysts cycled in KOH containing 1 mM Fe. These Fe peaks are also present in the spectra of NiO and NiNiO prepared by reduction cycled in 0.3 ppm Fe and 1 mM Fe. This is illustrated by the orange stars in Figure 6-1. From this figure it is clear that the presence of these peaks is directly correlated to a decrease in OER overpotential. Additionally, the overpotentials of Ni prepared by reduction do not decrease upon the addition of any amount of Fe to the electrolyte. Accordingly, no α -FeOOH peaks are observed in the in-situ Raman spectra for this electrocatalyst.

These peaks appear at around 303 cm⁻¹, 400 cm⁻¹ and 675 cm⁻¹, and are the three most prominent peaks in the Raman spectrum of α -FeOOH^{104,155}. Furthermore, the NiNiO sample cycled in 0.3 ppm Fe have peaks at 986 and 1062 cm⁻¹. As mentioned, there is a possibility that

these peaks arise due to Nafion¹⁵⁴. However, α -FeOOH also has clear peaks at similar wavenumbers¹⁵⁶. Based on the clear evidence that α -FeOOH is present with increased OER activity, these peaks will be assumed to arise due to its presence. What is also of interest, is that α -FeOOH is present and not γ -FeOOH, as reported in a similar study of surface Fe¹¹. α -FeOOH is crystalline and thermodynamically more stable than amorphous γ -FeOOH¹⁵⁶.

It is unlikely that the Fe peaks detected through Raman spectroscopy originate from Fe in the electrolyte (when higher concentrations of Fe are present in the electrolyte). The Raman spectra of the samples before they are cycled in the different Fe concentrations, contain no Fe peaks, regardless of the electrolytic Fe concentration. If the Fe peaks originated from the Fe in the electrolyte, they would have been visible in the spectra of these samples as well. However, the Fe peaks are only visible after cycling in higher concentrations of Fe, indicating that Fe adsorbs to the surface of Ni electrocatalysts during potential cycling.

Therefore, the Raman results clearly highlight that Fe is present on the surface of the electrocatalyst samples, which explains the absence of a NiFe LDH structure. From literature, it is known that Fe first adsorbs to the electrocatalyst surface and enhances the OER activity before incorporating into the bulk⁹. 30 CV cycles between 0.2 and 0.8 V vs Hg/HgO at 20 mV s⁻¹ takes about 30 minutes to complete. It is not yet clear whether applied potential or potential cycling is necessary for Fe incorporation. It is said that Fe incorporation is diffusion limited and therefore depends on the amount of time that the electrode is in contact with the Fe-containing electrolyte⁸. Studies reporting the presence of a NiFe LDH structure have aged a Ni electrode in KOH containing trace amounts of Fe for a minimum period of 24 hours⁶. This is considerably more time than the 30 minutes the electrodes in this study are in contact with Fe containing electrolyte. Therefore, a possibility is that the surface Fe observed in this study has not been allowed sufficient time to incorporate into the bulk structure to replace some of the Ni.

3. The oxidation states of Ni electrocatalysts do not affect OER activity

Another important finding of this study is that the oxidation state of Ni electrocatalysts have no effect on OER activity or Fe incorporation during cycling. This finding is supported by CV, in-situ Raman spectroscopy, XPS and EDX results. Different oxidation states were prepared for the two different morphologies of nanoparticles as well as for the sputtered samples. XRD showed that colloidal Ni was successfully prepared by the tailored synthesis method and colloidal NiO was obtained after annealing these particles in air. XRD also indicated that Ni, NiO were obtained by annealing particles prepared by the chemical reduction synthesis method in H₂/Ar and Air, respectively. The diffraction pattern for NiNiO prepared by reduction showed that consecutive annealing in H₂/Ar and Air successfully yields NiNiO, which is a mixture of Ni and NiO. Magnetron

sputtering allowed the preparation of Ni by using a Ni target, NiO by using reactive sputtering in Air, and NiNiO by using both Ni and NiO targets together. Even though different oxidation states were prepared, similar OER activities were seen for electrocatalysts of similar morphologies, regardless of the oxidation state as prepared. However, it should be kept in mind that various factors can have an influence on the ECSA or roughness factor of these electrocatalysts, which in turn can influence the OER activity. Factors such as crystallinity, structural defects and impurities can vary, and can be affected by annealing processes.

Furthermore, both colloidal Ni and NiO only showed an increase in OER activity after 1 mM Fe was added. For both of these oxidation states, only the samples cycled in 1 mM Fe displayed FeOOH peaks in the Raman spectra. Similarly, for NiO and NiNiO prepared by the reduction method, the OER activity increases when 0.3 ppm Fe is present in the electrolyte. These samples all have FeOOH peaks in the Raman spectra of the samples cycled in 0.3 ppm Fe and 1 mM Fe. These results implicate that electrocatalysts prepared by the chemical reduction synthesis method take up Fe easier from the electrolyte than the colloidal particles, regardless of the oxidation states prepared.

Furthermore, from the XPS results for nanoparticles in section 4.2.3, it was confirmed that different oxidation states are apparent for all the Ni-based nanoparticle samples cycled in different Fe concentrations. Colloidal Ni show almost the same ratio of $\text{Ni}^{2+} / \text{Ni}^{3+}$ for the samples cycled in pure KOH and 1 mM Fe, even though the OER activity of the sample cycled in 1 mM Fe is much higher. Colloidal Ni cycled in 0.007 ppm and 0.3 ppm have almost the same $\text{Ni}^{2+} / \text{Ni}^{3+}$ ratio, with a much smaller contribution from Ni^{2+} than the samples cycled in pure KOH and 1 mM Fe. Similarly, it can be said that the samples cycled in pure KOH and 0.007 ppm Fe have similar OER activities, but the oxidation states differ. Therefore, no link can be made between oxidation state and OER activity. NiO prepared by reduction follow the exact same trend as colloidal Ni, even though the OER activity of the NiO sample cycled in 0.3 ppm is much higher. Similarly, NiNiO prepared by reduction have the same oxidation state for all of the samples, regardless of the electrolytic Fe concentration. If the oxidation state influences the OER activity or vice versa, a variation in oxidation states would be expected for NiNiO cycled in pure KOH versus NiNiO cycled in 1 mM, for example.

XPS results for sputtered samples again show that the intended oxidation states were prepared. From the Ni 2p XPS spectra, no correlation between the oxidation states and OER activities can be seen. However, for these samples it was possible to also obtain and analyse a high resolution scan of the O 1s peak, since no other oxygen containing components are present in these samples (such as the Nafion binder for the nanoparticles). The O 1s XPS show that the pristine

sample and the sample cycled in 1 mM Fe are significantly less oxidized than the samples cycled in pure KOH, 0.007 ppm Fe and 0.3 ppm Fe. This is the case for all three sputtered electrocatalysts. This shows that cycling in KOH containing concentrated amounts of Fe results in films that are less oxidized. This is in direct agreement with what has previously been reported⁸.

For sputtered Ni samples, EDX analysis has also been done, which clearly shows the percentage oxygen relative to the percentage of Ni in each sample before and after electrochemical cycling. From these results, it can be seen that Ni, NiO and NiNiO have different starting concentrations of oxygen i.e., before the samples have been exposed to electrolyte. Even though they have different concentrations of oxygen, they have similar OER activities. Furthermore, for Ni, NiO and NiNiO samples that have been cycled in 0.9 ppm and 1 mM Fe, all have almost the same oxygen concentration. This could indicate that when Ni electrocatalysts are cycled in higher electrolytic Fe concentrations, these samples obtain a certain optimum concentration of oxygen. This optimum concentration is independent of the oxygen concentration started with.

Lastly, the redox features of Ni electrocatalysts can be observed to gain some insight into the oxidation states, and additionally the phases of Ni electrocatalysts. The nanoparticle electrocatalysts all have a single oxidation feature and a single reduction feature, except for colloidal NiO. This sample has an anodic doublet that is not very well pronounced, and in some cases a corresponding cathodic doublet. An anodic peak doublet likely points to the co-existence of both α -Ni(OH)₂ and β -Ni(OH)₂ in the electrocatalyst film, whereas a cathodic peak doublet may indicate that both α -NiOOH and γ -NiOOH are present. The presence of these phases do not alter the OER activity or Fe uptake regimes of this sample, as evidenced by CV. Furthermore, some of the sputtered samples also show the presence of anodic and cathodic peak doublets. Sputtered Ni samples cycled in 0.3 ppm, 0.9 ppm and 1 mM have cathodic peak doublets, and anodic peaks that appear to consist out of two peaks that are not well split. Sputtered NiO have anodic and cathodic doublets for samples that have been cycled in KOH containing 0.3 ppm 0.9 ppm and 1 mM. For both sputtered Ni and NiO, the anodic and cathodic peak doublets seem to be linked to higher electrolytic Fe content as they are only present from 0.3 ppm Fe and more. However, sputtered NiNiO only have a single oxidation and reduction feature in all of the Fe concentrations.

7. CONCLUSION

7.1 Summary

Electrochemical characterisation, in-situ Raman spectroscopy, XPS and SEM-EDX were used to evaluate the effect of electrolytic Fe on the structure and OER activity of Ni-based electrocatalysts. Ni nanoparticles with two different morphologies were investigated to observe the effect of morphology on the inclusion of Fe. Within each morphology, different oxidation states were investigated. In addition, sputtered Ni, NiO and NiNiO samples have also been investigated. Using three different morphologies helped to analyse the effect of Ni electrocatalyst morphology on Fe uptake and OER activity.

Cyclic voltammetry was successfully used to activate Ni electrocatalysts and allow time for Fe incorporation. Simultaneously, CVs served as an indication of the OER activity and redox processes. In-situ Raman spectroscopy proved to be an extremely efficient technique to monitor active sites of the OER as the reaction takes place. XPS was also effectively employed and yielded information about the Ni oxidation states before and after electrochemical cycling in Fe containing electrolytes. Another important role that the XPS results fulfilled in answering the research questions was to indicate the amount of Fe present in the surface layers of the electrocatalyst films. This could be compared with the amount of Fe detected by EDX, which is a semi quantitative indication of the amount of Fe in the bulk film.

7.2 Answering the research questions

This study found that Fe in the KOH electrolyte does not incorporate into the bulk structure of Ni nanoparticles prepared as nanosheets and colloidal particles, or sputtered thin films. This was primarily proven by the absence of a NiFe-LDH structure in the Raman spectra. Instead, peaks corresponding to α -FeOOH were found in the Raman spectra. Furthermore, the amount of Fe in sputtered samples was quantified by both EDX and XPS. The amount of Fe detected by EDX (bulk) was orders of magnitude less than the amount detected by XPS (surface), which show that the majority or all Fe in the thin films are located in the surface. Lastly, the redox features of nanoparticles and sputtered samples show that Fe is present in the surface and did not homogeneously incorporate into the bulk. The oxidation peak did not shift anodically and decrease in size as the Fe concentration increased, which is characteristic of Fe incorporating into the bulk.

It was also found that increased OER activity is linked to the presence of α -FeOOH peaks in the in-situ Raman spectra. Nanoparticle electrocatalysts that exhibited increased OER activities, also

had peaks corresponding to α -FeOOH in their Raman spectra. The results of SEM-EDX, XPS and in-situ Raman spectroscopy show that the Fe present is not homogeneously distributed.

The electrolytic Fe concentration at which the OER activity of the electrocatalyst stops increasing is determined by the morphology of the electrocatalyst. There exists an Fe saturation point after which further increasing the electrolytic Fe concentration will not lead to a further increase in OER activity. Interestingly, the nanoparticles prepared with the reduction synthesis method had a lower Fe saturation point than the colloidal nanoparticles. This could possibly be due to defects existing in the irregular morphology. Sputtered thin films were found to readily incorporate even ppb amounts of Fe.

Unlike the morphology, the Fe saturation point was not influenced by the as-prepared oxidation states (Ni, NiO and NiNiO). Similar morphologies have similar saturation points whether they were prepared as Ni, NiO or NiNiO. In addition, the O 1s XPS spectra of sputtered samples show that cycling in concentrated amounts of Fe results in less oxidised films.

To summarise, this investigation clearly shows that Fe on the surface of Ni electrocatalysts deposited from Fe-spiked electrolyte is responsible for enhancing the OER activity. Different morphologies require different concentrations of Fe to obtain enhanced activity.

7.3 Contributions

This study provided useful information that can be applied in research as well as industry. Firstly, this study has shown once again how important it is for researchers to report the amount of Fe in alkaline electrolyte when benchmarking new Ni electrocatalysts. Ideally, the electrolyte needs to be purified in a way that does not influence the electrocatalyst in question. Future studies can also obtain a rough estimation of how much a certain Fe concentration will increase the OER activity of their Ni electrocatalysts, since a wide range of Fe concentrations and different types of Ni electrocatalysts were studied.

As mentioned, controversy exists in literature about how electrolyte-bound Fe enhances the activity of Ni electrocatalysts. This study has made a significant contribution towards understanding this. It is shown here that the presence of FeOOH on the surface of electrocatalysts is directly correlated to the enhanced OER activity.

The knowledge about which Fe concentration optimally enhances each unique morphology can be applied to design more effective, cheaper OER electrocatalysts.

7.4 Limitations and recommendations

This study has paved the way for numerous possible future studies. Firstly, co-synthesised NiFe electrocatalysts produced by the same synthesis methods or sputtering, can be investigated. These samples can be investigated in KOH containing the same Fe concentrations used in this study, to observe the effect of electrolytic Fe of samples already containing certain amounts of Fe. This will show how crucial electrolyte-bound Fe is toward enhancing OER activity, or if catalysts of the same efficiency can be designed by co-synthesising NiFe electrocatalysts.

Furthermore, a wider range of in-situ techniques can be explored as it is difficult to gain information that accurately represents the system from analyses that are performed ex-situ. Using a modified setup, SEM can be performed in situ. Near ambient pressure (NAP) XPS could also be considered. In addition, surface enhanced Raman spectroscopy can be used to study sputtered thin films.

Future studies should explore different ways to purify KOH and repeat selected experiments with purified KOH. For the same reason it should be ensured that reagents for nanoparticle preparation are ultra-pure. Furthermore, similar electrocatalysts can also be tested in 1 M KOH to evaluate the effect of KOH concentration on Fe incorporation. Different KOH concentrations should also be used to gain mechanistic information.

Ultimately, the information in this study could be used to design and test a highly active OER electrocatalyst in an alkaline electrolyser.

BIBLIOGRAPHY

1. Lee, S., Bai, L. & Hu, X. Deciphering Iron-Dependent Activity in Oxygen Evolution Catalyzed by Nickel–Iron Layered Double Hydroxide. *Angew. Chemie Int. Ed.* **59**, 8072–8077 (2020).
2. Corrigan, D. A. The Catalysis of the Oxygen Evolution Reaction by Iron Impurities in Thin Film Nickel Oxide Electrodes. *J. Electrochem. Soc.* **134**, 377 (1987).
3. Edwards, P. P., Kuznetsov, V. L., David, W. I. F. & Brandon, N. P. Hydrogen and fuel cells: Towards a sustainable energy future. *Energy Policy* **36**, 4356–4362 (2008).
4. Tahir, M. *et al.* Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review. *Nano Energy* **37**, 136–157 (2017).
5. Trotochaud, L., Young, S., K. Ranney, J. & W. Boettcher, S. Nickel–Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **136**, 6744–6753 (2014).
6. Klaus, S., Cai, Y., W. Louie, M., Trotochaud, L. & T. Bell, A. Effects of Fe Electrolyte Impurities on Ni(OH)₂/NiOOH Structure and Oxygen Evolution Activity. *J. Phys. Chem. C* **119**, 7243–7254 (2015).
7. Gong, M. & Dai, H. A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts. *Nano Res.* **8**, 23–39 (2015).
8. Nardi, K. L., Yang, N., Dickens, C. F., Strickler, A. L. & Bent, S. F. Creating Highly Active Atomic Layer Deposited NiO Electrocatalysts for the Oxygen Evolution Reaction. *Adv. Energy Mater.* **5**, 1500412 (2015).
9. Burke Stevens, M., D. M. Trang, C., J. Enman, L., Deng, J. & W. Boettcher, S. Reactive Fe-Sites in Ni/Fe (Oxy)hydroxide Are Responsible for Exceptional Oxygen Electrocatalysis Activity. *J. Am. Chem. Soc.* **139**, 11361–11364 (2017).
10. Farhat, R., Dhainy, J. & Halaoui, L. I. OER Catalysis at Activated and Codeposited NiFe-Oxo/Hydroxide Thin Films Is Due to Postdeposition Surface-Fe and Is Not Sustainable without Fe in Solution. *ACS Catal.* **10**, 20–35 (2019).
11. Bai, L., Lee, S. & Hu, X. Spectroscopic and electrokinetic evidence for a bifunctional mechanism of the oxygen evolution reaction. *Angew. Chemie* **133**, 3132–3140 (2020).

12. Louie, M. W. & Bell, A. T. An Investigation of Thin-Film Ni–Fe Oxide Catalysts for the Electrochemical Evolution of Oxygen. *J. Am. Chem. Soc.* **135**, 12329–12337 (2013).
13. Peng, C. *et al.* Engineering Active Fe Sites on Nickel–Iron Layered Double Hydroxide through Component Segregation for Oxygen Evolution Reaction. *ChemSusChem* **13**, 811–818 (2020).
14. Fominykh, K. *et al.* Iron-doped nickel oxide nanocrystals as highly efficient electrocatalysts for alkaline water splitting. *ACS Nano* **9**, 5180–5188 (2015).
15. Lee, S., Banjac, K., Lingenfelder, M. & Hu, X. Oxygen isotope labeling experiments reveal different reaction sites for the oxygen evolution reaction on nickel and nickel iron oxides. *Angew. Chemie* **131**, 10401–10405 (2019).
16. Steimecke, M. *et al.* Higher-Valent Nickel Oxides with Improved Oxygen Evolution Activity and Stability in Alkaline Media Prepared by High-Temperature Treatment of Ni(OH)₂. *ACS Catal.* **10**, 3595–3603 (2020).
17. Gorlin, Y. *et al.* In situ X-ray absorption spectroscopy investigation of a bifunctional manganese oxide catalyst with high activity for electrochemical water oxidation and oxygen reduction. *J. Am. Chem. Soc.* **135**, 8525–8534 (2013).
18. Streibel, V. *et al.* In situ electrochemical cells to study the oxygen evolution reaction by near ambient pressure X-ray photoelectron spectroscopy. *Top. Catal.* **61**, 2064–2084 (2018).
19. Cleveland, C. J. & Morris, C. *Handbook of Energy*. (Elsevier, 2013).
20. LeRoy, R. L. Industrial water electrolysis: present and future. *Int. J. Hydrogen Energy* **8**, 401–417 (1983).
21. Chi, J. & Yu, H. Water electrolysis based on renewable energy for hydrogen production. *Chinese J. Catal.* **39**, 390–394 (2018).
22. Zeng, K. & Zhang, D. Recent progress in alkaline water electrolysis for hydrogen production and applications. *Prog. Energy Combust. Sci.* **36**, 307–326 (2010).
23. Wei, C. *et al.* Recommended Practices and Benchmark Activity for Hydrogen and Oxygen Electrocatalysis in Water Splitting and Fuel Cells. *Adv. Mater.* **31**, 1806296 (2019).

24. Song, F. *et al.* Transition metal oxides as electrocatalysts for the oxygen evolution reaction in alkaline solutions: an application-inspired renaissance. *J. Am. Chem. Soc.* **140**, 7748–7759 (2018).
25. Zhou, D. *et al.* Recent Advances in Non-Precious Metal-Based Electrodes for Alkaline Water Electrolysis. *ChemNanoMat* **6**, 336–355 (2020).
26. Lyons, M. E. G. & Brandon, M. P. The oxygen evolution reaction on passive oxide covered transition metal electrodes in aqueous alkaline solution. Part 1-Nickel. *Int. J. Electrochem. Sci* **3**, 1386–1424 (2008).
27. Miller, E. L. & Rocheleau, R. E. Electrochemical Behavior of Reactively Sputtered Iron-Doped Nickel Oxide. *J. Electrochem. Soc.* **144**, 3072–3077 (1997).
28. Lyons, M. & Doyle, R. Oxygen Evolution at Oxidised Iron Electrodes: A Tale of Two Slopes. *Int. J. Electrochem. Sci.* **7**, (2012).
29. Shinagawa, T., Garcia-Esparza, A. T. & Takanabe, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. *Sci. Rep.* **5**, 13801 (2015).
30. Wang, F. *et al.* Recent advances in transition-metal dichalcogenide based nanomaterials for water splitting. *Nanoscale* **7**, 19764–19788 (2015).
31. Anantharaj, S., Kundu, S. & Noda, S. “The Fe Effect”: A review unveiling the critical roles of Fe in enhancing OER activity of Ni and Co based catalysts. *Nano Energy* **80**, 105514 (2021).
32. Juodkazis, K., Juodkazytė, J., Vilkauskaitė, R. & Jasulaitienė, V. Nickel surface anodic oxidation and electrocatalysis of oxygen evolution. *J. Solid State Electrochem.* **12**, 1469–1479 (2008).
33. Bockris, J. O. Kinetics of Activation Controlled Consecutive Electrochemical Reactions: Anodic Evolution of Oxygen. *J. Chem. Phys.* **24**, 817–827 (1956).
34. Bockris, J. O. & Otagawa, T. The electrocatalysis of oxygen evolution on perovskites. *J. Electrochem. Soc.* **131**, 290 (1984).
35. Anantharaj, S. *et al.* Precision and correctness in the evaluation of electrocatalytic water splitting: revisiting activity parameters with a critical assessment. *Energy Environ. Sci.* **11**, 744–771 (2018).

36. Diaz-Morales, O., Ferrus-Suspedra, D. & Koper, M. T. M. The importance of nickel oxyhydroxide deprotonation on its activity towards electrochemical water oxidation. *Chem. Sci.* **7**, 2639–2645 (2016).
37. Zhang, M., De Respinis, M. & Frei, H. Time-resolved observations of water oxidation intermediates on a cobalt oxide nanoparticle catalyst. *Nat. Chem.* **6**, 362–367 (2014).
38. Song, F. *et al.* An unconventional iron nickel catalyst for the oxygen evolution reaction. *ACS Cent. Sci.* **5**, 558–568 (2019).
39. Kibria, M. F. & Mridha, M. S. Electrochemical studies of the nickel electrode for the oxygen evolution reaction. *Int. J. Hydrogen Energy* **21**, 179–182 (1996).
40. Hahn, F., Beden, B., Croissant, M. J. & Lamy, C. In situ uv visible reflectance spectroscopic investigation of the nickel electrode-alkaline solution interface. *Electrochim. Acta* **31**, 335–342 (1986).
41. Karpinski, A. *et al.* Deposition of nickel oxide by direct current reactive sputtering: Effect of oxygen partial pressure. *Thin Solid Films* **520**, 3609–3613 (2012).
42. Wruck, D. A., Dixon, M. A., Rubin, M. & Bogy, S. N. As-sputtered electrochromic films of nickel oxide. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **9**, 2170–2173 (1991).
43. Carenco, S. *et al.* Controlled Design of Size-Tunable Monodisperse Nickel Nanoparticles. *Chem. Mater.* **22**, 1340–1349 (2010).
44. Carenco, S. Designing Nanoparticles and Nanoalloys with Controlled Surface and Reactivity. *Chem. Rec.* **18**, 1114–1124 (2018).
45. K. Bates, M., Jia, Q., Ramaswamy, N., J. Allen, R. & Mukerjee, S. Composite Ni/NiO-Cr₂O₃ Catalyst for Alkaline Hydrogen Evolution Reaction. *J. Phys. Chem. C* **119**, 5467–5477 (2015).
46. Faid, A. Y., Barnett, A. O., Seland, F. & Sunde, S. Ni/NiO nanosheets for alkaline hydrogen evolution reaction: In situ electrochemical-Raman study. *Electrochim. Acta* **361**, 137040 (2020).
47. Sadiq, I. M., Mohammad, A. M., El-Shakre, M. E. & El-Deab, M. S. Electrocatalytic activity of nickel oxide nanoparticles-modified electrodes: Optimization of the loading level and operating pH towards the oxygen evolution reaction. *Int. J. Hydrogen Energy* **37**, 68–77 (2012).

48. Chekin, F., Tahermansouri, H. & Besharat, M. R. Nickel oxide nanoparticles prepared by gelatin and their application toward the oxygen evolution reaction. *J. Solid State Electrochem.* **18**, 747–753 (2014).
49. Boudart, M. Catalysis by Supported Metals. in (eds. Eley, D. D., Pines, H. & Weisz, P. B. B. T.-A. in C.) vol. 20 153–166 (Academic Press, 1969).
50. Gao, M. *et al.* Efficient Water Oxidation Using Nanostructured α -Nickel-Hydroxide as an Electrocatalyst. *J. Am. Chem. Soc.* **136**, 7077–7084 (2014).
51. Silva, V. D., Simões, T. A., Grilo, J. P. F., Medeiros, E. S. & Macedo, D. A. Impact of the NiO nanostructure morphology on the oxygen evolution reaction catalysis. *J. Mater. Sci.* **55**, 6648–6659 (2020).
52. Ganesan, P., Sivanantham, A. & Shanmugam, S. Inexpensive electrochemical synthesis of nickel iron sulphides on nickel foam: super active and ultra-durable electrocatalysts for alkaline electrolyte membrane water electrolysis. *J. Mater. Chem. A* **4**, 16394–16402 (2016).
53. Oshchepkov, A. G., Bonnefont, A. & Savinova, E. R. On the Influence of the Extent of Oxidation on the Kinetics of the Hydrogen Electrode Reactions on Polycrystalline Nickel. *Electrocatalysis* **11**, 133–142 (2020).
54. Dong, Y., Dang, J., Wang, W., Yin, S. & Wang, Y. First-principles determination of active sites of Ni metal-based electrocatalysts for hydrogen evolution reaction. *ACS Appl. Mater. Interfaces* **10**, 39624–39630 (2018).
55. Fominykh, K. *et al.* Ultrasmall dispersible crystalline nickel oxide nanoparticles as high-performance catalysts for electrochemical water splitting. *Adv. Funct. Mater.* **24**, 3123–3129 (2014).
56. Siang Yeo, B. & T. Bell, A. In Situ Raman Study of Nickel Oxide and Gold-Supported Nickel Oxide Catalysts for the Electrochemical Evolution of Oxygen. *J. Phys. Chem. C* **116**, 8394–8400 (2012).
57. Portemer, F., Delahaye-Vidal, A. & Figlarz, M. Characterization of active material deposited at the nickel hydroxide electrode by electrochemical impregnation. *J. Electrochem. Soc.* **139**, 671 (1992).
58. Beverskog, B. & Puigdomenech, I. Revised Pourbaix diagrams for nickel at 25–300 C.

- Corros. Sci.* **39**, 969–980 (1997).
59. Bode, H., Dehmelt, K. & Witte, J. _ . Zur kenntnis der nickelhydroxidelektrode—I. Über das nickel (II)-hydroxidhydrat. *Electrochim. Acta* **11**, 1079-IN1 (1966).
 60. Friebe, D. *et al.* Identification of highly active Fe sites in (Ni, Fe) OOH for electrocatalytic water splitting. *J. Am. Chem. Soc.* **137**, 1305–1313 (2015).
 61. Song, F. & Hu, X. Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. *Nat. Commun.* **5**, 4477 (2014).
 62. Kostecki, R. & McLarnon, F. Electrochemical and in situ Raman spectroscopic characterization of nickel hydroxide electrodes: I. Pure nickel hydroxide. *J. Electrochem. Soc. - J Electrochem SOC* **144**, 485–492 (1997).
 63. Francàs, L. *et al.* Spectroelectrochemical study of water oxidation on nickel and iron oxyhydroxide electrocatalysts. *Nat. Commun.* **10**, 1–10 (2019).
 64. Visscher, W. & Barendrecht, E. The anodic oxidation of nickel in alkaline solution. *Electrochim. Acta* **25**, 651–655 (1980).
 65. Li, N. *et al.* Influence of iron doping on tetravalent nickel content in catalytic oxygen evolving films. *Proc. Natl. Acad. Sci.* **114**, 1486–1491 (2017).
 66. Fan, L. *et al.* Promoting the Fe (VI) active species generation by structural and electronic modulation of efficient iron oxide based water oxidation catalyst without Ni or Co. *Nano Energy* **72**, 104656 (2020).
 67. Stern, L.-A. & Hu, X. Enhanced oxygen evolution activity by NiOx and Ni (OH) 2 nanoparticles. *Faraday Discuss.* **176**, 363–379 (2015).
 68. Roy, C. *et al.* Impact of nanoparticle size and lattice oxygen on water oxidation on NiFeOxHy. *Nat. Catal.* **1**, 820–829 (2018).
 69. Yang, Z. & Liang, X. Self-magnetic-attracted Ni x Fe (1– x)@ Ni x Fe (1– x) O nanoparticles on nickel foam as highly active and stable electrocatalysts towards alkaline oxygen evolution reaction. *Nano Res.* **13**, 461–466 (2020).
 70. Li, J., Lian, R., Wang, J., He, S. & Rui, Z. Oxygen vacancy defects modulated electrocatalytic activity of iron-nickel layered double hydroxide on Ni foam as highly active electrodes for oxygen evolution reaction. *Electrochim. Acta* **331**, 135395 (2020).

71. Wang, R. *et al.* Hierarchically devising NiFeOxHy catalyst with surface Fe active sites for efficient oxygen evolution reaction. *Catal. Today* **364**, (2020).
72. Schlögl, R. Heterogeneous Catalysis. *Angew. Chemie Int. Ed.* **54**, 3465–3520 (2015).
73. Suen, N.-T. *et al.* Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. *Chem. Soc. Rev.* **46**, 337–365 (2017).
74. Pan, Y., Shen, X., Yao, L., Bentalib, A. & Peng, Z. Active sites in heterogeneous catalytic reaction on metal and metal oxide: theory and practice. *Catalysts* **8**, 478 (2018).
75. Taylor, H. S. A theory of the catalytic surface. *Proc. R. Soc. London. Ser. A, Contain. Pap. a Math. Phys. Character* **108**, 105–111 (1925).
76. Garlyyev, B. *et al.* Revealing the nature of active sites in electrocatalysis. *Chem. Sci.* **10**, 8060–8075 (2019).
77. Medford, A. J. *et al.* From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. *J. Catal.* **328**, 36–42 (2015).
78. S. Burke, M., J. Enman, L., S. Batchellor, A., Zou, S. & W. Boettcher, S. Oxygen Evolution Reaction Electrocatalysis on Transition Metal Oxides and (Oxy)hydroxides: Activity Trends and Design Principles. *Chem. Mater.* **27**, 7549–7558 (2015).
79. Rossmeisl, J., Qu, Z.-W., Zhu, H., Kroes, G.-J. & Nørskov, J. K. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* **607**, 83–89 (2007).
80. Man, I. C. *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159–1165 (2011).
81. Stevens, M. B. *et al.* Measurement techniques for the study of thin film heterogeneous water oxidation electrocatalysts. *Chem. Mater.* **29**, 120–140 (2017).
82. Fu, S. *et al.* Ultrafine and highly disordered Ni₂Fe₁ nanofoams enabled highly efficient oxygen evolution reaction in alkaline electrolyte. *Nano Energy* **44**, 319–326 (2018).
83. Chung, D. Y. *et al.* Dynamic stability of active sites in hydr (oxy) oxides for the oxygen evolution reaction. *Nat. Energy* **5**, 222–230 (2020).
84. Hu, H.-S., Si, S., Liu, R.-J., Wang, C.-B. & Feng, Y.-Y. Iron-nickel hydroxide nanoflake arrays supported on nickel foam with dramatic catalytic properties for the evolution of

- oxygen at high current densities. *Int. J. Energy Res.* **44**, 9222–9232 (2020).
85. Boettcher, S. W. Oxygen stays put during water oxidation. *Nat. Catal.* **1**, 814–815 (2018).
 86. Welch, C. M. & Compton, R. G. The use of nanoparticles in electroanalysis: a review. *Anal. Bioanal. Chem.* **384**, 601–619 (2006).
 87. Kriek, R. J. *et al.* On the electrocatalytic symbiotic synergism between Pt, Ni and Al in plasma vapour deposited PtxNiyAlz thin metal films for water electrolysis. *J. Power Sources* **494**, 229344 (2021).
 88. Kjartansdóttir, C., Caspersen, M., Egelund, S. & Møller, P. Electrochemical investigation of surface area effects on PVD Al-Ni as electrocatalyst for alkaline water electrolysis. *Electrochim. Acta* **142**, 324–335 (2014).
 89. Mattox, D. M. *The Foundations of Vacuum Coating Technology*. (Noyes Publications, UK, USA, 2003).
 90. Baptista, A. *et al.* On the physical vapour deposition (PVD): Evolution of magnetron sputtering processes for industrial applications. *Procedia Manuf.* **17**, 746–757 (2018).
 91. Pierozynski, B., Mikolajczyk, T., Luba, M. & Zolfaghari, A. Kinetics of oxygen evolution reaction on nickel foam and platinum-modified nickel foam materials in alkaline solution. *J. Electroanal. Chem.* **847**, 113194 (2019).
 92. Ganeshchandra Prabhu, V., Paloly, A. R., Divya, N. G. & Bushiri, M. J. Photocatalytic and ferromagnetic properties of electrically conducting multifunctional Ni/NiO nanocomposites in amorphous carbon matrix. *Mater. Sci. Eng. B* **228**, 132–141 (2018).
 93. Ju, H., Li, Z. & Xu, Y. Electro-catalytic activity of Ni–Co-based catalysts for oxygen evolution reaction. *Mater. Res. Bull.* **64**, 171–174 (2015).
 94. Xue, X. *et al.* One-step synthesis of nickel–iron layered double hydroxides with tungstate acid anions via flash nano-precipitation for the oxygen evolution reaction. *Sustain. energy fuels* **3**, 237–244 (2019).
 95. Peter Atkins, P. & De Paula, J. *Atkins' Physical Chemistry*. (OUP Oxford, 2014).
 96. Jones, R. R., Hooper, D. C., Zhang, L., Wolverson, D. & Valev, V. K. Raman techniques: Fundamentals and frontiers. *Nanoscale Res. Lett.* **14**, 1–34 (2019).

97. HORIBA. What is Raman Spectroscopy? https://www.horiba.com/en_en/raman-imaging-and-spectroscopy/.
98. Zhu, K., Zhu, X. & Yang, W. Application of In Situ Techniques for the Characterization of NiFe-Based Oxygen Evolution Reaction (OER) Electrocatalysts. *Angew. Chemie Int. Ed.* **58**, 1252–1265 (2019).
99. Michael, J. D. *et al.* Alkaline electrolyte and Fe impurity effects on the performance and active-phase structure of NiOOH thin films for OER catalysis applications. *J. Phys. Chem. C* **119**, 11475–11481 (2015).
100. Beverskog, B. & Puigdomenech, I. Revised pourbaix diagrams for iron at 25–300 °C. *Corros. Sci.* **38**, 2121–2135 (1996).
101. Shang, Y. & van Weert, G. Iron control in nitrate hydrometallurgy by autoclave hydrolysis of iron(III) nitrate. *Hydrometallurgy* **33**, 273–290 (1993).
102. Zhang, F. *et al.* In situ electrochemically converting Fe₂O₃-Ni(OH)₂ to NiFe₂O₄-NiOOH: a highly efficient electrocatalyst towards water oxidation. *Sci. China Mater.* **60**, 324–334 (2017).
103. Lu, Z. *et al.* Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction. *Chem. Commun.* **50**, 6479–6482 (2014).
104. Abrashev, M. V *et al.* Raman spectroscopy of alpha-FeOOH (goethite) near antiferromagnetic to paramagnetic phase transition. *J. Appl. Phys.* **127**, 205108 (2020).
105. Wang, D., Jin, L., Li, Y. & Hu, H. Partial oxidation of vacuum residue over Al and Zr-doped α -Fe₂O₃ catalysts. *Fuel* **210**, 803–810 (2017).
106. Yi, Y. *et al.* Electrochemical corrosion of a glassy carbon electrode. *Catal. Today* **295**, 32–40 (2017).
107. Trześniewski, B. J. *et al.* In situ observation of active oxygen species in Fe-containing Ni-based oxygen evolution catalysts: the effect of pH on electrochemical activity. *J. Am. Chem. Soc.* **137**, 15112–15121 (2015).
108. Mironova-Ulmane, N., Kuzmin, A., Sildos, I. & Pärs, M. Polarisation dependent Raman study of single-crystal nickel oxide. *Open Phys.* **9**, 1096–1099 (2011).
109. Thema, F. T., Manikandan, E., Gurib-Fakim, A. & Maaza, M. Single phase Bunsenite NiO

- nanoparticles green synthesis by *Agathosma betulina* natural extract. *J. Alloys Compd.* **657**, 655–661 (2016).
110. Hall, D. S., Lockwood, D. J., Bock, C. & MacDougall, B. R. Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **471**, 20140792 (2015).
 111. Van der Heide, P. X-Ray photoelectron spectroscopy. *An Introd. to Princ. Pract.* (2011).
 112. Regonini, D. Anodised TiO₂ nanotubes: synthesis, growth mechanism and thermal stability. (2008).
 113. Liu, Q. *et al.* Crystal-Plane-Dependent Activity of Spinel Co₃O₄ Towards Water Splitting and the Oxygen Reduction Reaction. *ChemElectroChem* **5**, 1080–1086 (2018).
 114. McIntyre, N. S. & Zetaruk, D. G. X-ray photoelectron spectroscopic studies of iron oxides. *Anal. Chem.* **49**, 1521–1529 (1977).
 115. Biesinger, M. C. *et al.* Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **257**, 2717–2730 (2011).
 116. Allen, G. C., Curtis, M. T., Hooper, A. J. & Tucker, P. M. X-Ray photoelectron spectroscopy of iron–oxygen systems. *J. Chem. Soc. Dalt. Trans.* 1525–1530 (1974) doi:10.1039/DT9740001525.
 117. Major, G. H. *et al.* Practical guide for curve fitting in X-ray photoelectron spectroscopy. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **38**, 61203 (2020).
 118. Dutta, S., Indra, A., Feng, Y., Song, T. & Paik, U. Self-supported nickel iron layered double hydroxide-nickel selenide electrocatalyst for superior water splitting activity. *ACS Appl. Mater. Interfaces* **9**, 33766–33774 (2017).
 119. Huang, Z. *et al.* All-room-temperature solution-processed new nanocomposites based hole transport layer from synthesis to film formation for high-performance organic solar cells towards ultimate energy-efficient fabrication. *Nano Energy* **47**, 26–34 (2018).
 120. Yao, T. *et al.* Preparation of magnetically recyclable yolk/shell Fe_xO_y/PdPt@ CeO₂ nanoreactors with enhanced catalytic activity. *Chem. Asian J.* **12**, 1400–1407 (2017).
 121. Pan, L., Zhu, X., Xie, X. & Liu, Y. Smart Hybridization of TiO₂ Nanorods and Fe₃O₄

- Nanoparticles with Pristine Graphene Nanosheets: Hierarchically Nanoengineered Ternary Heterostructures for High-Rate Lithium Storage. *Adv. Funct. Mater.* **25**, 3341–3350 (2015).
122. Zhang, W. *et al.* Multifunctional glucose biosensors from Fe₃O₄ nanoparticles modified chitosan/graphene nanocomposites. *Sci. Rep.* **5**, 1–9 (2015).
 123. Meng, X. *et al.* Graphene oxide sheets-induced growth of nanostructured Fe₃O₄ for a high-performance anode material of lithium ion batteries. *J. Mater. Chem. A* **3**, 12938–12946 (2015).
 124. Martinez, L. *et al.* Electrochemical growth of diverse iron oxide (Fe₃O₄, α-FeOOH, and γ-FeOOH) thin films by electrodeposition potential tuning. *J. Electrochem. Soc.* **154**, D126 (2007).
 125. Liu, A. *et al.* Hole mobility modulation of solution-processed nickel oxide thin-film transistor based on high-k dielectric. *Appl. Phys. Lett.* **108**, 233506 (2016).
 126. Koshtyal, Y. *et al.* Atomic layer deposition of NiO to produce active material for thin-film lithium-ion batteries. *Coatings* **9**, 301 (2019).
 127. Arrigo, R. *et al.* In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS. *Angew. Chemie Int. Ed.* **52**, 11660–11664 (2013).
 128. Atkins, P. & Overton, T. *Shriver and Atkins' inorganic chemistry*. (Oxford University Press, USA, 2010).
 129. Chen, P. *et al.* Nitrogen-doped nanoporous carbon nanosheets derived from plant biomass: an efficient catalyst for oxygen reduction reaction. *Energy Environ. Sci.* **7**, 4095–4103 (2014).
 130. Skoog, D. A., West, D. M., Holler, F. J. & Crouch, S. R. *Fundamentals of Analytical Chemistry*. (Brooks/Cole, Cengage Learning, 2014).
 131. Pedersen, C. M. *et al.* Benchmarking Pt-based electrocatalysts for low temperature fuel cell reactions with the rotating disk electrode: oxygen reduction and hydrogen oxidation in the presence of CO (review article). *Electrochim. Acta* **179**, 647–657 (2015).
 132. Skoog, D. A., Holler, F. J. & Crouch, S. R. *Principles of instrumental analysis*. (Cengage learning, 2017).

133. Vidal-Iglesias, F. J., Solla-Gullón, J., Rodes, A., Herrero, E. & Aldaz, A. Understanding the Nernst Equation and Other Electrochemical Concepts: An Easy Experimental Approach for Students. *J. Chem. Educ.* **89**, 936–939 (2012).
134. Görlin, M. *et al.* Oxygen evolution reaction dynamics, faradaic charge efficiency, and the active metal redox states of Ni–Fe oxide water splitting electrocatalysts. *J. Am. Chem. Soc.* **138**, 5603–5614 (2016).
135. Kear, G. & Walsh, F. The characteristics of a true Tafel slope. *Corros. Mater.* **30**, (2005).
136. Fabbri, E., Haberer, A., Waltar, K., Kötz, R. & Schmidt, T. J. Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. *Catal. Sci. Technol.* **4**, 3800–3821 (2014).
137. Oldham, K., Myland, J. & Bond, A. *Electrochemical science and technology: fundamentals and applications*. (John Wiley & Sons, 2011).
138. Lian, K. K., Kirk, D. W. & Thorpe, S. J. Investigation of a “Two-State” Tafel Phenomenon for the Oxygen Evolution Reaction on an Amorphous Ni-Co Alloy. *J. Electrochem. Soc.* **142**, 3704–3712 (1995).
139. Wan, K., Luo, J., Zhang, X., Subramanian, P. & Fransaer, J. In-situ formation of Ni (oxy)hydroxide on Ni foam as an efficient electrocatalyst for oxygen evolution reaction. *Int. J. Hydrogen Energy* **45**, 8490–8496 (2020).
140. Liang, J., Wang, Y.-Z., Wang, C.-C. & Lu, S.-Y. In situ formation of NiO on Ni foam prepared with a novel leaven dough method as an outstanding electrocatalyst for oxygen evolution reactions. *J. Mater. Chem. A* **4**, 9797–9806 (2016).
141. McCrory, C. C. L., Jung, S., Peters, J. C. & Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **135**, 16977–16987 (2013).
142. Anantharaj, S. & Noda, S. Appropriate use of electrochemical impedance spectroscopy in water splitting electrocatalysis. *ChemElectroChem* **7**, 2297–2308 (2020).
143. Swierk, J. R., Klaus, S., Trotochaud, L., Bell, A. T. & Tilley, T. D. Electrochemical study of the energetics of the oxygen evolution reaction at nickel iron (oxy) hydroxide catalysts. *J. Phys. Chem. C* **119**, 19022–19029 (2015).
144. Spanos, I. *et al.* Facile protocol for alkaline electrolyte purification and its influence on a

- Ni–Co oxide catalyst for the oxygen evolution reaction. *ACS Catal.* **9**, 8165–8170 (2019).
145. Nsanzimana, J. M. V. *et al.* Facile synthesis of amorphous ternary metal borides–reduced graphene oxide hybrid with superior oxygen evolution activity. *ACS Appl. Mater. Interfaces* **11**, 846–855 (2018).
 146. El-Kemary, M., Nagy, N. & El-Mehasseb, I. Nickel oxide nanoparticles: Synthesis and spectral studies of interactions with glucose. *Mater. Sci. Semicond. Process.* **16**, 1747–1752 (2013).
 147. García-Cerda, L. A. *et al.* Preparation of hcp and fcc Ni and Ni/NiO Nanoparticles Using a Citric Acid Assisted Pechini-Type Method. *J. Nanomater.* **2011**, 162495 (2011).
 148. Sneha, K., Esterle, A., Sharma, N. & Sahi, S. Yucca-derived synthesis of gold nanomaterial and their catalytic potential. *Nanoscale Res. Lett.* **9**, 627 (2014).
 149. Andrews, J. & Doddathimmaiah, A. K. 9 - Regenerative fuel cells. in *Woodhead Publishing Series in Electronic and Optical Materials* (ed. Gasik, M. B. T.-M. for F. C.) 344–385 (Woodhead Publishing, 2008). doi:<https://doi.org/10.1533/9781845694838.344>.
 150. Schulze, M., Lorenz, M., Wagner, N. & Gülzow, E. XPS analysis of the degradation of Nafion. *Fresenius. J. Anal. Chem.* **365**, 106–113 (1999).
 151. Hoffmann, E. A., Fekete, Z. A., Korugic-Karasz, L. S., Karasz, F. E. & Wilusz, E. Theoretical and experimental X-ray photoelectron spectroscopy investigation of ion-implanted nafion. *J. Polym. Sci. Part A Polym. Chem.* **42**, 551–556 (2004).
 152. Loeian, M. S., Ziolkowska, D. A., Khosravi, F., Jasinski, J. B. & Panchapakesan, B. Exfoliated WS₂-Nafion Composite based Electromechanical Actuators. *Sci. Rep.* **7**, 1–18 (2017).
 153. Lyons, M. E. G., Cakara, A., O'Brien, P., Godwin, I. & Doyle, R. L. Redox, pH sensing and electrolytic water splitting properties of electrochemically generated nickel hydroxide thin films in aqueous alkaline solution. *Int. J. Electrochem. Sci* **7**, 711–768 (2012).
 154. Logette, S., Eysseric, C., Huguet, P., Gavach, C. & Pourcelly, G. Oxidation by electrogenerated mediator: influence of perfluorosulfonic separator on process performance. *J. Appl. Electrochem.* **29**, 371–382 (1999).
 155. Hedenstedt, K., Bäckström, J. & Ahlberg, E. In-Situ Raman Spectroscopy of α - and γ -FeOOH during Cathodic Load. *J. Electrochem. Soc.* **164**, H621–H627 (2017).

156. Luo, W. *et al.* Highly crystallized α -FeOOH for a stable and efficient oxygen evolution reaction. *J. Mater. Chem. A* **5**, 2021–2028 (2017).
157. Nathan, M. I., Smith, J. E. & Tu, K. N. Raman spectra of glassy carbon. *J. Appl. Phys.* **45**, 2370 (1974).
158. Upare, D., Yoon, S. & Lee, C. W. Nano-structured porous carbon materials for catalysis and energy storage. *Korean J. Chem. Eng.* **28**, 731–743 (2011).

APPENDIX A

Appendix A includes experimental results pertaining to Ni-based nanoparticle electrocatalysts.

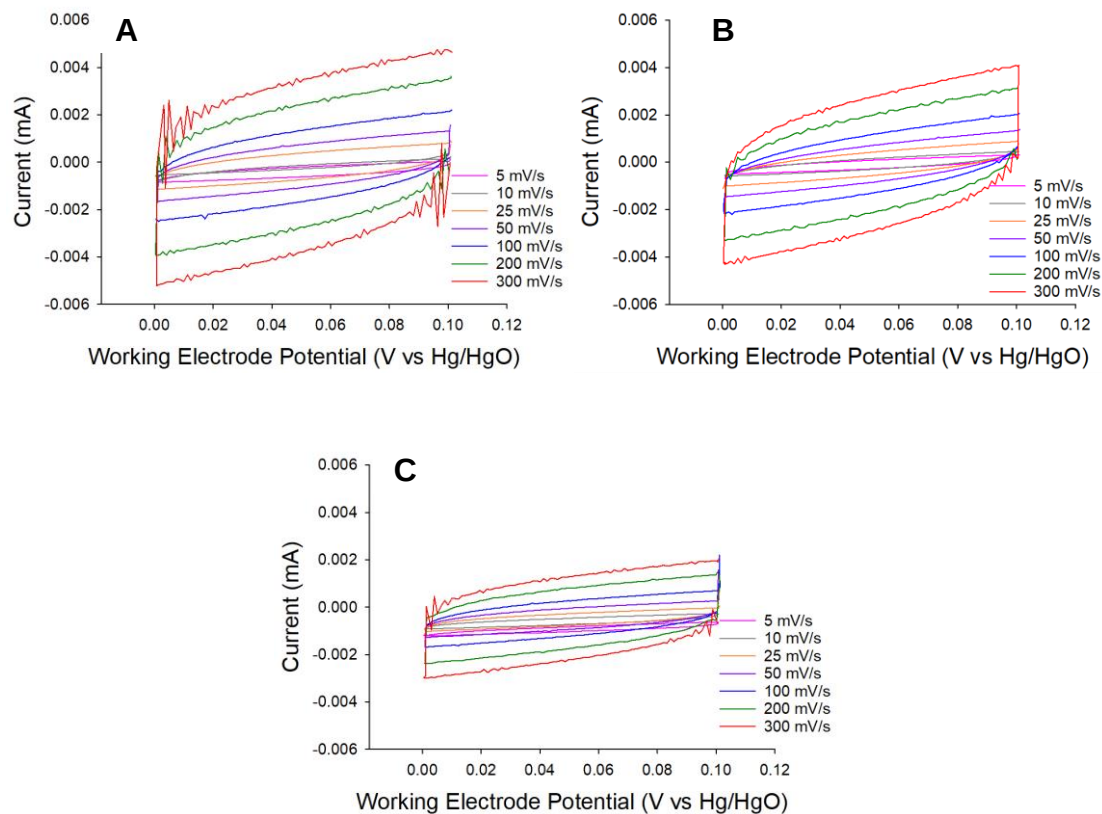


Figure A-1: CVs of colloidal Ni in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

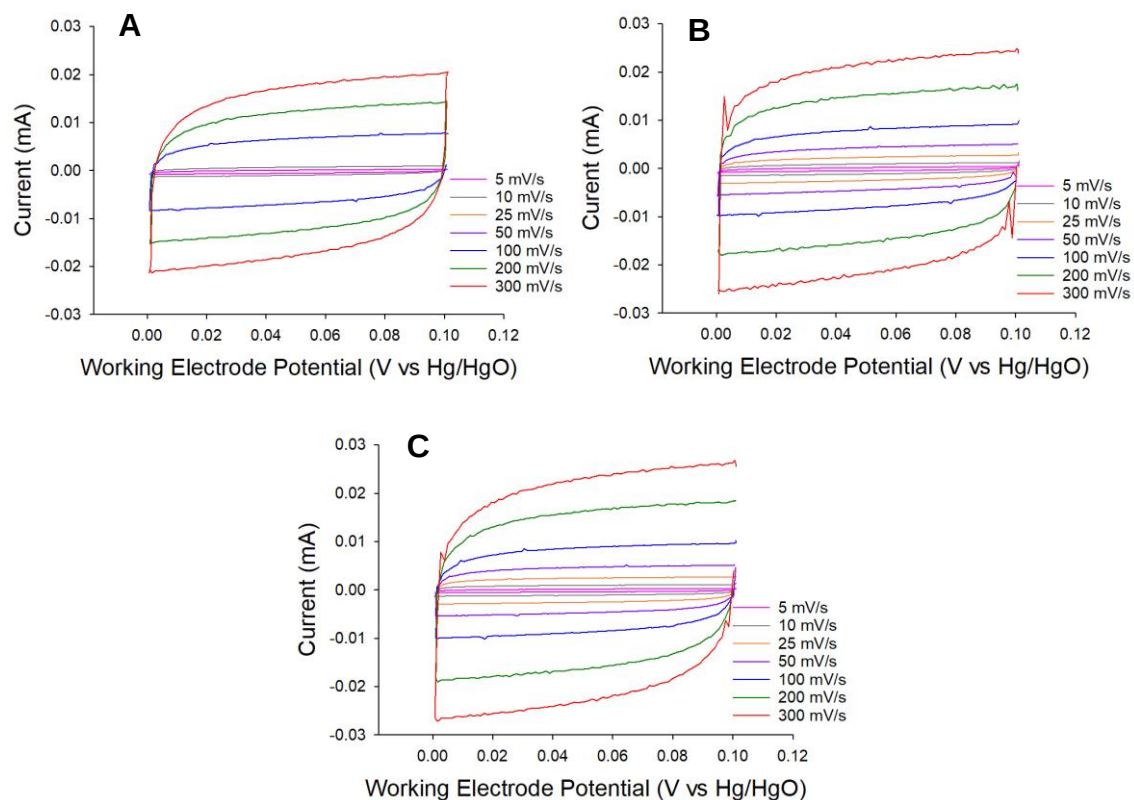


Figure A-2: CVs of colloidal NiO in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

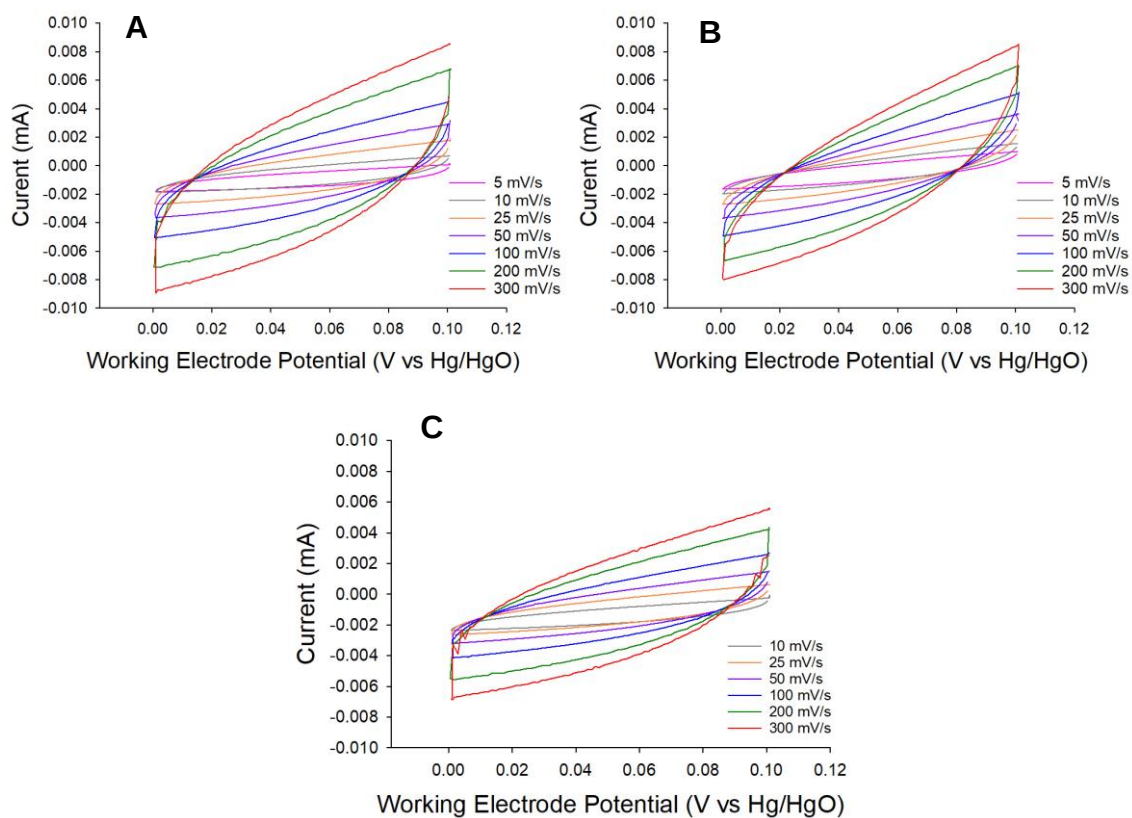


Figure A-3: CVs of NiO prepared by reduction in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

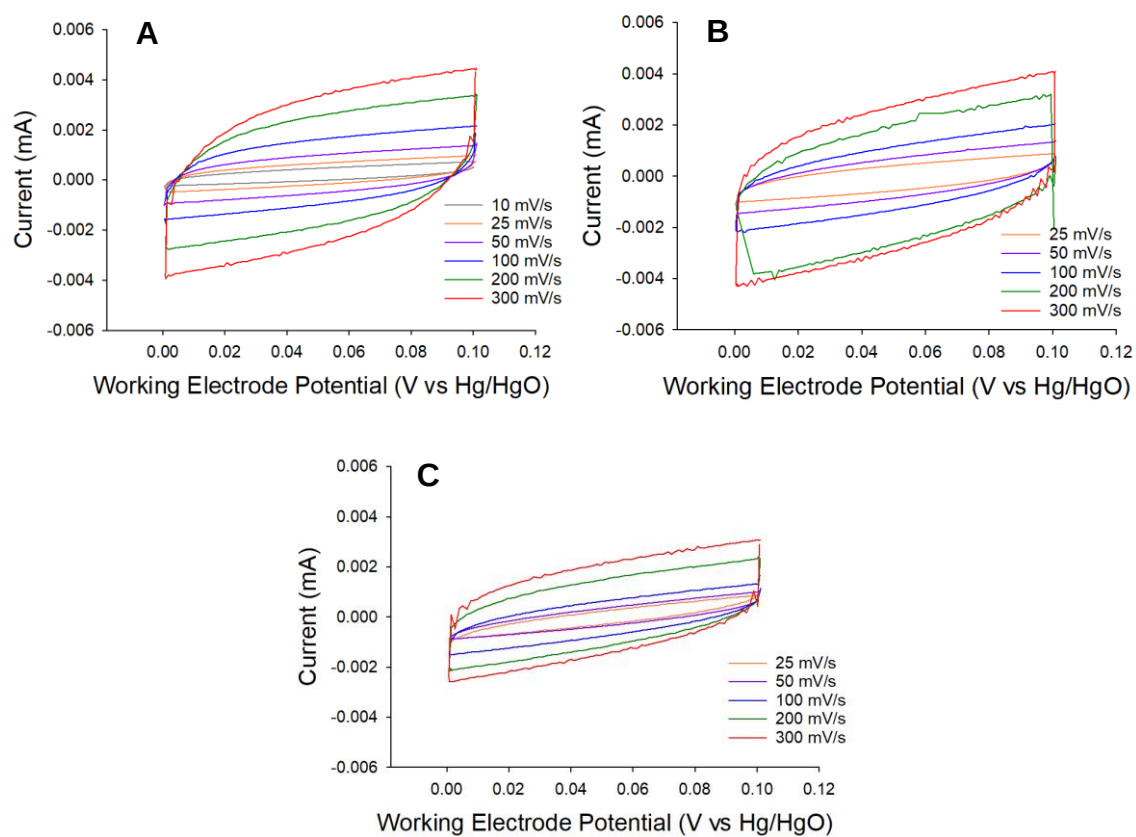


Figure A-4: CVs of NiNiO prepared by reduction in (a) pure KOH, (b) 0.3 ppm Fe and (c) 1 mM Fe performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

Figure A-5 to Figure A-13 illustrates the Raman spectra of Ni-based nanoparticles before and after cycling in different concentrations of Fe. The three peaks at 1340, 1590 and 2700 cm^{-1} , that can be observed throughout most of the spectra in this study arise due to the glassy carbon substrate used^{157,158}. A broad maximum from about 3000 to 3600 cm^{-1} obscures any peaks in the high-frequency region. This broad feature arises due to the O-H stretching vibration from the aqueous electrolyte present in the electrocatalyst film⁶².

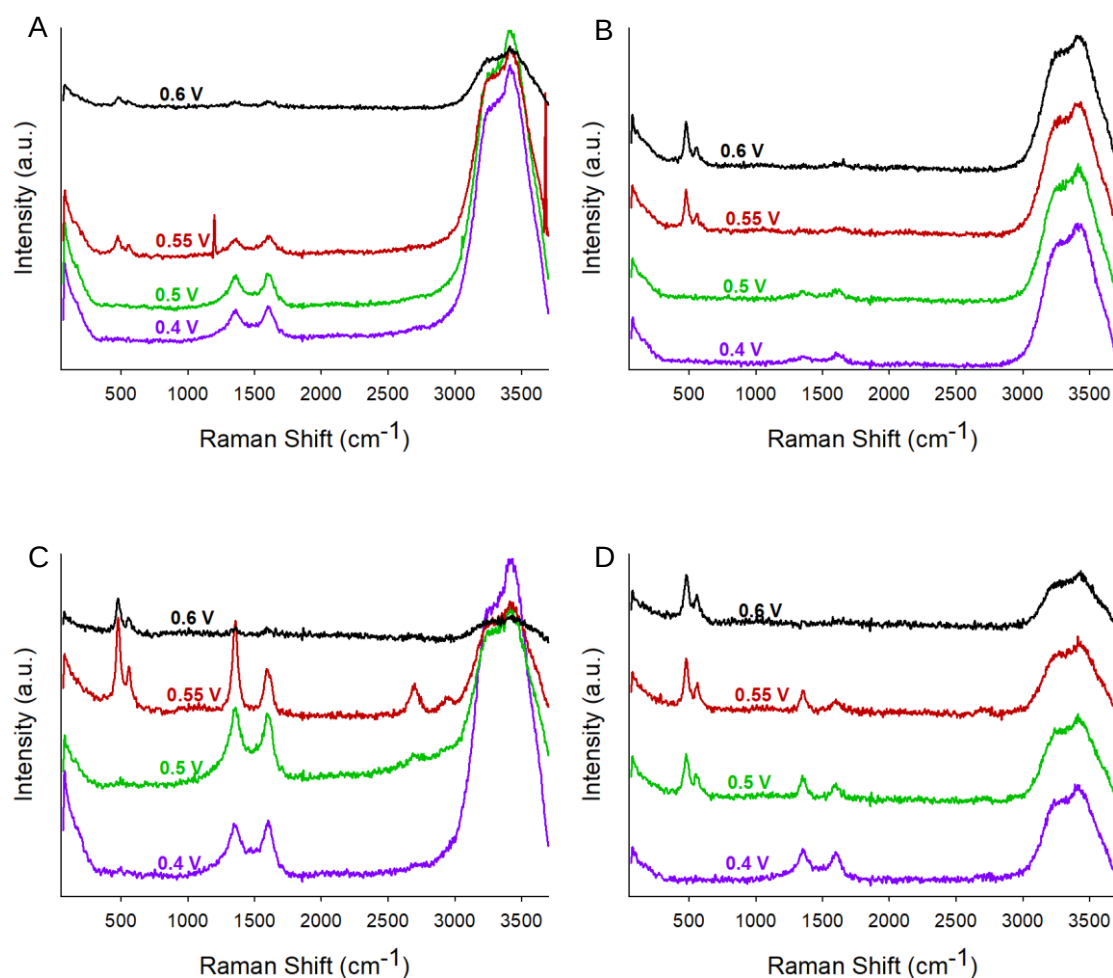


Figure A-5: In-situ Raman spectra of Colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.

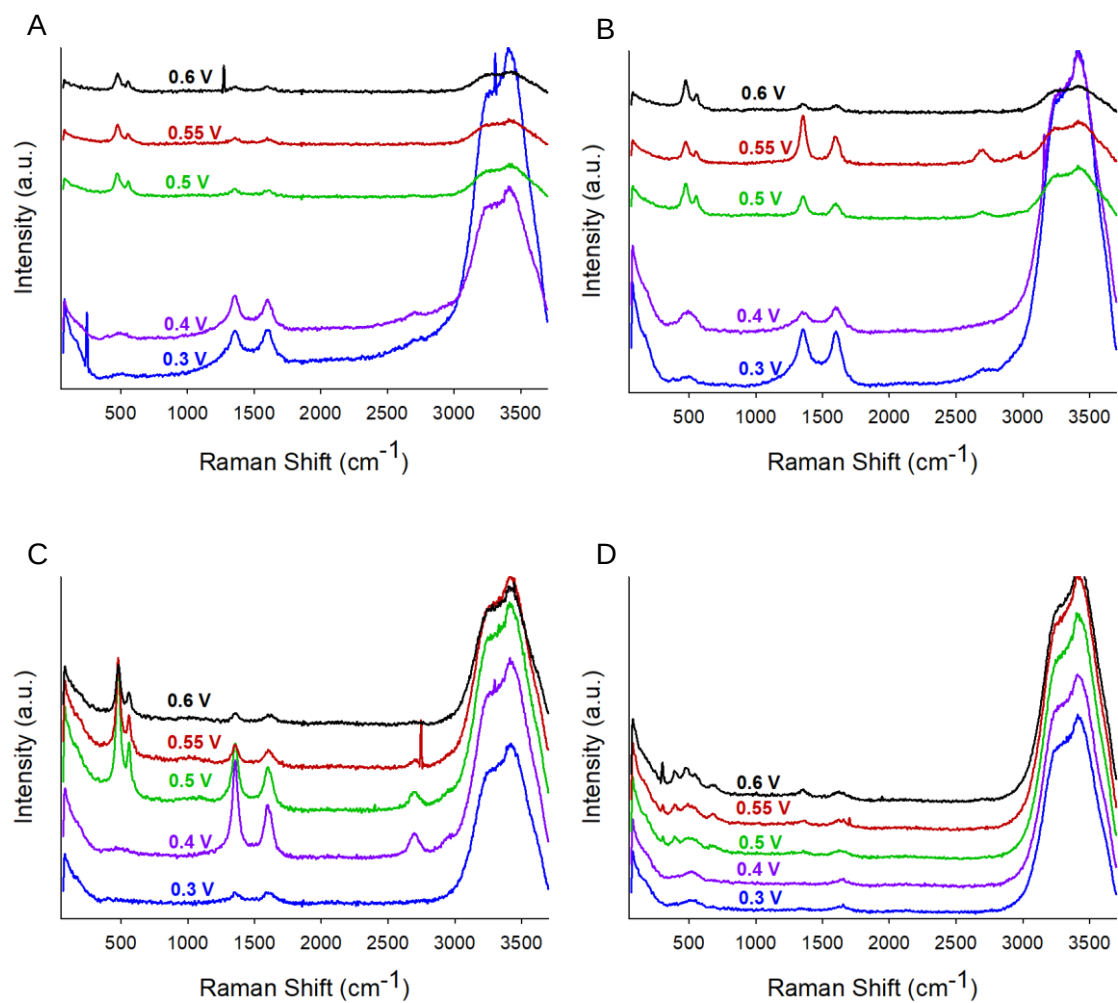


Figure A-6: In-situ Raman spectra of Colloidal Ni in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.

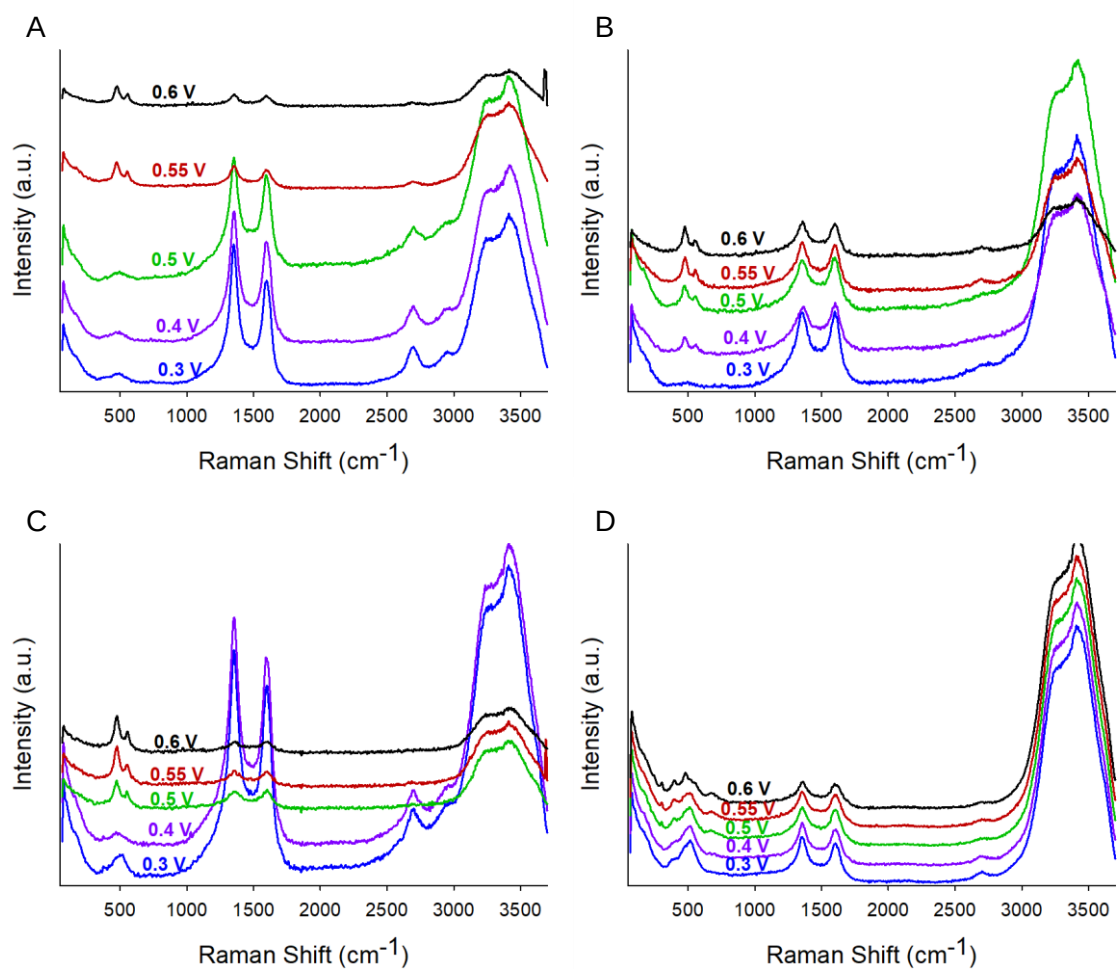


Figure A-7: In-situ Raman spectra of Colloidal NiO in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.

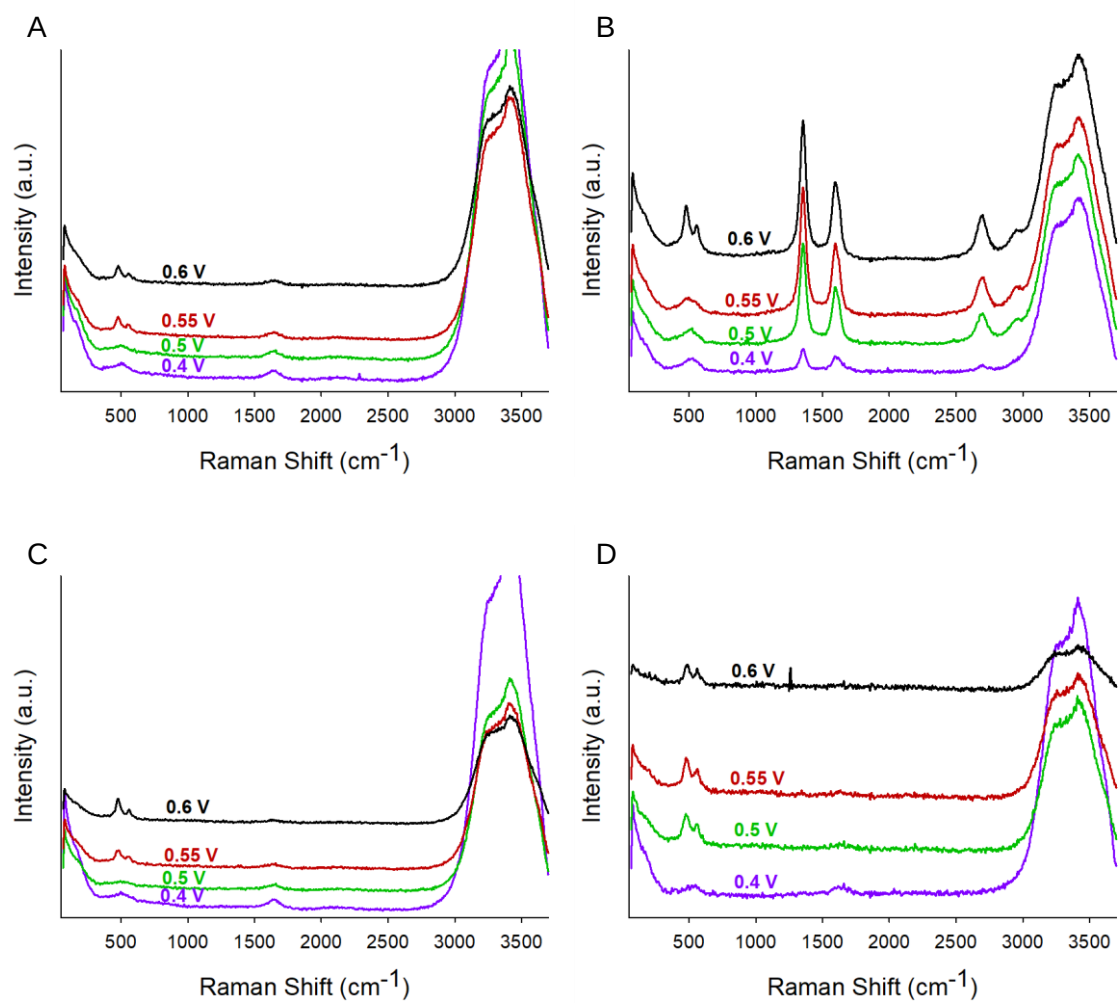


Figure A-8: In-situ Raman spectra of Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.

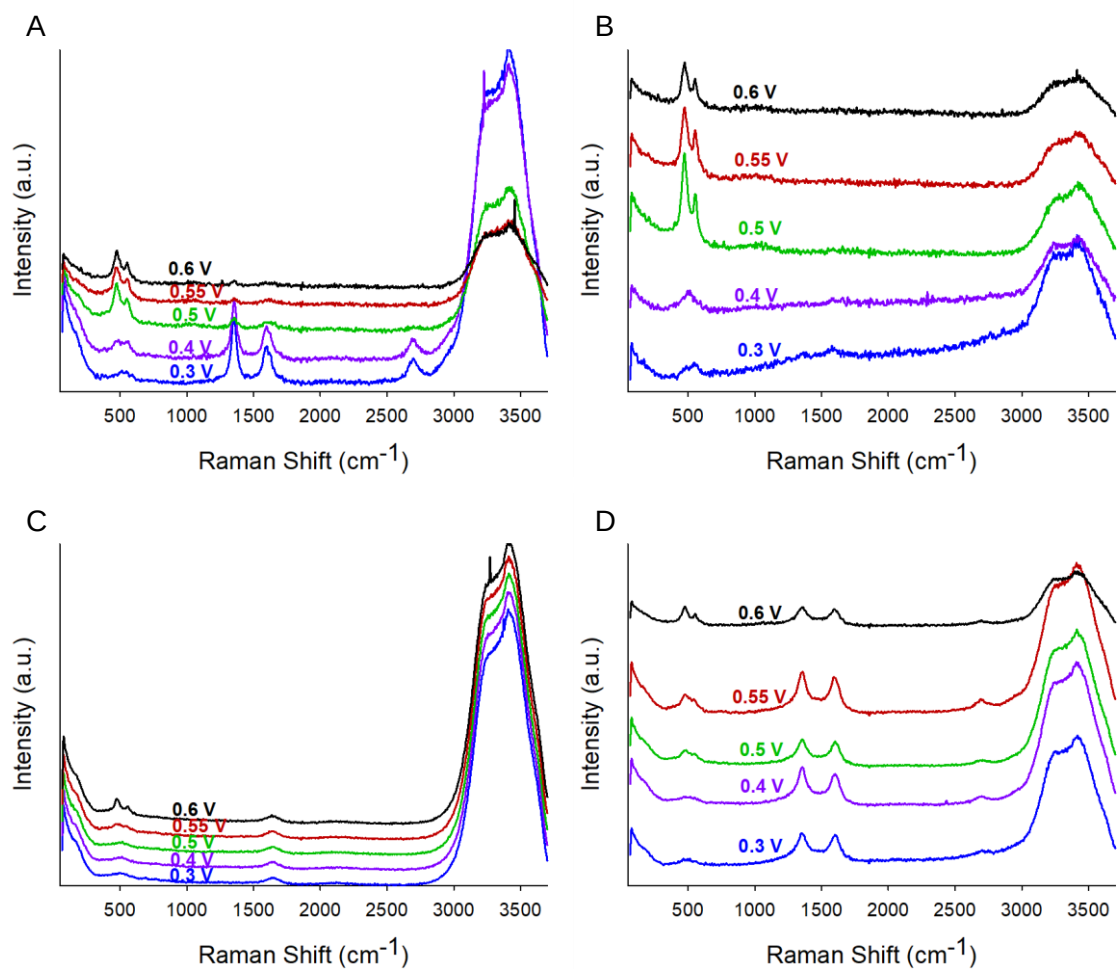


Figure A-9: In-situ Raman spectra of Ni prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.

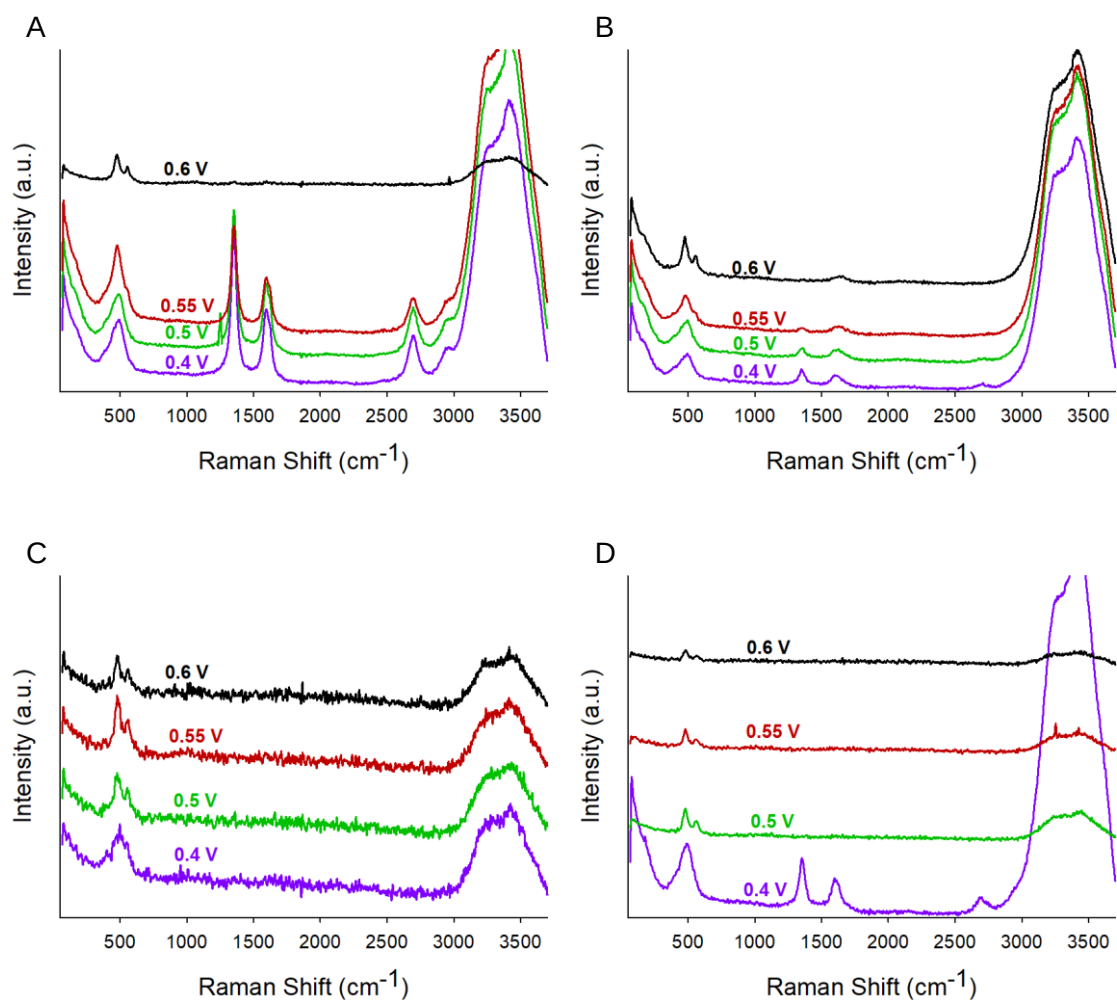


Figure A-10: In-situ Raman spectra of NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.

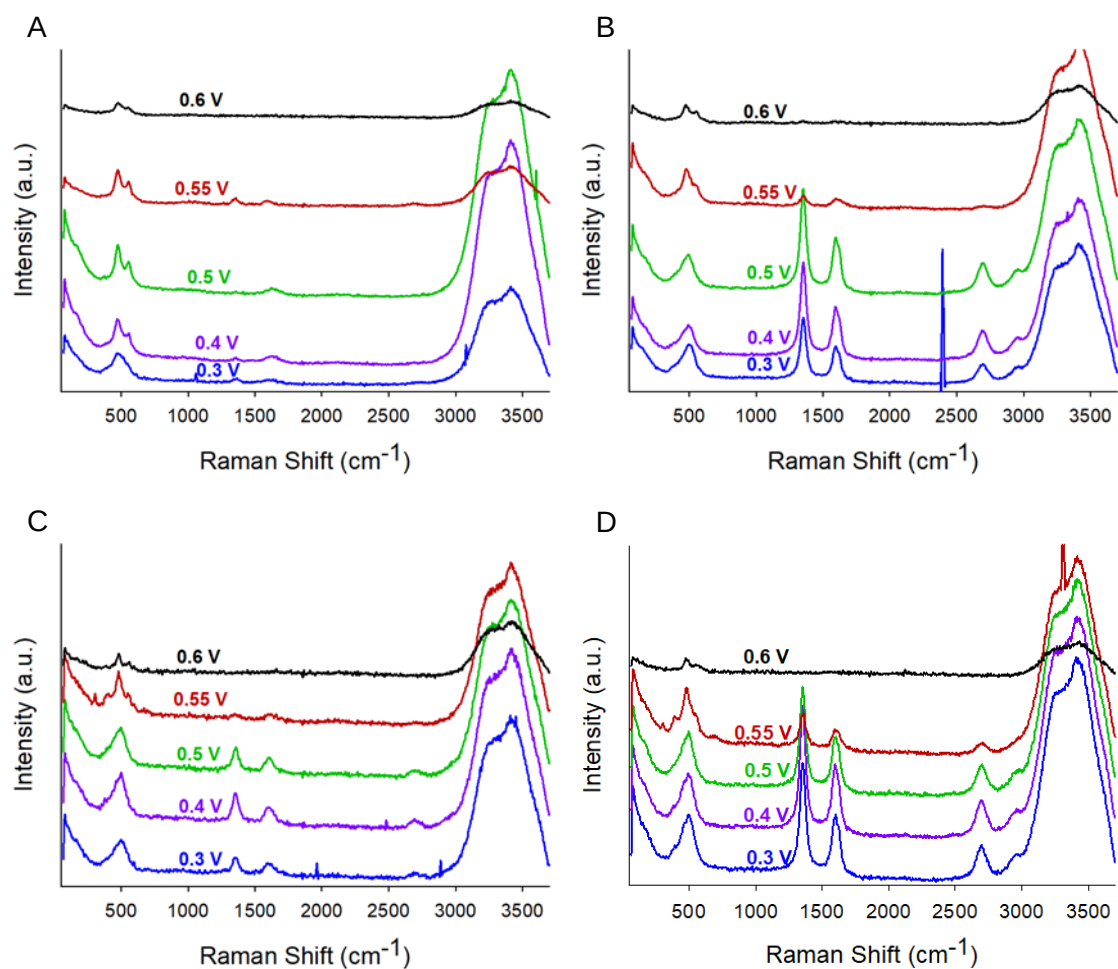


Figure A-11: In-situ Raman spectra of NiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.

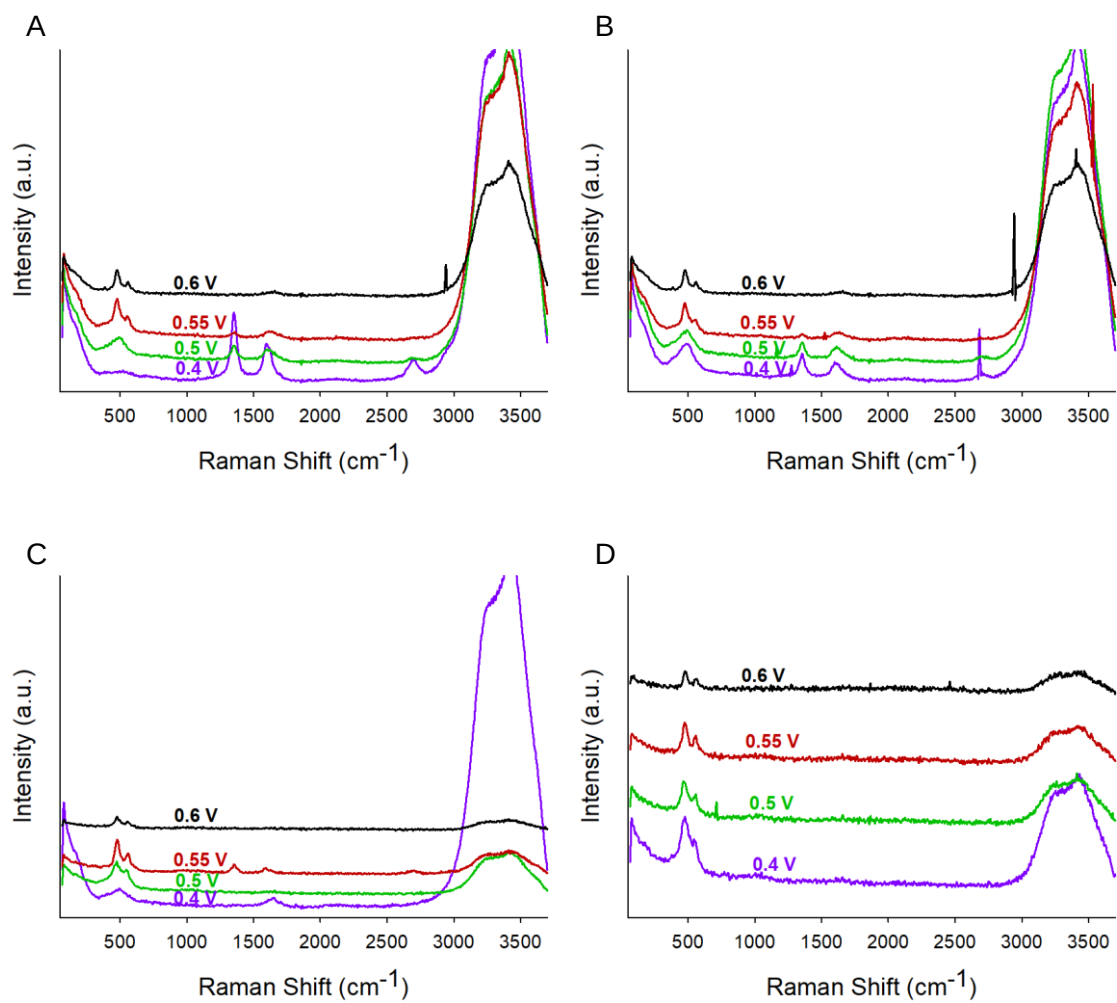


Figure A-12: In-situ Raman spectra of NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, before electrochemical cycling.

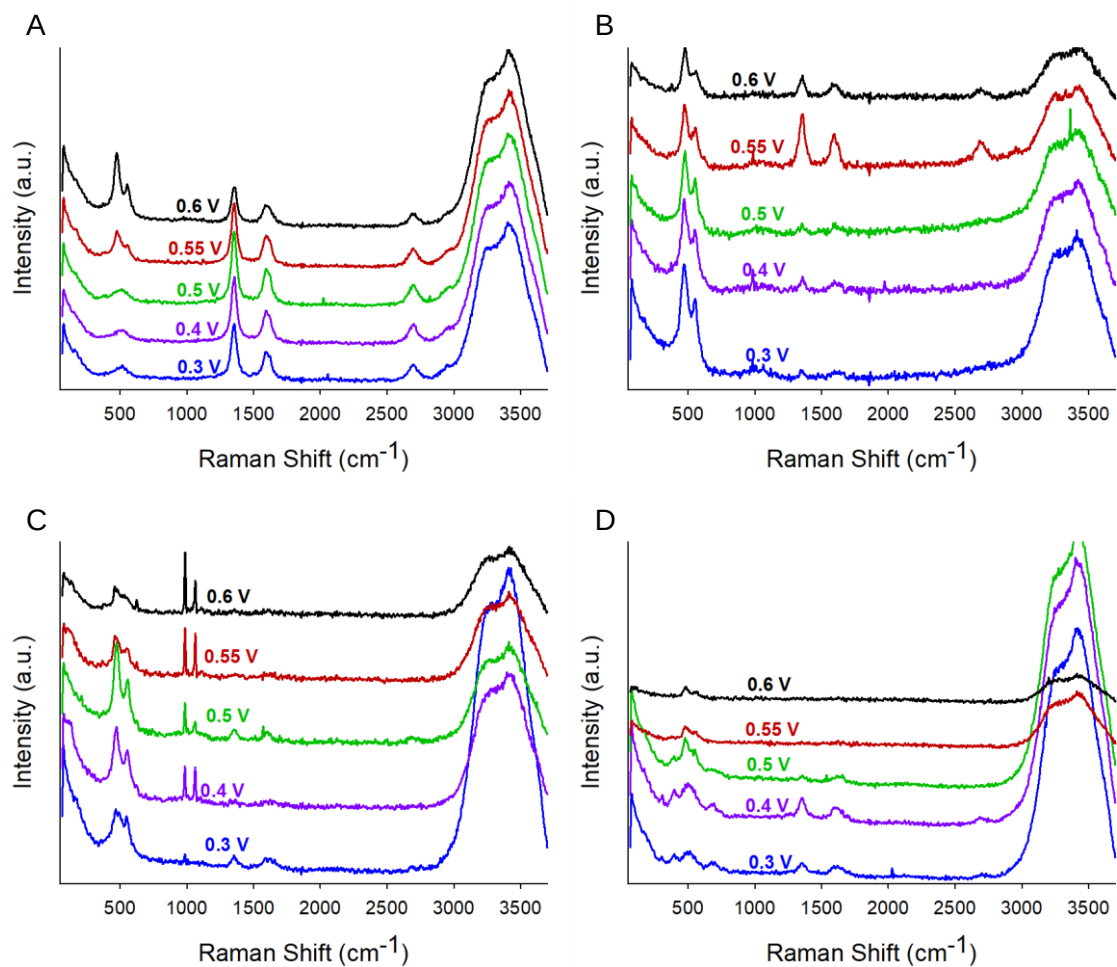


Figure A-13: In-situ Raman spectra of NiNiO prepared by reduction in (a) pure 0.1 M KOH, and 0.1 M KOH containing (b) 0.007 ppm Fe, (c) 0.3 ppm Fe and (d) 1mM Fe, after electrochemical cycling.

APPENDIX B

Appendix B contains results pertaining to sputtered electrocatalysts samples.

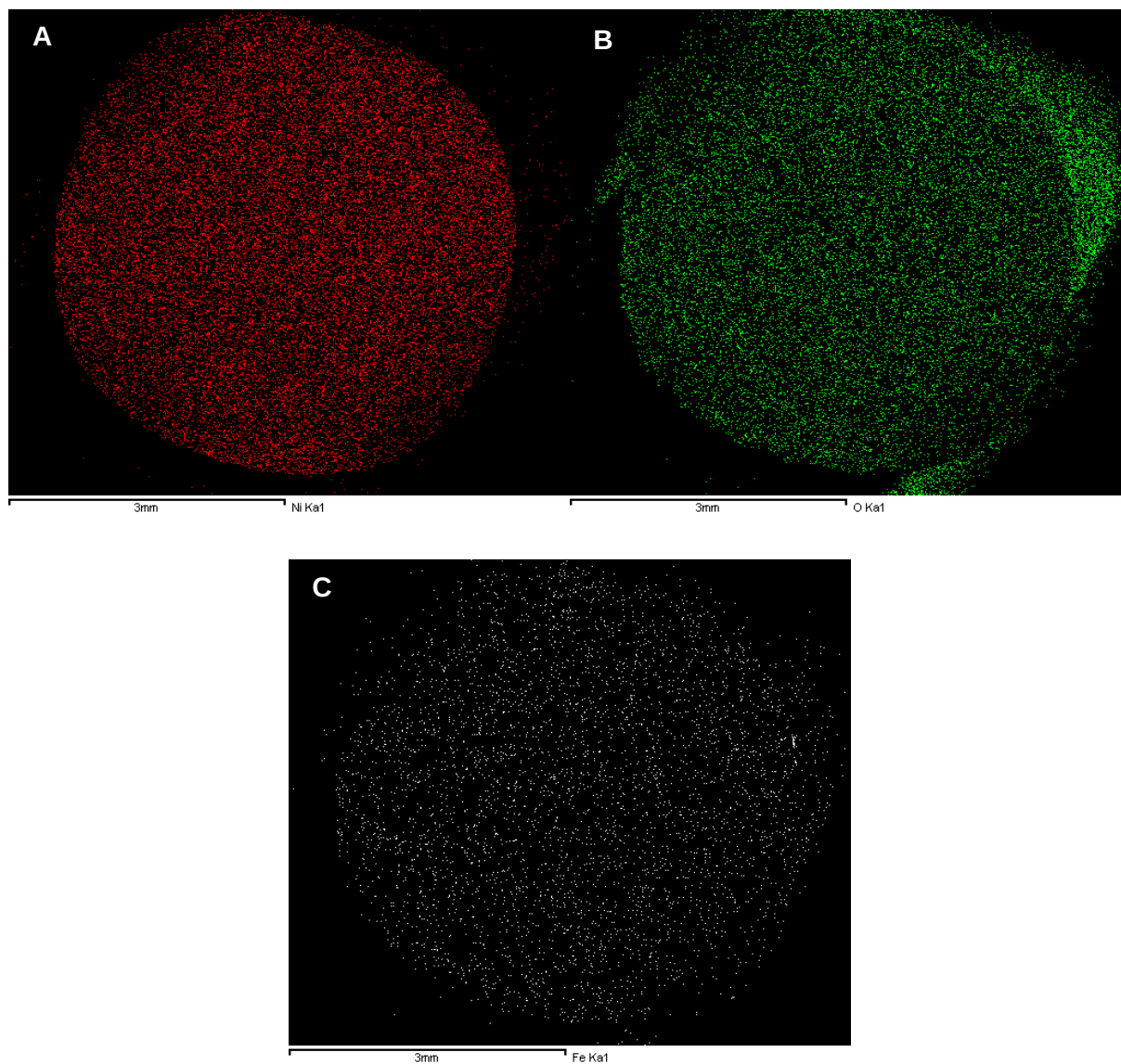


Figure B-1: SEM-EDX mapping analysis of the entire surface of a sputtered Ni thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.

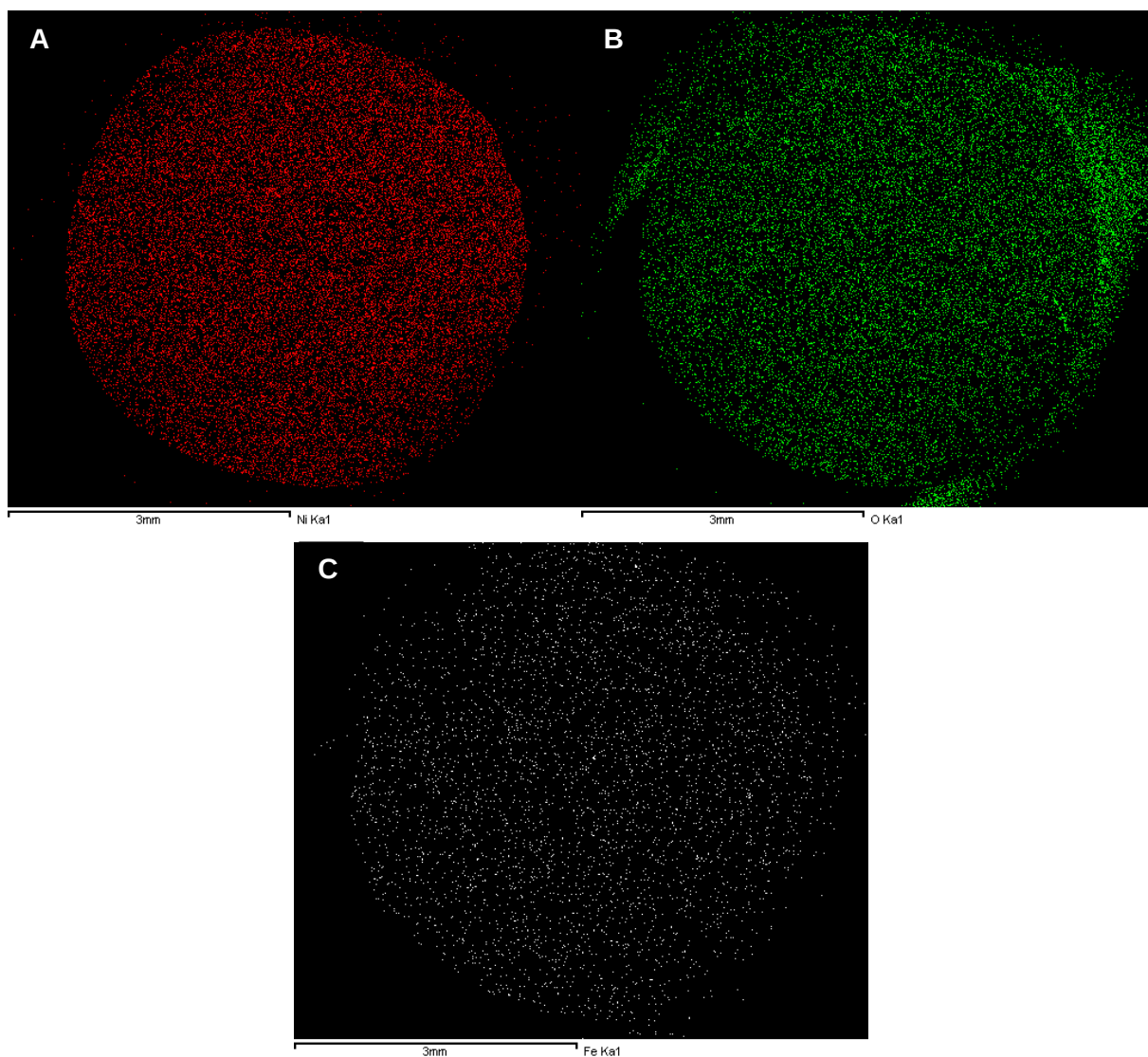


Figure B-2: SEM-EDX mapping analysis of the entire surface of a sputtered NiO thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.

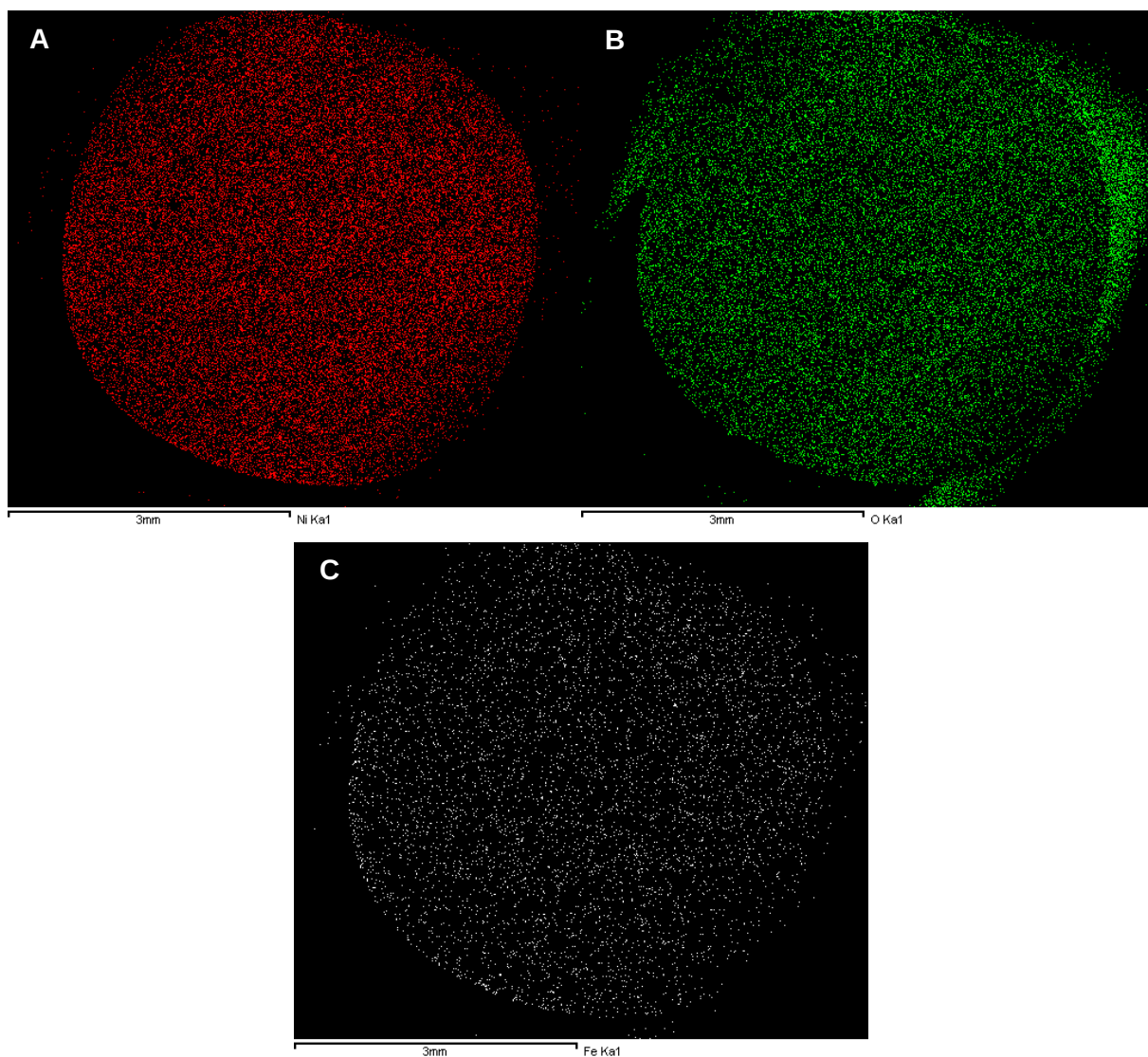


Figure B-3: SEM-EDX mapping analysis of the entire surface of a sputtered NiO thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.

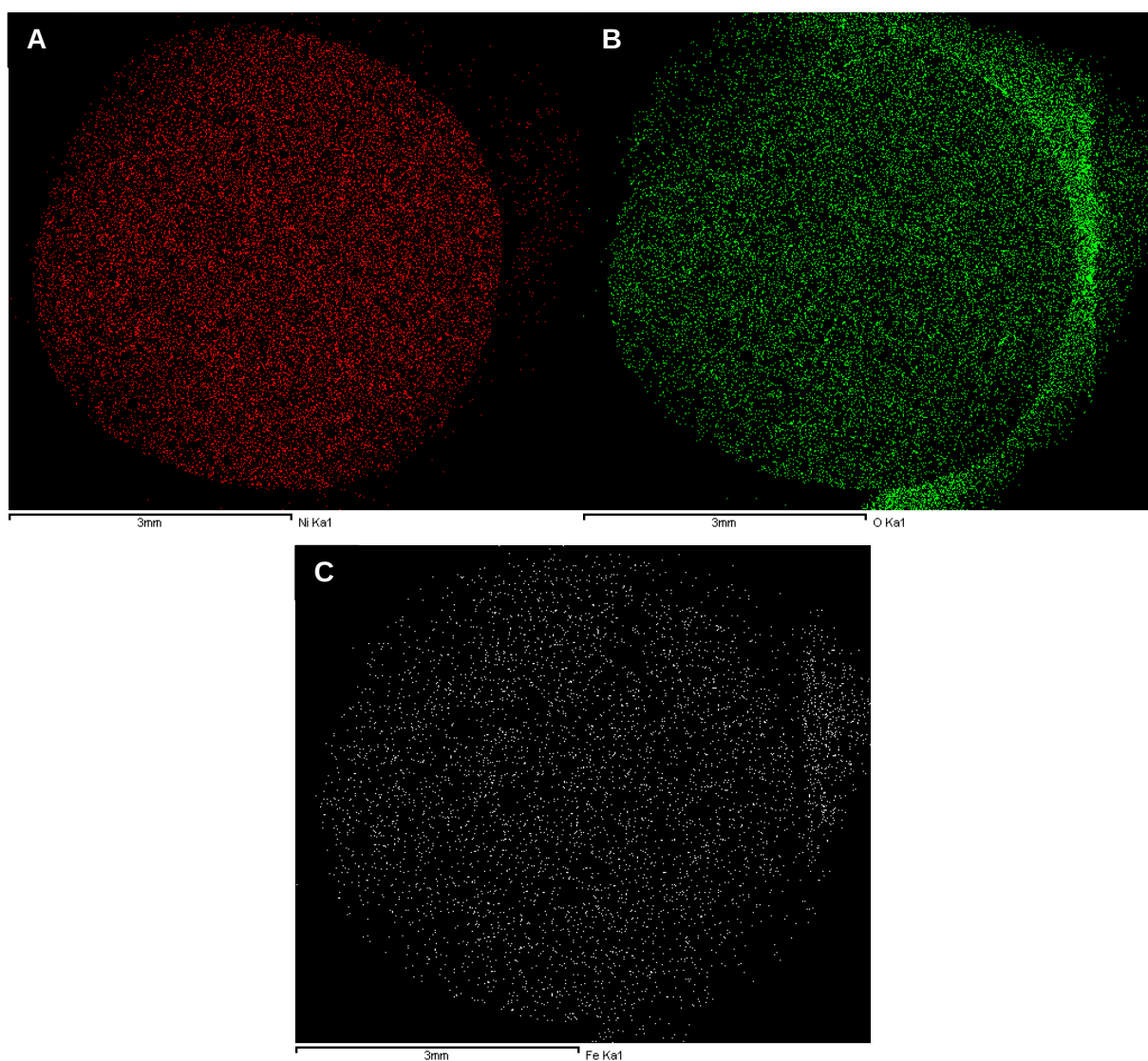


Figure B-4: SEM-EDX mapping analysis of the entire surface of a sputtered NiNiO thin film cycled in 0.9 ppm Fe for (a) Ni, (b) O and (c) Fe.

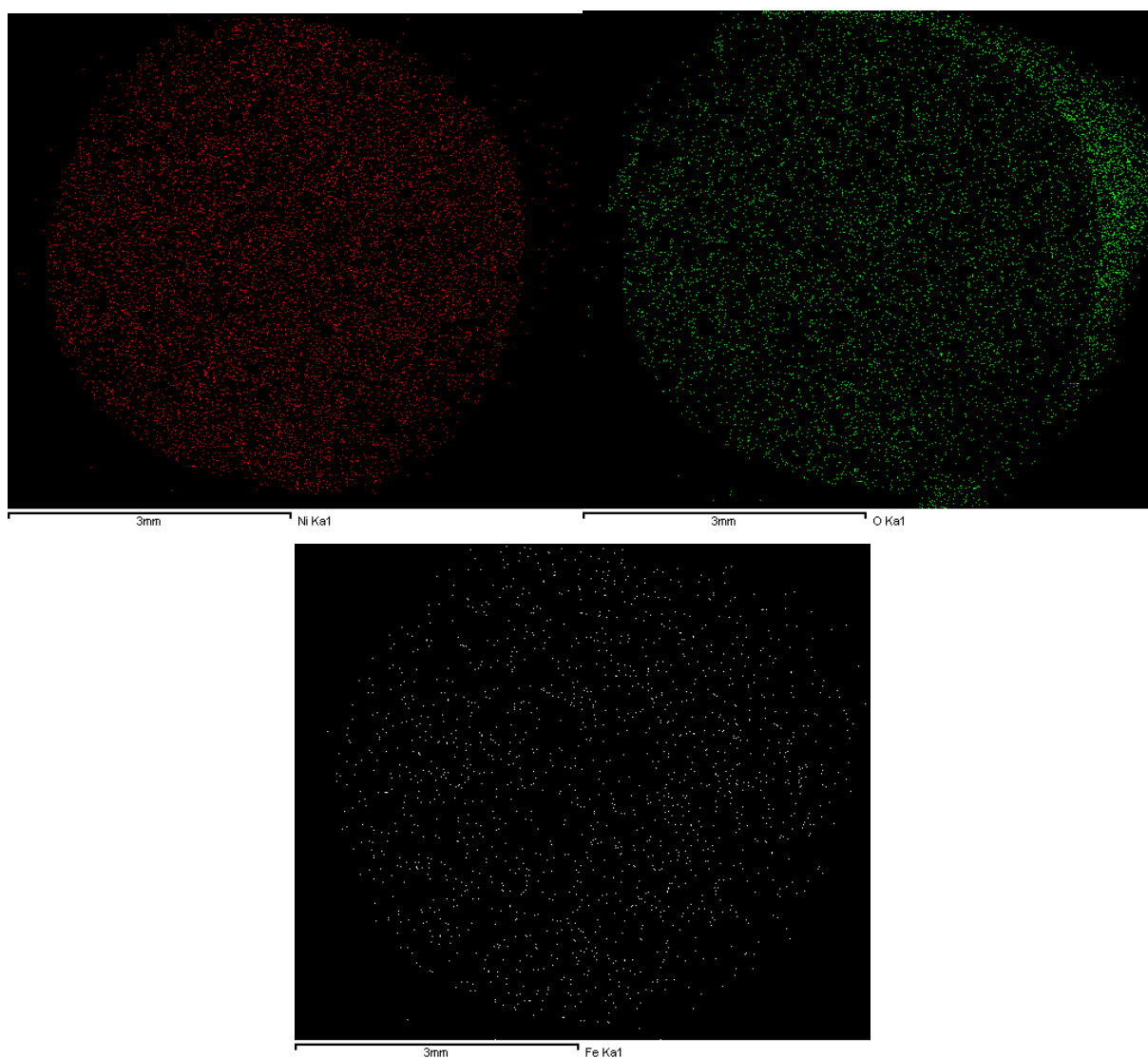


Figure B-5: SEM-EDX mapping analysis of the entire surface of a sputtered NiNiO thin film cycled in 1 mM Fe for (a) Ni, (b) O and (c) Fe.

Table B-1: Binding energies of the peaks in the Ni 2p XPS spectra of the Ni electrocatalysts cycled in pure and Fe containing KOH.

	Ni 2p _{3/2} (eV)	Ni 2p _{3/2} (eV)	Ni 2p _{3/2} (eV)	Ni 2p _{1/2} (eV)	Ni 2p _{1/2} (eV)	Ni 2p _{1/2} (eV)	Satellite (eV)	Satellite (eV)
Ni								
As- prep	852.48	853.79	855.50	869.80	872.29	873.19	860.56	879.89
Pure KOH			855.46			872.56	860.93	878.54
0.007 ppm			855.53			873.17	860.93	879.14
0.3 ppm	851.97		854.86	872.0		872.87	860.26	878.63
1 mM	852.6		855.69	870.89		872.51	860.19	879.58
NiO								
As- prep		853.59	855.38		870.89	872.72	860.73	878.96
Pure KOH		853.14	855.36		871.54	872.90	860.63	879.00
0.007 ppm		853.19	855.39		870.49	872.85	860.86	879.00
0.3 ppm		853.31	855.39		870.42	872.81	860.79	878.81
1 mM		853.28	855.21		871.04	872.90	860.68	878.76
NiNiO								
As- prep	852.14	853.56	855.48	869.36	870.79	873.46	859.96	879.95
Pure KOH			855.40			872.94	860.81	878.78
0.007 ppm	852.72		855.65	872.85		873.5	861.10	879.49
0.3 ppm			855.74			873.38	861.07	879.30
1 mM	852.6		855.80	873.0		873.6	861.30	879.70

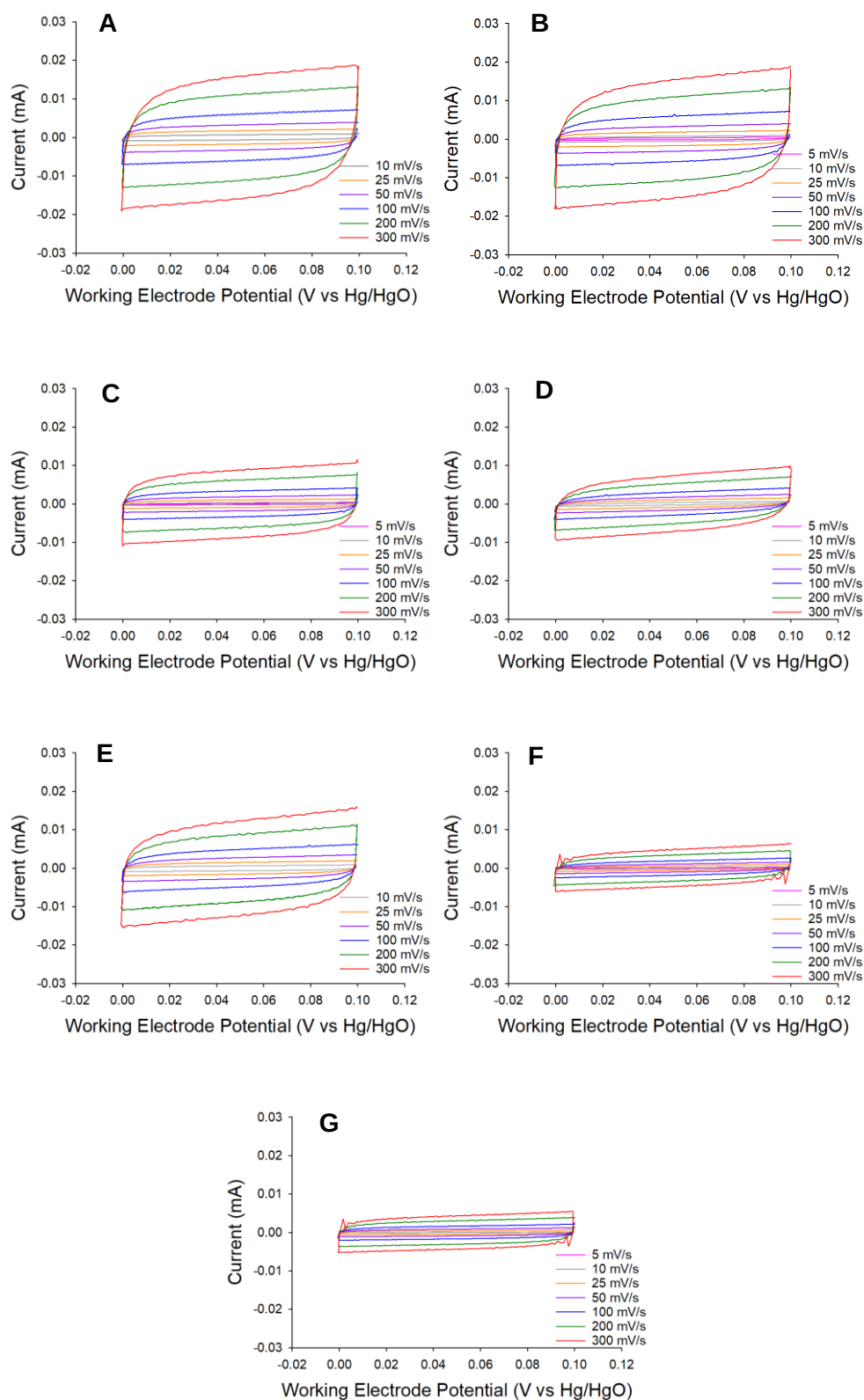


Figure B-6: CVs of sputtered Ni in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

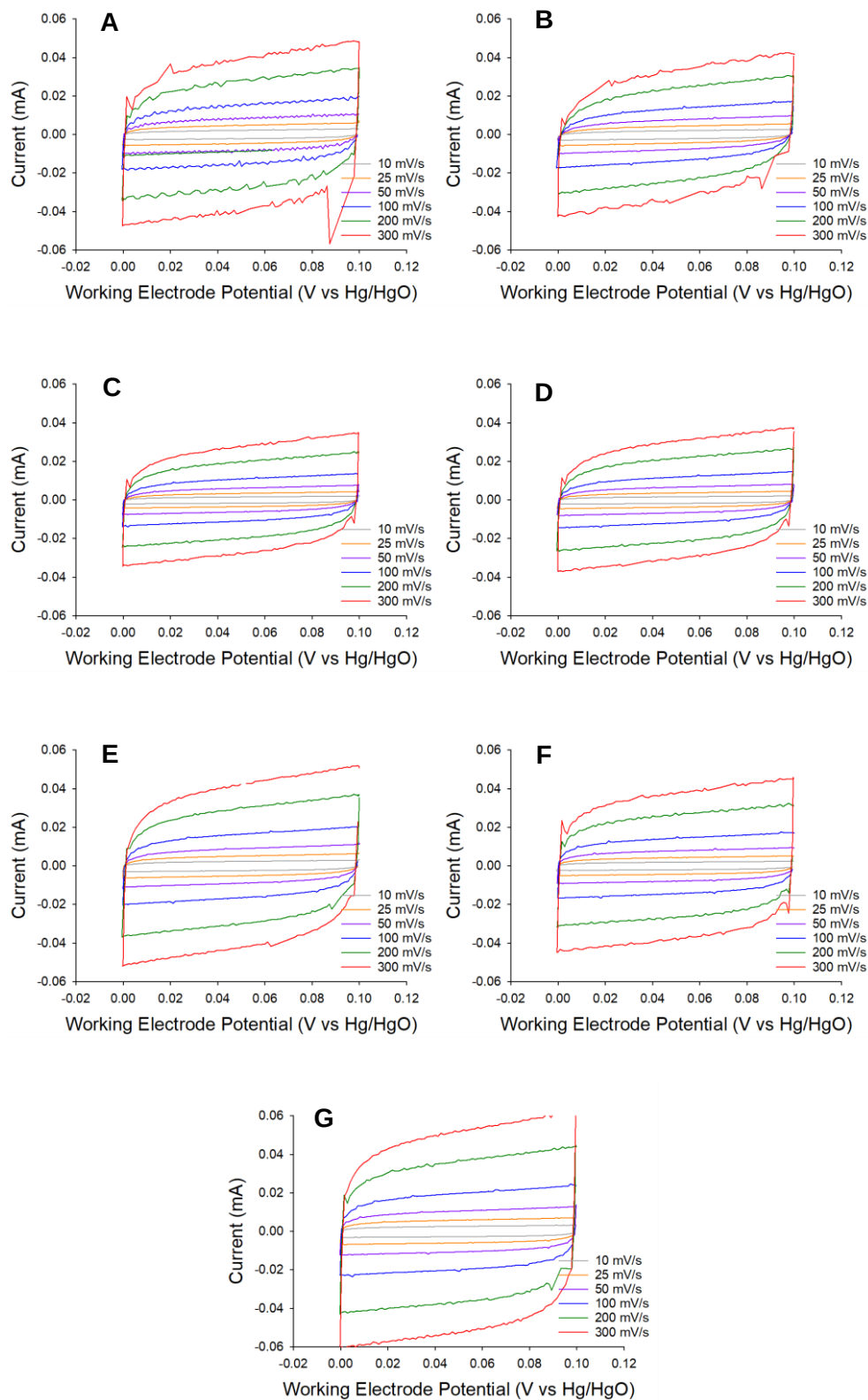


Figure B-7: CVs of sputtered NiO in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.

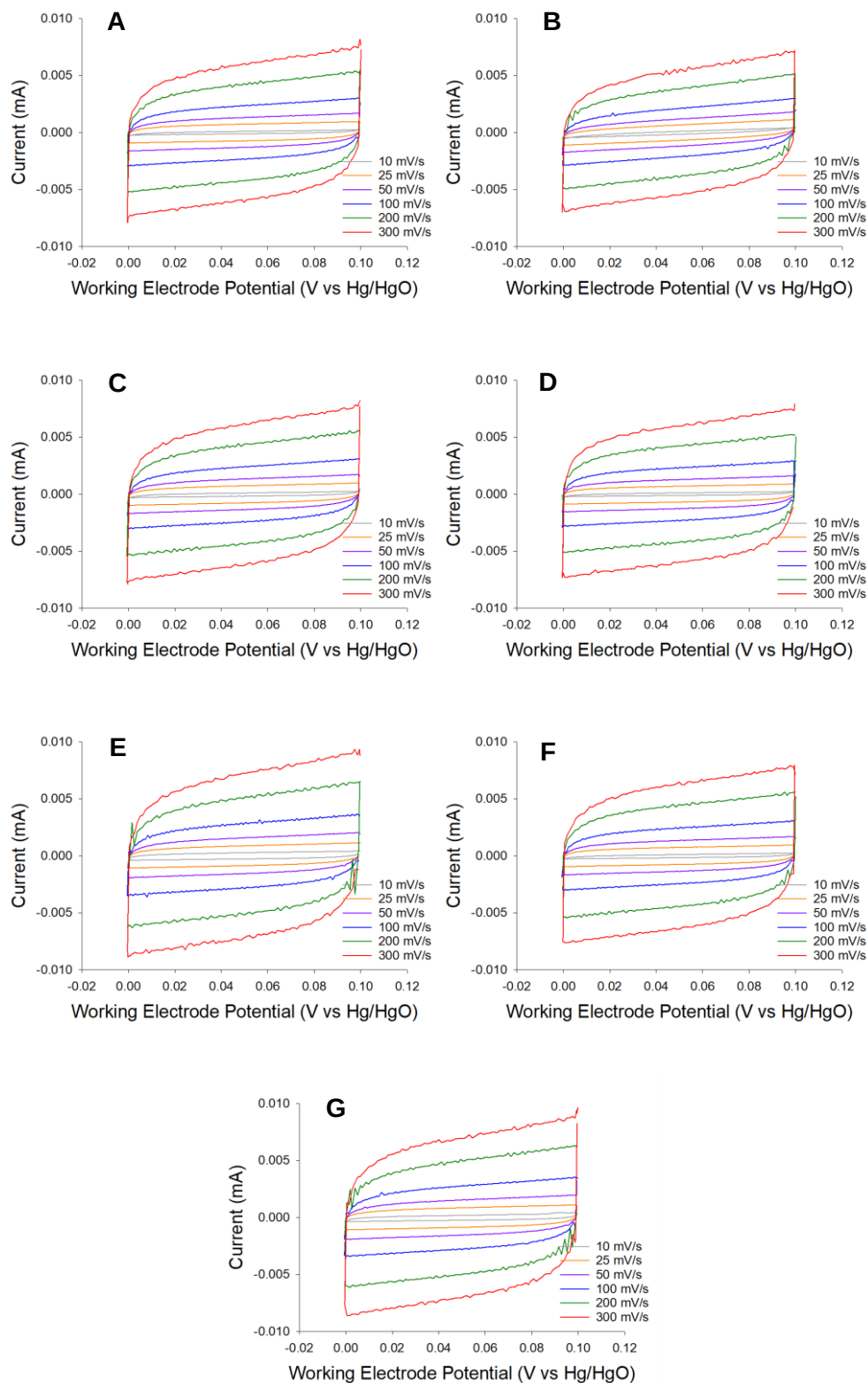


Figure B-8: CVs of sputtered NiNiO in (a) pure KOH, and KOH containing (b) 0.003 ppm Fe, (c) 0.007 ppm, (d) 0.09 ppm, (e) 0.3 ppm, (f) 0.9 ppm and (g) 1 mM Fe, performed at different scan rates in the non-Faradaic potential window 0 to 0.1 V vs Hg/HgO.