

Development and Characterisation of Anode Materials for Polysulphide-Air Redox Flow Battery

Yuhua Xia

Department of Earth Science and Engineering

Imperial College London

Submitted in part fulfilment of the requirements for the degree of Doctor of
Philosophy at Imperial College London

January 2019

Declaration

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given in the list of sources.

Yuhua Xia, January 2019

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Abstract

The aim of this thesis is to develop a highly active negative electrode for the polysulphide-air RFB. The investigation started from a fundamental understanding of the aqueous polysulphide electrolyte, including the speciation and redox reactions. A numerical model was shown to be a valuable method to approximate the equilibrium concentrations of sulphur species within aqueous polysulphide solutions. S_3^{2-} and S_4^{2-} are shown to be the predominant polysulphide species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH and the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolytes. Possible aqueous S_x^{2-}/HS^- redox reactions were summarized from previous studies, whose potentials were calculated using the numerical model derived ionic concentrations.

Electrochemical measurements were mostly performed in a three-electrode cell setup. CV measurements of glassy carbon and nickel disk electrodes showed multiple peaks during the anodic and cathodic polarizations of a dilute polysulphide electrolyte, corresponding to the formation of an initial sulphur or NiS_x layer and the subsequent electrochemical formation and dissolution of polysulphide and sulphur species on the initial sulphur or NiS_x layer. Passivation of both disk electrodes at high anodic potentials was observed. Polarization tests of the two disk electrodes in a concentrated polysulphide electrolyte suggested nickel as a better catalyst than glassy carbon towards aqueous S_x^{2-}/HS^- redox reactions.

A number of NiS_x/carbon paper electrodes were prepared, using electrodeposition, impregnation and electroless deposition methods, and characterized for their electrocatalytic performance in a concentrated polysulphide electrolyte. Those composite electrodes exhibited much better catalytic activities than the catalyst-free carbon paper electrodes, however lower than a sulphidised acid-treated Ni foam which was demonstrated in a 5 cm² single-cell polysulphide-air RFB. A maximum power density of ~4.8 mW cm⁻² was achieved. The performance of the polysulphide-air RFB was largely limited by the polysulphide-side half-cell, due to the large charge transfer resistance associated with the negative electrode, as indicated by the EIS measurements.

Acknowledgement

First and foremost, I would like to express my sincere thankfulness to my supervisor Professor Nigel Brandon for his kind support, advice and patience throughout my PhD study! I am extremely grateful for the opportunities he gave me to attend the numerous conferences and workshops, which have greatly broadened my horizon and networking. His knowledge, wisdom and diplomatic skills have also set a great example for me in both life and work.

I would also like to extend my gratitude to my co-supervisor Dr Vladimir Yufit. His broad knowledge and expertise in electrochemistry and electrochemical engineering have been a greatly valuable support to my research. This PhD work wouldn't have been the same without him.

I feel proud and grateful for being part of the excellent Electrochemical Science and Engineering group at Imperial College London where I have the most brilliant, friendly and warm-hearted colleagues and friends accompanying me over the past few years. Dr Harini Hewa Dewage, Dr Enrique Ruiz-Trejo, Dr Paul Boldrin, Dr Barun Chakrabarti, Dr Farid Tariq, Dr Zadariana Jamil, Dr Xinhua Liu, Dr Jingyi Chen, Dr Mengzheng Ouyang, Dr Xiaolong Chen and many others have offered me great support in and out of the lab. Thanks to them the LG23, LG27 and RSM open office have become the most pleasant place to work in. We also shared loads of laughter playing badminton, working out in the gym, watching movies and travelling together. All of those good times spent with them had made my PhD life much more enjoyable.

Last but not least, it is beyond words that how grateful I am to my dear parents, Zhengyong Xia and Ping Hua, for their selfless contributions to my study and life mentally and financially. I would have never achieved what I have now without their selfless dedication and determined support.

To my dear parents:

Zhengyong Xia and Ping Hua

Contents

Abstract.....	4
Acknowledgement.....	5
List of Tables.....	10
List of Figures.....	12
Nomenclature.....	17
Dissemination.....	21
1 Chapter 1 Introduction.....	23
1.1 Overview.....	23
1.2 Research Background.....	26
1.3 Objectives of This work.....	29
1.4 Thesis Outline.....	30
2 Chapter 2 Literature Review.....	31
2.1 Fundamentals of RFBs.....	31
2.1.1 Concept and Principles.....	31
2.1.2 System Configuration and Components.....	32
2.1.3 RFB Chemistries.....	35
2.1.4 Evaluation of RFBs.....	39
2.2 Sulphur Chemistry in Aqueous Solutions.....	48
2.2.1 Equilibria within Aqueous Polysulphides Solutions.....	49
2.2.2 Numerical Modelling of Aqueous Polysulphide Speciation.....	56
2.2.3 Aqueous Polysulphide Electrolyte.....	57
2.3 Electrochemistry of Aqueous Polysulphide Solutions.....	61
2.3.1 Aqueous S_x^{2-}/HS^- Redox Reaction.....	61
2.3.2 Reaction Mechanisms.....	64
2.3.3 Electrodes for Aqueous S_x^{2-}/HS^- Redox Reactions.....	67

2.3.4	Electrochemical Characterization of Polysulphide Electrodes	80
2.4	Conclusions	81
3	Chapter 3 Experimental Methods	84
3.1	Experimental Setups	84
3.1.1	Three-electrode Cell	84
3.1.2	Single-cell Polysulphide-air RFB.....	85
3.2	Preparation of Electrolytes.....	88
3.2.1	Sodium hydroxide solution.....	88
3.2.2	Aqueous polysulphide Electrolytes	89
3.3	Pre-treatment of Membranes	89
3.3.1	Nafion® 117 CEM.....	90
3.3.2	Fumapem® FAA-3-PK-75 AEM.....	90
3.4	Preparation of Electrodes	91
3.4.1	Nickel and Glassy Carbon Disk Electrodes.....	91
3.4.2	Porous Electrodes.....	92
3.4.3	Sulphidisation of Ni-based Electrodes.....	97
3.5	Electrochemical Measurements.....	97
3.5.1	Three-electrode cell Experiments.....	98
3.5.2	Single-cell Polysulphide-air RFB Tests.....	100
4	Chapter 4 Fundamentals of Aqueous Polysulphide Electrolytes.....	102
4.1	Speciation of Aqueous Polysulphide Electrolyte.....	102
4.1.1	Results of the Numerical Modelling.....	102
4.1.2	Discussion of the Numerical Modelling.....	109
4.2	Electrochemistry of Aqueous Polysulphide Electrolyte	112
4.2.1	Potentials of Aqueous S_x^{2-}/HS^- Redox Reactions	112
4.2.2	Eh-pH Diagram of Metastable S-H ₂ O System at 25 °C.....	114
4.3	Conclusions	116

5	Chapter 5 Study of Glassy Carbon and Nickel in Aqueous Polysulphide Electrolytes	118
5.1	CV Measurements.....	118
5.1.1	Glassy Carbon.....	119
5.1.2	Nickel.....	133
5.2	Polarization Tests.....	143
5.2.1	Potentiodynamic Polarization Tests	143
5.2.2	Potentiostatic Polarization Tests.....	144
5.2.3	Exchange Current Densities.....	145
5.3	Conclusions.....	148
6	Chapter 6 Electrodes for aqueous polysulphide electrolyte.....	150
6.1	Carbon Paper.....	150
6.2	Ni Foam	154
6.3	NiS _x /carbon paper Electrodes	158
6.3.1	Electrodeposition Method.....	158
6.3.2	Impregnation Method	165
6.3.3	Electroless Deposition Method.....	173
6.4	Demonstration of Polysulphide-Air Redox RFB	176
6.5	Conclusions	178
7	Chapter 7 Conclusion	182
7.1	Future Work	184
	References	186
8	Appendices.....	199

List of Tables

<i>Table 2.2-1 Equilibrium constants among polysulphides in aqueous solutions</i>	55
<i>Table 2.2-2 Aqueous solubility of NaOH, KOH, Na₂S, K₂S and K₂S₄ at 25 °C</i>	58
<i>Table 2.3-1 Reported redox reactions within aqueous polysulphide solutions</i>	63
<i>Table 2.3-2 Current densities of Co/Ni mesh and MoS₂/Mo mesh electrodes at -50 mV overpotential [181]</i>	71
<i>Table 2.3-3 Exchange current density of different electrode materials in a 1.3 mol l⁻¹ Na₂S₄ electrolyte at 25 °C</i>	79
<i>Table 3.1-1 List of components for the polysulphide/air RFB single cell</i>	87
<i>Table 3.1-2 Compositions and flow rates of the electrolytes used in the single-cell polysulphide/air RFB tests</i>	87
<i>Table 3.1-3 List of components for the electrolyte pumping system</i>	88
<i>Table 3.4-1 Thermal treatment of SGL 10 AA carbon paper</i>	93
<i>Table 3.4-2 Properties of the 0.9 mm thick Ni foams</i>	94
<i>Table 3.4-3 Experimental design for the electrodeposition of nickel onto carbon paper</i>	95
<i>Table 3.4-4 Experimental design for the impregnation of Ni(NO₃)₂ onto carbon paper</i> ..	96
<i>Table 3.4-5 Solutions used to prepare the NiOOH deposition bath</i>	96
<i>Table 4.1-1 Equilibrium constants associated with aqueous polysulphide solutions</i> ...	102
<i>Table 4.1-2 Calculated equilibrium concentrations of OH⁻ and major sulphur species in two aqueous polysulphide solutions at 20 °C</i>	103
<i>Table 4.1-3 Calculated equilibrium concentrations of OH⁻ and major sulphur species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at 20 °C with the modified numerical model replacing activities of OH⁻ and H₂O by their concentrations</i>	110
<i>Table 4.1-4 Calculated equilibrium concentrations of OH⁻ and major sulphur species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at 20 °C with the modified numerical model using K_A, K_B and K_C from [[77]]</i>	111
<i>Table 4.2-1 Calculated potentials of the reported aqueous S_x²⁻/HS⁻ redox reactions</i>	113
<i>Table 4.2-2 Standard Gibbs energies of formation of species in aqueous polysulphide solutions at 25 °C [93]</i>	115
<i>Table 5.2-1 Potentiostatic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte</i>	145

Table 5.2-2 Exchange current densities of glassy carbon and nickel disk electrodes in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte	148
<i>Table 6.1-1 Exchange current densities and current densities at ±200 mV of the untreated and 450°C-6hr treated carbon paper electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte</i>	<i>152</i>
<i>Table 6.2-1 Exchange current densities and current densities at ±200 mV of the three Ni foam electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte</i>	<i>156</i>
Table 6.3-1 Ni/carbon paper electrodes prepared by electrodeposition method	161
<i>Table 6.3-2 Exchange current densities and current densities at ±200 mV of the NiS_x/carbon paper electrodes prepared by electrodeposition method in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte</i>	<i>164</i>
Table 6.3-3 NiS _x /carbon paper electrodes prepared by the impregnation method	166
Table 6.3-4 Exchange current densities and current densities at ±200 mV of the NiS _x /carbon paper electrodes prepared by impregnation method in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte	171
<i>Table 6.5-1 Catalytic performances of various porous electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte</i>	<i>181</i>

List of Figures

Figure 1.2-1 A schematic illustration of the polysulphide-air RFB with double-membrane design	27
Figure 1.2-2 Polarisation curve and power density curve of the 5 cm ² single-cell polysulphide-air RFB at 20±3 °C [21]	28
Figure 1.2-3 EIS measurement without load of the 5 cm ² single-cell polysulphide-air RFB with an amplitude of 0.2 mA and frequency range of 0.01~10000 Hz at 20±3 °C [21]	29
Figure 2.1-1 Schematic view of a typical RFB with electron/ion/solvent transport and the redox reactions of each half-cell.....	32
<i>Figure 2.1-2 Components of a RFB (a) cell and (b) stack [22]</i>	<i>33</i>
Figure 2.1-3 A summary of inorganic redox couples with their standard potentials (vs standard hydrogen electrode (SHE))	35
<i>Figure 2.1-4 Generalized polarization curve and power density curve, with the indication of different sources of potential losses along the increasing current density</i>	<i>42</i>
<i>Figure 2.1-5 Nyquist plot (a) and Bode plot (b) for a parallel RC circuit with R = 100 Ω and C = 1 μF [57]</i>	<i>45</i>
<i>Figure 2.1-6 Randles circuit model with mixed kinetic and finite diffusion control</i>	<i>46</i>
<i>Figure 2.2-1 Temperature dependence of K_{a,2} from 10-70 °C [96].....</i>	<i>52</i>
<i>Figure 2.2-2 pK_{a,2} vs NaOH concentration for data obtained in different studies [78]</i>	<i>54</i>
<i>Figure 2.2-3 Aqueous solubilities of Na₂S, K₂S, NaOH and KOH as a function of temperature [114]</i>	<i>58</i>
<i>Figure 2.3-1 Polarization curves of various Teflon-bonded high surface area carbon electrodes in 1 mol l⁻¹ Na₂S, S and NaOH electrolyte at 27 °C with Ar atmosphere and no stirring. B.D.H. Carbon was used in each case except for the Co/Vulcan Carbon Black XC-72 electrode [166].....</i>	<i>69</i>
<i>Figure 2.3-2 Polarization curves of various electrodes in 1 mol l⁻¹ Na₂S, S and KOH at 30 °C with Ar atmosphere and no stirring [64].....</i>	<i>70</i>
Figure 2.3-3 Polarization tests of pyrite-phase FeS ₂ , CoS ₂ , NiS ₂ and PyS ₂ thin film electrodes towards the aqueous S _x ²⁻ /HS ⁻ redox reaction [174].	72
<i>Figure 2.3-4 Steady-state polarization of Fe, Co, Ni, Pb, Graphite (φ 6 disk) in a 1.3 mol l⁻¹ Na₂S₄ electrolyte at 25 °C and a scan rate of 1 mV s⁻¹ [217].</i>	<i>78</i>

Figure 2.3-5 Polarization curves of different negative electrodes in PSB: ($\blacklozenge, \blacklozenge$) graphite felt; ($\blacksquare, \square$) carbon felt; ($\blacktriangle, \triangle$) activated carbon; ($\bullet, \circ$) Co-activated carbon; ($\blacktriangledown, \triangledown$) Co-graphite felt [44].	80
Figure 3.1-1 (a) Schematic view: (1) $\text{Ag}/\text{AgCl}_{(\text{sat})}$ RE, (2) WE, (3) Pt CE, (4, 6) gas inlets, (5) gas outlet, (7) electrolyte, (8) three-neck flask; and (b) laboratory setup of the three-electrode cell	84
Figure 3.1-2 (a) Exploded view of the single cell design: (1, 16) end plates, (2, 15) body plates, (4, 13) flow channel plates, (7) CEM, (9) mesh flow channels (10) AEM, (6) negative electrode, (11) positive electrode and (3, 5, 8, 12, 14) gaskets; and (b) laboratory setup of the 5 cm ² single-cell polysulphide/air RFB	86
Figure 3.4-1 Glassy carbon (a) and nickel (b) disk electrodes with a diameter of 5 mm	91
Figure 3.4-2 (a) 1×3 cm ² nickel foam electrode, (b) 1×3 cm ² carbon paper electrode and (c) sheet electrode holder	92
Figure 3.5-1 Procedures for cleaning disk electrodes	99
Figure 4.1-1 Effects of initial S/S^{2-} on the speciation of aqueous polysulphide solutions containing 1 mol kg ⁻¹ Na ₂ S, 1 mol kg ⁻¹ NaOH and various concentrations of S	104
Figure 4.1-2 Effects of NaOH addition on the speciation of aqueous polysulphide electrolytes containing 1 mol kg ⁻¹ Na ₂ S ₂	106
Figure 4.1-3 Effect of temperature on the speciation of 1 mol kg ⁻¹ Na ₂ S ₂ / 1 mol kg ⁻¹ NaOH solution	107
Figure 4.1-4 Speciation of sulphur species of an aqueous polysulphide electrolyte containing initially 1 mol kg ⁻¹ of Na ₂ S, S and NaOH at various SoC	108
Fig. 4.2-1 Calculated metastable Eh-pH Diagram of S-H ₂ O system excluding all oxy-sulphur anions at 25°C with a dissolved total sulphur concentration of 2 mol kg ⁻¹	115
Figure 5.1-1 Cyclic voltammograms (5 cycles) of the glassy carbon disk electrode in the 0.02 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s ⁻¹ and within the potential window of: (a) -1.0 V ~ -0.4 V, (b) -1.0 V ~ -0.3 V, (c) -1.0 V ~ -0.2 V, (d) -1.0 V ~ -0.1 V, (e) -1.0 V ~ 0 V, (f) -1.0 V ~ 0.1 V, (g) -1.0 V ~ 0.2 V, (h) -1.0 V ~ 0.3 V.	123
Figure 5.1-2 Cyclic voltammograms (10 cycles) of the glassy carbon disk electrode in the 0.02 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s ⁻¹ and within the potential window of: (a) -0.9 V ~ -0.3 V, (b) -0.9 V ~ -0.1 V, (c) -0.9 V ~ 0.1 V, (d) -0.9 V ~ -0.3 V.	129

Figure 5.1-3 Cyclic voltammograms (10 cycles) of the glassy carbon disk electrode in the 0.02 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s ⁻¹ and within the potential window of : (a) -1.1 V ~ -0.3 V, (b) -1.1 V ~ -0.1 V, (c) -1.1 V ~ 0.1 V, (d) -1.1 V ~ -0.3 V.	131
Figure 5.1-4 Cyclic voltammogram of the glassy carbon disk electrode in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s ⁻¹ and within the potential window of -0.9 V ~ 0.3 V vs Ag AgCl _(sat)	132
Figure 5.1-5 Cyclic voltammograms (5 cycles) of glassy carbon disk electrode in the 1 mol kg ⁻¹ NaOH electrolyte, at the scan rate of 20 mV s ⁻¹ and within the potential window of -1.1 ~ 0.3 V vs Ag AgCl _(sat)	133
Figure 5.1-6 Cyclic voltammograms (10 cycles) of the nickel disk electrode in the 0.02 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s ⁻¹ and within the potential window of: (a) -0.9 V ~ -0.3 V, (b) -0.9 V ~ -0.1 V, (c) -0.9 V ~ 0.1 V, (d) -0.9 V ~ 0.3 V.	136
Figure 5.1-7 Cyclic voltammograms of nickel disk electrode in the 0.02 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte at the scan rate of 20 mV s ⁻¹ within a variety of potential windows: (a) -1.1 V ~ -0.3 V, (b) -1.1 V ~ -0.1 V, (c) -1.1 V ~ 0.1 V, (d) -1.1 V ~ -0.3 V.	140
Figure 5.1-8 Cyclic voltammogram of nickel disk electrode in 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte at the scan rate of 20 mV s ⁻¹ within the potential window of -0.9 V ~ 0.3 V vs Ag AgCl _(sat)	142
Figure 5.1-9 Cyclic voltammograms (5 cycles) nickel disk electrode in the 1 mol kg ⁻¹ NaOH electrolyte at the scan rate of 20 mV s ⁻¹ and within the potential window of -1.1 V ~ 0.3 V vs Ag AgCl _(sat)	143
Figure 5.2-1 Potentiodynamic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte	144
Figure 5.2-2 Tafel plots of the potentiodynamic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte.....	146
Figure 5.2-3 Tafel plots of the potentiostatic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte.....	147
<i>Figure 6.1-1 Drop test with deionized water of SGL 10AA carbon papers heat-treated under various conditions: (a) untreated, (b) 400°C - 30 hr treated, (c) 450°C - 6 hr treated, and (d) 500°C - 6 hr treated.</i>	<i>150</i>

<i>Figure 6.1-2 Cross-section SEM images of the untreated and 450°C-6hr treated SGL 10AA carbon papers: (a) surface of the untreated carbon paper, (b) cross-section of the untreated carbon paper, (c) surface of the 450°C-6hr treated carbon paper, and (d) cross-section of the 450°C-6hr treated carbon paper</i>	151
Figure 6.1-3 Potentiodynamic polarization of the untreated and 450°C-6hr treated carbon papers in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte: (a) linear plot, (b) Tafel plot.....	153
Fig. 6.2-1 SEM images of Ni foams: (a) untreated, (b) acid-treated, (c) acid-treated and impregnated at room temperature for 72 hr, (d) acid-treated and boiled for 30 min ..	154
<i>Figure 6.2-2 Potentiodynamic polarization of the three Ni foam electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte: (a) linear plot and (b) Tafel plot.</i>	155
Figure 6.2-3 SEM image of the acid-treated Ni foam boiled in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte for 30 min	157
Figure 6.3-1 Cross-section SEM images of the Ni/carbon paper electrodes prepared by electrodeposition method with various nickel loading: (a, b) 7.82 wt%, (c, d) 9.90 wt%, (e, f) 16.32 wt%, (g, h) 10.55 wt%, (i, j) 20.85 wt%, and (k, l) 26.22 wt%.	160
Figure 6.3-2 Cross-section SEM images of the 7.82 wt% Ni/carbon paper electrode (a) before and (b) after sulphidisation treatment.....	161
Figure 6.3-3 Potentiodynamic polarization of the NiS _x /carbon paper electrodes, prepared by electrodeposition method, in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte: (a) linear plot and (b) Tafel plot.....	163
Figure 6.3-4 Exchange current densities against nickel loading before sulphidisation of the NiS _x /carbon paper electrodes prepared by the electrodeposition method	165
Figure 6.3-5 Cross-section SEM images of the Ni/carbon paper electrodes prepared by impregnation method using a Ni(NO ₃) ₂ /ethanol solution with various nickel loading: (a, b) 2.6 wt%, (c, d) 13.6 wt%, (e, f) 23.2 wt%.....	167
Figure 6.3-6 Cross-section SEM images of the Ni/carbon paper electrodes prepared by impregnation method using a Ni(NO ₃) ₂ /isopropanol solution with various nickel loading: (a, b) 7.5 wt%, (c, d) 12.5 wt%, (e, f) 25.8 wt%	168
Figure 6.3-7 Cross-section SEM images of the 23.2 wt% Ni/carbon paper electrode prepared using Ni(NO ₃) ₂ /ethanol solution (a) before and (b) after sulphidisation treatment and the 25.8 wt% Ni/carbon paper electrode prepared using Ni(NO ₃) ₂ /isopropanol solution (a) before and (b) after sulphidisation treatment.	169

Figure 6.3-8 Potentiodynamic polarization of the NiS _x /carbon paper electrodes, prepared by impregnation method, in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte: (a) linear plot and (b) Tafel plot.....	170
Figure 6.3-9 Exchange current densities against nickel loading before sulphidisation of the NiS _x /carbon paper electrodes prepared by impregnation method.....	172
Figure 6.3-10 SEM images of: (a, b) as-deposited NiOOH/carbon paper, (c, d) reduced NiOOH/carbon paper, and (e, f) sulphidised Ni/carbon paper. Note: (a), (c) and (e) are surface SEM images; (b), (d) and (f) are cross-section SEM images.....	173
Figure 6.3-11 Potentiodynamic polarization of the NiS _x /carbon paper electrodes, prepared by electroless deposition method, in the 1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH electrolyte: (a) linear plot and (b) Tafel plot.....	175
<i>Figure 6.4-1 Polarization curve and power density curve of the 5 cm² single-cell polysulphide-air RFB at 20±3 °C.....</i>	<i>176</i>
<i>Figure 6.4-2 EIS measurements at OCV of the 5 cm² single-cell polysulphide-air RFB at 20±3 °C</i>	<i>177</i>

Nomenclature

A	Active surface area [m]
a	Activity [mol kg^{-1} or mol l^{-1}]
c	concentration [mol kg^{-1} or mol l^{-1}]
E	Potential [V]
E^0	Standard reduction potential [V]
F	Faraday Constant [96485 C mol^{-1}]
i_0	Exchange current density [A cm^{-2}]
I	Ionic strength [mol l^{-1} or mol kg^{-1}]
I	Current [A]
k^0	Standard rate constant [$\text{mol cm}^{-2} \text{ s}^{-1}$]
K_w	Ionic product of water
$K_{a,1}$	First dissociation constant of hydrogen sulphide
$K_{a,2}$	First dissociation constant of hydrogen sulphide
K_A	Equilibrium constant between S_2^{2-} and S_3^{2-}
K_B	Equilibrium constant between S_3^{2-} and S_4^{2-}
K_C	Equilibrium constant between S_4^{2-} and S_5^{2-}
n	Number of electrons
P	Power [W]
Q	Capacity [Ah]
R	Resistance [Ω]
R	universal gas constant [$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
R_{ct}	Charge transfer resistance [Ω]
T	Temperature [$^{\circ}\text{C}$ or K]
V	volume [L]
Z	Impedance [Ω]
Z_{re}	Real impedance [Ω]
Z_{im}	Imaginary impedance [Ω]

Acronym	Description
AC	Alternating current
AEM	Anion-exchange membrane

CCS	Carbon capture and storage
CEM	Cation-exchange membrane
CNC	Computerized Numerical Control
CPE	Constant phase elements
CV	Cyclic voltammetry
DECC	Department of Energy & Climate Change
DICP	Dalian Institute of Chemical Physics, China
DOE	Department of Energy
EDX	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EPDM	Ethylenepropylenedienemonomer
ESI MS	Electrospray Ionization Mass Spectrometry
ETFE	Ethylene tetrafluoroethylene
FEG-SEM	Field emission gun scanning electron microscopy
FTO	fluorine doped tin oxide
GDL	Gas diffusion layer
HDPE	High-density polyethylene
HER	Hydrogen evolution reaction
HFR	high frequency resistance
HRR	Hydrogen reduction reaction
IC	Ion Chromatography
IEM	Ion-exchange membrane
IF	Inorganic fullerene-like
LSV	Linear scan voltammetry
NASA	the National Aeronautics and Space Administration
NMR	Nuclear magnetic resonance
OCP	Open circuit potential
OCV	Open circuit voltage
OECD	the Organisation for Economic Co-operation and Development
OER	Oxygen evolution reaction
PAN	Polyacrylonitrile
PE	Polyethylene
PEDOT	Poly(3,4-ethylenedioxythiophene)

PEC	Photoelectrochemical solar cell
PEEK	Polyetheretherketone
PFA	Perfluoro alkoxy alkanes
PP	Polypropylene
PSB	Polysulphide-bromine redox flow battery
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
PVC	Polyvinylchloride
PVDF	Polyvinylidene
QDSSC	Quantum Dot-Sensitized Solar Cell
RDE	Rotating disk electrode
RE	Reference electrode
RFB	Redox flow battery
SEM	Scanning electron microscopy
SHE	Standard Hydrogen Electrode
SILAR	Successive ionic layer adsorption and reaction
SoC	State of charge
TVA	Tennessee Valley Authority
T&D	Transmission and distribution
UV	Ultraviolet
Vis	Visible
VRB	All-vanadium redox flow battery
W	Warburg diffusion
XPS	X-ray photoelectron spectroscopy
3D	three-dimensional

Greek Symbol

η	Overpotential [V]
η_v	Voltage efficiency [%]
η_c	Coulombic efficiency [%]
η_E	Energy efficiency [%]
γ	Activity coefficient
ϕ	diameter [m]

Φ	Phase angle [°]
ω	Frequency [Hz]
ΔG_f^0	Standard Gibbs energy of formation [kJ mol ⁻¹]

Dissemination

Papers

Y. Xia, V. Yufit and N. P. Brandon, "Study of Nickel and Glassy Carbon in Aqueous Polysulphide Electrolytes", *In preparation*

Y. Xia, V. Yufit, E. Ruiz-Trejo, P. Boldrin, J. Chen, A. Regoutz and N. P. Brandon, "Development of Negative Electrodes for the Polysulphide-air Redox Flow Battery", *In preparation*

B. Chakrabarti, V. Yufit, **Y Xia**, F. Tariq, O. Taiwo, A. Kavei, and N. Brandon, "Performance Enhancements in the Regenerative Hydrogen/Vanadium Fuel Cell with Reduced Graphene Oxide Modified Carbon Paper Electrodes", *Submitted*

Chen, X., Liu, X., Ouyang, M., Chen, J., Taiwo, O., **Xia, Y.**, Childs, P.R., Brandon, N.P. and Wu, B., Multi-metal 4D printing with a desktop electrochemical 3D printer. Scientific reports, 2019, 9(1), p.3973.

Conferences

Oral presentation

Y. Xia, V. Yufit and N. P. Brandon, "Development of A Novel Polysulphide-Air Redox Flow Battery", SCI Electrochemistry Postgraduate Conference (May 2017, Southampton).

Poster presentation

Y. Xia, V. Yufit and N. P. Brandon, "Polysulphide Air Redox Flow Battery - a Novel Solution for Grid Scale Energy Storage", International Flow Battery Forum 2015 (June, Glasgow).

Y. Xia, V. Yufit and N. P. Brandon, "Polysulphide Air Redox Flow Battery - a Novel Solution for Grid Scale Energy Storage", ECS Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV (July 2015, Glasgow).

Y. Xia, V. Yufit and N. P. Brandon, “Polysulphide Air Redox Flow Battery - a Novel Solution for Grid Scale Energy Storage”, UK Energy Storage 2015 (November, Birmingham).

Y. Xia, V. Yufit and N. P. Brandon, “Polysulphide Air Redox Flow Battery - a Novel Solution for Grid Scale Energy Storage”, UK Energy Storage 2016 (November, Birmingham).

Y. Xia, V. Yufit and N. P. Brandon, “Development of A Novel Polysulphide-Air Redox Flow Battery”, UK Energy Storage 2018 (March, Newcastle).

Chapter 1 Introduction

1.1 Overview

Developing alternative energy sources has been a critical issue since the last century due to growing energy demand and the rapid consumption of traditional fossil fuels. The fast depletion of fossil fuels also causes great concerns among governments and societies in terms of energy security. Despite the continuous increase in energy efficiencies, by 2040 the world total primary energy supply is predicted to rise by around 30% compared to today [1]. Based on proven reserves and current production rates, crude oil, natural gas and coal would be exhausted within 50.2 years, 52.6 years and 134 years respectively [2].

Rapid consumption of fossil fuels also greatly contributes to the growing problem of global warming since massive amounts of carbon dioxide (CO_2) is released into the atmosphere during the processes of utilising fossil fuels, which is the dominant contributor of greenhouse effect caused by human activities [3]. Global warming, which potentially increases the risk and significance of climate change, has received great attentions from across the globe. A main objective as stated in the Paris Agreement is to limit the increase of global average temperature to well below 2°C above pre-industrial levels [4]. To achieve this goal decarbonisation of fossil fuel utilisations, such as electricity generation and transportation fuels, is crucial. The decarbonisation of energy sectors can be achieved through carbon capture and storage (CCS) or by replacing fossil fuels with cleaner energy sources.

Renewable energies, which are abundant, sustainable and clean, are promising alternatives to traditional fossil fuels. Renewable energies not only can help to mitigate climate change by decarbonizing energy consumption, but also contribute to a more secure and healthier energy supply by reducing the dependence on fossil fuels. Renewable energies appear in a variety of types, such as hydro power, wind energy, solar energy, geothermal energy, tide and biomass. Although found in lower energy densities in comparison to traditional fossil fuels such as coal and oil, renewable energies are

greatly abundant and capable of supplying the whole world provided enough capacity is installed.

Nuclear power, another form of low carbon energy, is another energy source which could potentially replace fossil fuels in the future energy mix. Due to the low flexibility of generation, nuclear power usually serves as a baseline source of electricity production. As an important component in the current energy mix, nuclear power accounted for 10.4% of world total electricity generation and 5% of world total primary energy supply in 2016 [5, 6]. However, successive nuclear disasters such as Chernobyl and Fukushima have raised great concerns among the public and within governments towards the potential safety hazard of nuclear power plants. Nevertheless, due to the high capital cost and long service life nuclear power plants in commission will continue as an indispensable baseline of the energy mix in the near future.

Renewable energies have seen rapid development in the past decade and have become an important part in the energy mix of today. 13.7% of the world total primary energy supply in 2016 came from renewable energy sources (excluding nuclear which accounted for 4.9% of the world total primary energy supply in 2016), among which 69.5% came from biofuels and waste and 18.6% came from hydro power [7]. The large share of biofuels and waste in the total renewable energy supply is mainly due to the wide use of biomass as fuels in developing countries especially in African, Non-OECD American and Non-OECD Asian countries. Whereas, wind, solar, tide and geothermal only made up 1.6% of the world total primary energy supply in 2016 [7].

Despite the relatively small installed capacities compared to biomass, the growth of solar photovoltaic (PV) and wind energies had been the fastest among all types of renewable energies from 1990 to 2016 [7]. In 2016, the growth of installed solar PV capacity was the largest among all forms of generation [1]. With a growth rate of around 50% the total installed capacity of solar PV by 2016 had reached 74 GW [8]. This is largely due to the rapid deployment of solar PV in China because of the cost reduction of technology and policy support.

Apart from the rise of world total primary energy supply, the share of electricity in world total final energy consumption also increased in recent years owing to the growing electrification of end-use applications. It has been predicted that electricity could make

up roughly 40% of the rise in total energy consumption to 2040 [1]. Renewable energies offer a great solution to the increasing demand of electricity in the future. In 2016, 23.8% of the world electricity generation was produced from renewables [7]. It is predicted that by 2040, 40% of world total electricity generation would come from renewable energies [1].

Despite the increase in electricity generation, deployment of large amounts of renewable energies, mainly solar PV and wind, also introduces substantial instability to the grid due to the intermittency of renewable energy sources. System balancing is therefore crucial when considerable amounts of renewable energy are integrated into the grid. In general, there are four techniques to balance the supply and demand of electricity, namely advanced network technologies and interconnection, demand side response, flexible generation and energy storage [9].

The value of energy storage in the future low carbon energy system is predicted to be very large. Taking the UK as an example, it was indicated that with the high renewable scenario (DECC's carbon plan) energy storage could generate a maximum system saving for the UK of £0.8bn/year in 2020, £2.1bn/year in 2030 and £4.7bn-£14.9bn/year in 2050, if other balancing technologies are also available at reasonably cheap prices [10].

Energy storage has a variety of applications, such as seasonal storage, inter-seasonal or weekly storage, arbitrage, grid integration of renewables, frequency regulation, load following, reserve capacity, voltage support, black start, transmission and distribution (T&D) congestion management, T&D infrastructure investment deferral and off-grid applications. [11]. Depending on the characteristics of a particular energy storage technology, such as mobility (site-dependency), response time, size (power/energy), discharge time, safety, efficiency, cost and lifetime, it could be utilised in one or more applications [11, 12].

According to the storage media, energy storage technologies can be divided into the following five types, including electrical storage, electrochemical storage, chemical storage, mechanical storage and thermal storage [13].

Among various energy storage technologies rechargeable batteries offer a variety of advantages, such as site independency, high efficiency, fast response and high power and energy density [14]. A number of rechargeable batteries have been demonstrated for

energy storage purposes, including conventional secondary batteries, metal-ion batteries, metal-air batteries, high temperature batteries, and redox flow batteries (RFBs) [15].

Apart from the prior common benefits of rechargeable batteries, RFBs also possess some unique advantages, such as modularity, independence of power and energy, tolerance of deep charge and discharge, very little self-discharge, long cycle life, low cost and enhanced safety [16]. The modular design of stacks and systems allows RFBs to be scaled up easily. The power and energy capacity of RFB systems are associated with cell size (active area) and tank size (volume of electrolytes) respectively and independently, allowing customized manufactures of RFB systems. RFBs can undergo deep charge and discharge operations without adverse effects on the system. The self-discharge of RFBs is small because the anolyte and catholyte are stored separately in two tanks which avoids the mixing and neutralization of these two electrolytes. Since electrolytes are stored outside the cell, the potential amount of energy generated during accidents of RFB systems are relatively low which therefore cause less hazards. Lastly, RFBs are expected to have a lifetime of up to 20 years subject to the use of durable membrane technologies, whereas the lifetime of li-ion battery is much shorter mainly due to the degradation of electrodes caused by repeated expansion and contraction of the electrodes over the charge/discharge cycles [17].

1.2 Research Background

Studies of RFBs date back to the 1970s when the first RFB system, namely the iron-chromium RFB, was invented by the National Aeronautics and Space Administration (NASA) [18]. Since then, a great variety of RFB systems have been developed and demonstrated, such as all-vanadium RFB (VRB), zinc-bromine RFB (Zn/Br) and polysulphide-bromine RFB (PSB). However, the prices of current RFB systems remain too high for large scale deployment. Taking the US as an example, the Department of Energy (DOE) had established target costs of \$250/kWh and \$150/kWh for short-term and long-term grid storage systems respectively. In contrast, the most advanced RFB technology today, namely the VRB, has an installation cost of \$400-500/kWh [19]. As a result, great efforts have been devoted to the cost reduction of RFBs in the past few years, including the discovery of cheaper alternative chemistries to vanadium.

In 2012, Brandon et al. patented an alkaline gas-liquid hybrid RFB system with a variety of alkaline redox chemistries being proposed for this novel RFB system, among which the polysulphide-air (oxygen) system was particularly attractive due to the low material costs [20]. Half-cell reactions and the overall reaction of this novel polysulphide-air RFB are described below.

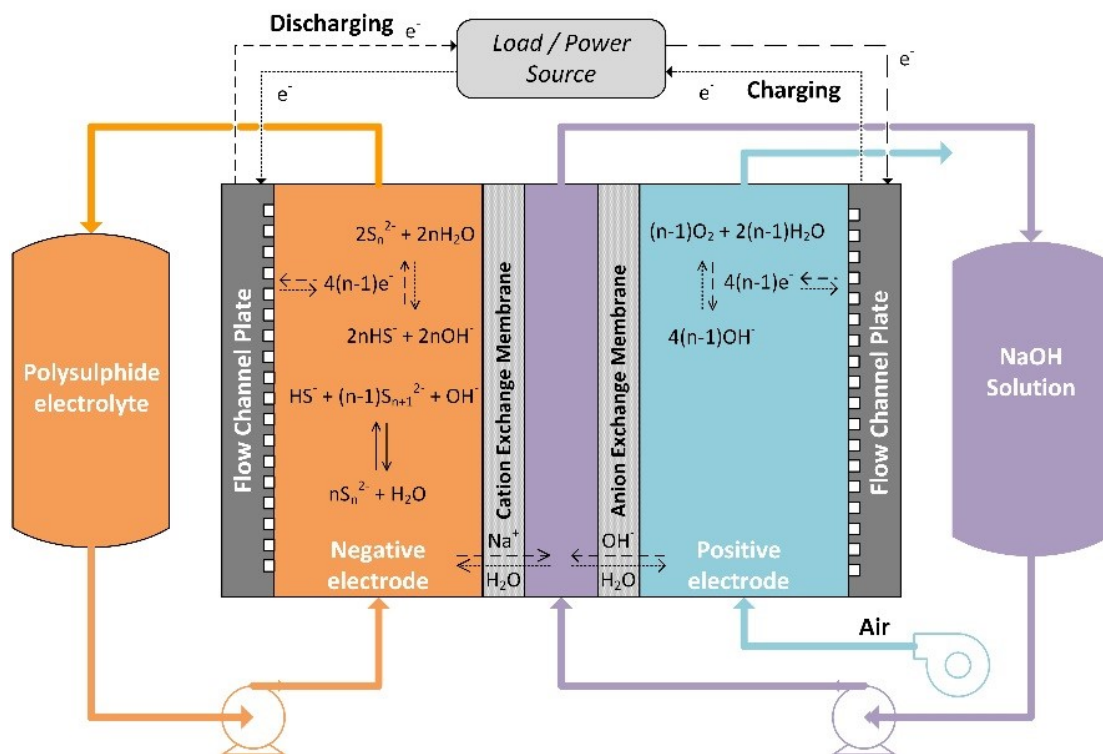
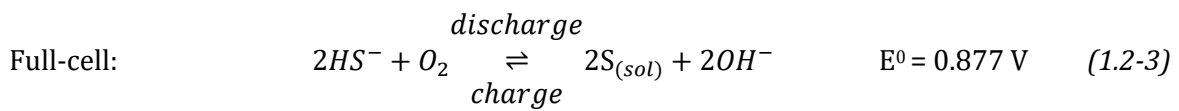
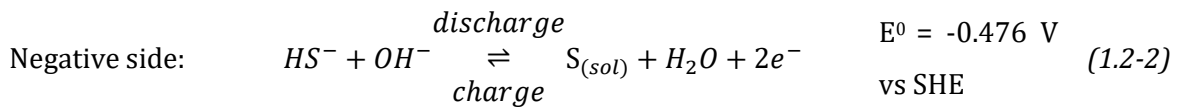
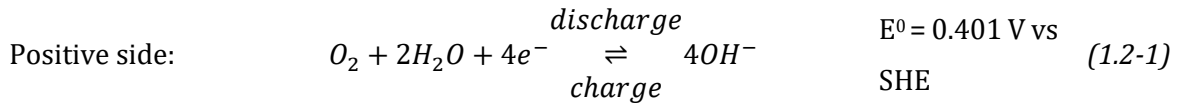


Figure 1.2-1 A schematic illustration of the polysulphide-air RFB with double-membrane design

This polysulphide-air RFB was demonstrated by the Xia et al in 2014 with a 5 cm² sing-cell RFB system [21]. A novel double membrane design, as shown in Figure 1.2-1, was

utilised to mitigate the sulphur crossover issue within the system which was proved effective in previous studies. An open circuit voltage (OCV) of 0.68 V and a peak power density of 2.1 mW cm⁻² were achieved for the 5 cm² sing-cell polysulphide-air RFB, as shown in Figure 1.2-2, when using a 0.5 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH anolyte, a 2 mol kg⁻¹ NaOH intermediate electrolyte (the electrolyte pumped through the compartment between the two membranes, as shown in Figure 1.2.1) and air catholyte. Electrochemical impedance spectroscopy (EIS) measurements indicated that performance of the polysulphide-air RFB was limited by the large polarization resistance of the polysulphide-side half-cell, as shown in Figure 1.2-3. Hence, the aim of this work is to develop highly active and long-term stable anode materials for the polysulphide-air RFB applications.

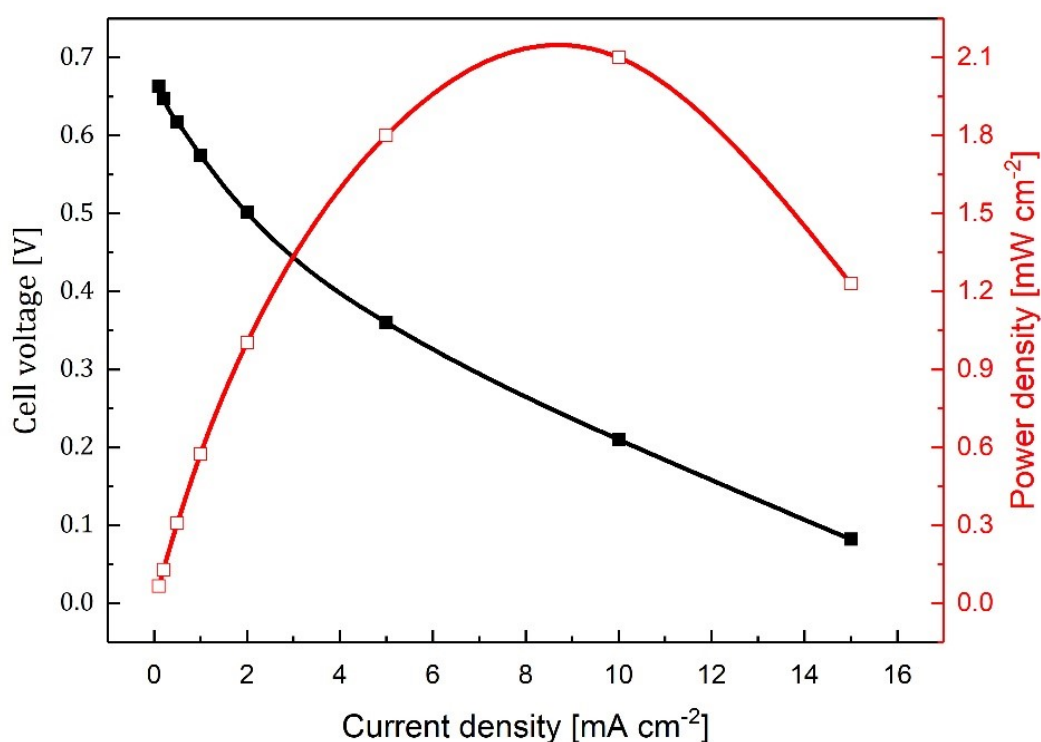


Figure 1.2-2 Polarisation curve and power density curve of the 5 cm² single-cell polysulphide-air RFB at 20±3 °C [21]

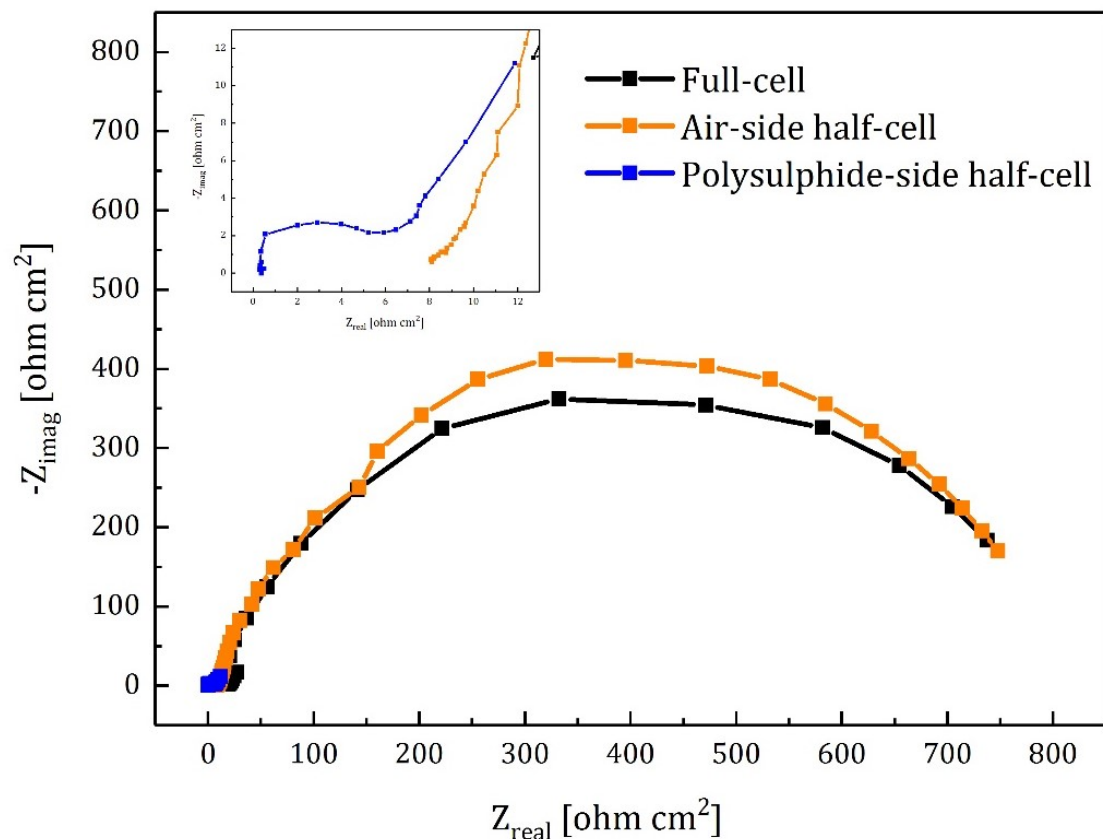


Figure 1.2-3 EIS measurement without load of the 5 cm² single-cell polysulphide-air RFB with an amplitude of 0.2 mA and frequency range of 0.01~10000 Hz at 20±3 °C [21]

1.3 Objectives of This work

1. Understanding of the aqueous polysulphide speciation by means of numerical modelling;
2. Understanding of aqueous polysulphide/sulphide (S_x^{2-}/HS^-) redox reactions, by cyclic voltammetry (CV) studies of glassy carbon and nickel disk electrodes in aqueous polysulphide electrolytes;
3. Preparation of nickel based high-surface-area electrodes using different methods;
4. Finding out suitable sulphidisation methods for nickel-based high-surface-area electrodes;
5. Determination of the catalytic activities of the various prepared Ni/NiS_x modified high-surface-area electrodes by linear scan voltammetry (LSV) in a concentrated aqueous polysulphide electrolyte.

1.4 Thesis Outline

Chapter 1 introduces the world energy mix of today and explains why energy storage technologies especially RFBs are important to the future energy systems. It also discusses the outcomes of a previous demonstration of the polysulphide-air RFB, which leads to the research question of this work.

Chapter 2 contains the review of (i) fundamentals of RFBs including the concept and principles, system configuration and components, RFB technologies and the evaluation criteria and methods for RFBs, (ii) the basics of aqueous polysulphide electrolytes, the chemical equilibria within aqueous polysulphide electrolytes and a numerical model used to approximate the equilibrium concentrations of sulphur species, and (iii) possible aqueous S_x^{2-}/HS^- redox reactions, the electrodes (electrocatalysts) and reaction mechanisms for aqueous S_x^{2-}/HS^- redox reactions, and the electroanalytical techniques used in the three-electrode cell experiments.

Chapter 3 introduces the experimental setups, methods and conditions in this study.

Chapter 4 discusses the speciation of aqueous polysulphide electrolytes using the numerical model and re-evaluated the potentials of possible aqueous S_x^{2-}/HS^- redox reactions. A metastable Eh-pH diagram of the S-H₂O system was also built to facilitate the understanding of aqueous polysulphide electrolytes.

Chapter 5 presents the results of CV measurements and polarization tests of glassy carbon and nickel disk electrodes in aqueous polysulphide electrolytes.

Chapter 6 discusses the results of polarization tests of a variety of porous electrodes including carbon papers, Ni foams and various NiS_x/carbon papers electrodes prepared using electrodeposition, impregnation and electroless deposition methods. It also presents the results of demonstrating a NiS_x/Ni foam negative electrode in a 5 cm² single-cell polysulphide-air RFB.

Chapter 7 presents the conclusions of this thesis and suggestions for future work.

Chapter 2 Literature Review

2.1 Fundamentals of RFBs

2.1.1 Concept and Principles

RFBs, also known as regenerative fuel cells, usually comprise a negative electrode compartment and a positive electrode (cathode) compartment separated by an ion-exchange membrane (IEM). In each compartment, an electrolyte that dissolves a redox couple is pumped through/by the electrode at which the electroactive species (or electroactive species) are oxidized or reduced during the charge and discharge of the battery. Energy conversion in a RFB is achieved by the reversible electrochemical reactions of the two redox couples ($A^{n+}/A^{(n+x)+}$ and $C^{(m-y)+}/C^{m+}$), as generalized below.

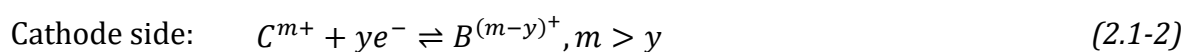


Figure 2.1-1 illustrates a typical RFB system with electron/ion/solvent transport and redox reactions on each side. In discharge mode, the electroactive species in the negative electrolyte (anolyte) are oxidized (from A^{n+} to $A^{(n+x)+}$) and the electroactive species in the positive electrolyte (catholyte) are reduced (from C^{m+} to $C^{(m-y)+}$); in the charge mode, the electroactive species in the anolyte are reduced (from $A^{(n+x)+}$ to A^{n+}) and the electroactive species in the catholyte are oxidized (from $C^{(m-y)+}$ to C^{m+}). The electric circuit is completed by the transport of charge-carrying species through the IEM which separates the anolyte and catholyte.

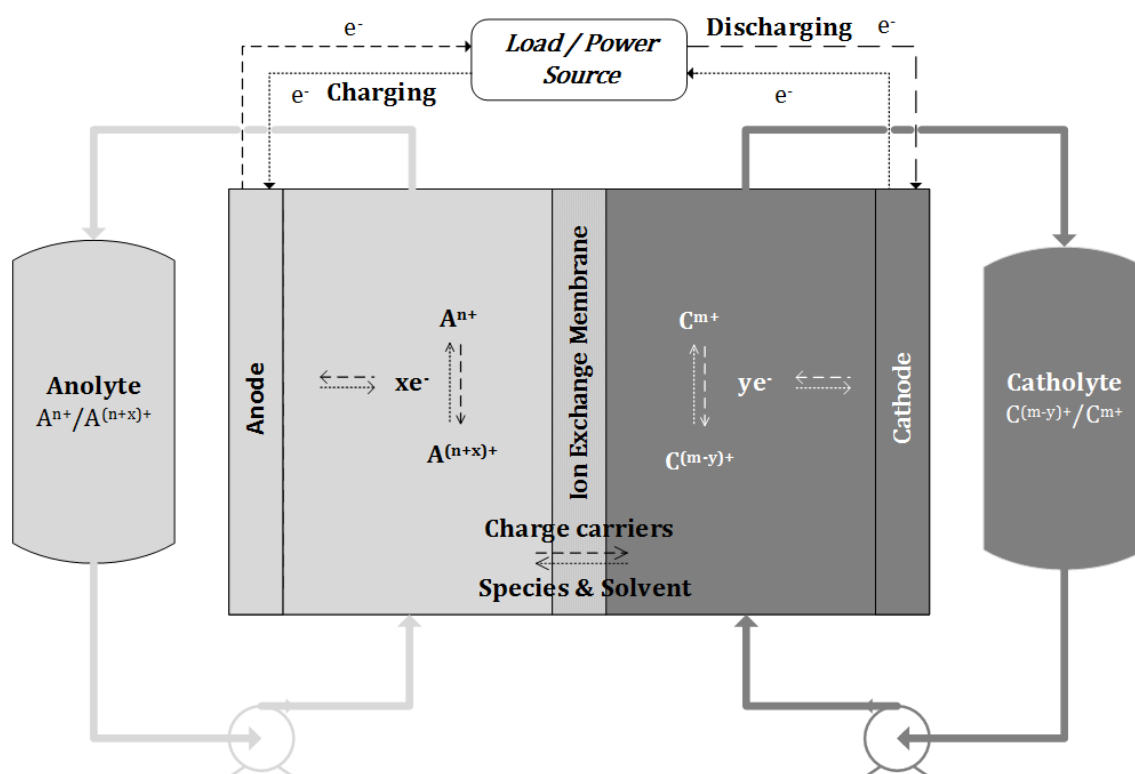


Figure 2.1-1 Schematic view of a typical RFB with electron/ion/solvent transport and the redox reactions of each half-cell.

2.1.2 System Configuration and Components

An RFB system usually consists of the stack and the electrolyte storage (tank) and pumping system. A typical unit cell of an RFB stack comprises an anode and a cathode separated by an IEM. A stack is made up of a number of unit cells connected in series in a bipolar fashion. In addition to the electrodes and the membrane, (bipolar) flow channel plates, current collectors, gaskets and end plates are also necessary components of an RFB stack. Figure 2.1-2 illustrates (a) the exploded view of a unit cell within a RFB stack and (b) the assembled view of a RFB stack [22].

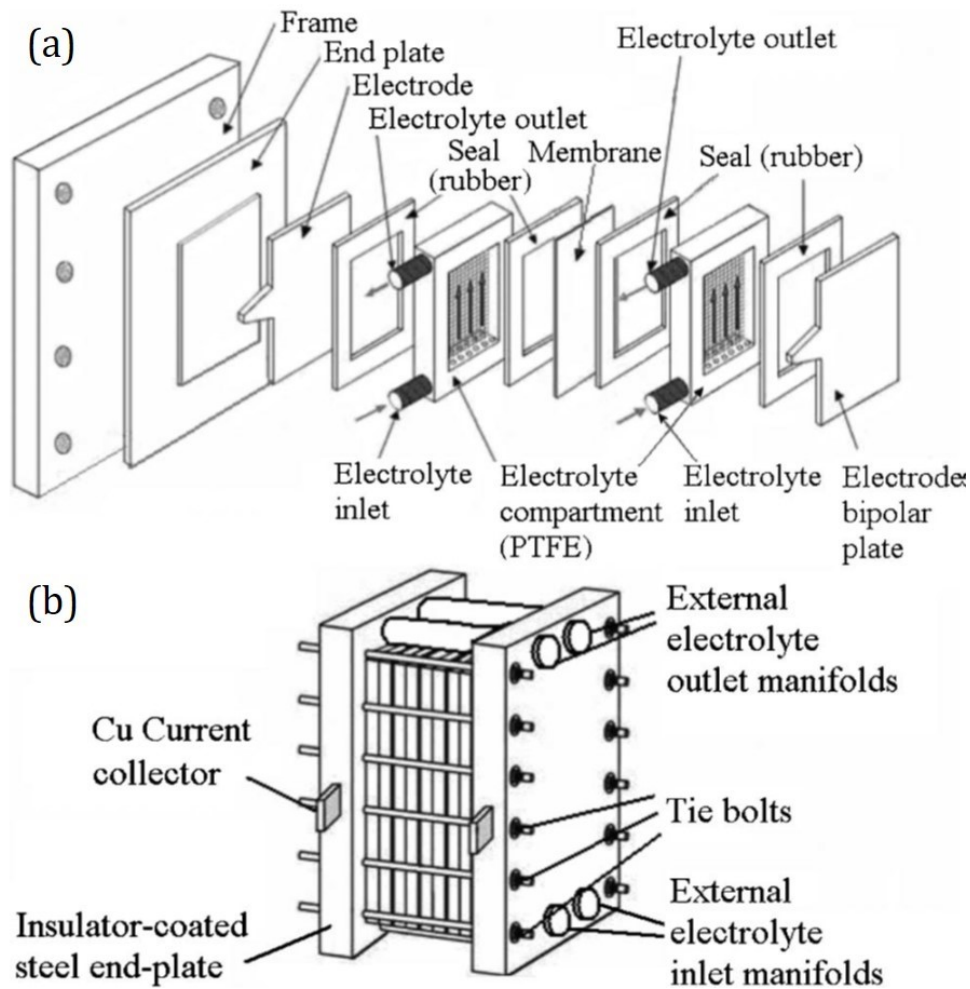


Figure 2.1-2 Components of a RFB (a) cell and (b) stack [22]

Electrolytes are the media where the energy is stored for RFB systems. The open circuit potential (OCP), often referred as open circuit voltage (OCV), of an RFB system is defined as the potential difference between the anodic and cathodic redox reactions, which is intrinsic to the redox couples dissolved in the electrolytes. The storage capacity of an RFB system depends on the volume and concentration (solubility) of the redox species, while the energy density is determined by the cell potential and storage capacity. The choice of electrolyte greatly affects the overall cost, operational temperature, stability and safety of RFB systems.

Electrodes are another important component of RFB systems, whose size (active area), catalytic activity and resistance have great effects on the power output and efficiencies of RFBs. An ideal electrode should have a high surface area, low electrical resistance,

suitable porosity, high electrochemical activity towards the redox reactions and high chemical, electrochemical and mechanical stabilities in the electrolyte [23].

Carbon- or graphite-based papers, felts, cloths as well as carbon black have been the most commonly used electrode materials in RFB applications due to their high surface areas, great stabilities in both acidic and alkaline environment and low costs. However, the hydrophobicity of carbon or graphite materials often leads to the poor wetting of these electrodes by aqueous electrolytes and hence low utilisation of the electrode surface areas. As a result, carbon or graphite materials are often treated thermally [24-27], chemically [28, 29], electrochemically [30] and by doping or depositing metals [31, 32] before being used as electrodes for aqueous RFBs, among which thermal treatment is the simplest and most adopted method. The pre-treatments often introduce increased oxygen-based groups, mainly C-O-H and C=O, on the surface of carbon or graphite materials which enhances both the hydrophilicity and catalytic activity of the carbon/graphite electrodes [23].

For redox couples towards which carbon or graphite materials have low catalytic activities, the electrodes are often prepared by loading highly catalytically active catalysts onto the carbon/graphite substrates [33]. On the other hand, porous metals such as Ni foam are also being widely used as electrodes in RFBs due to their high catalytic activities and high surface areas [34].

The **Membrane** is a separator which divides the anode and cathode compartments preventing anolyte and catholyte from mixing and meanwhile allowing the charge-carrying species to transport across in order to complete the electric circuit. Good membranes should have high ionic conductivity and selectivity, low water intake, good ion exchange capacity and good chemical and mechanical stability, as well as low cost [35]. Membranes are a three-dimensional (3D) network made up of cross-linked linear polymer chains with ionic functional groups fixed on the backbones surrounded by counter ions [35]. According to the ionic functional groups attached to the membrane matrix, IEM can be classified as cation-exchange membrane (CEM) and anion-exchange membrane (AEM). So far, the most widely used RFB membranes are the Nafion® series CEMs produced by DuPont. These perfluorinated membranes exhibit great performances and stabilities, whose application however are largely limited by their high cost [35].

Flow channels (turbulence promoters) are often employed inside the electrode compartments to enhance the mass transport and exchange of electroactive species [22]. **Current collectors** often use copper due to its high electrical conductivity. **Gaskets** (sealing components) are usually made from chemically resistant polymers, such as polytetrafluoroethylene (PTFE), polyvinylchloride (PVC) and polyvinylidene (PVDF). **End plates** usually use metals such as aluminium and stainless steel due to their high mechanical strength and corrosion resistance.

2.1.3 RFB Chemistries

In general, RFBs can be divided into two categories, namely all-liquid RFBs and hybrid RFBs. All-liquid RFBs can be further divided into aqueous RFBs and non-aqueous RFBs according to the solvent used to dissolve the redox couples; hybrid RFBs can be further classified into solid-liquid, gas-liquid and semi-solid RFBs [36]. Although increasing efforts have been seen in the development of non-aqueous and hybrid RFB systems in the past decade [37-42], conventional RFBs utilising aqueous inorganic redox couples in both anodic and cathodic compartments are the most developed to date.

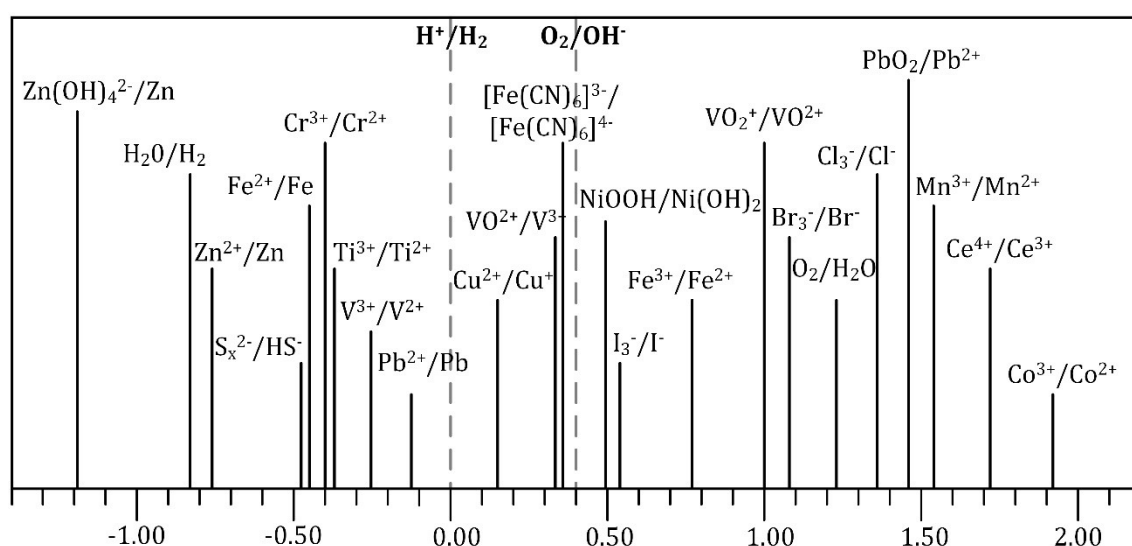


Figure 2.1-3 A summary of inorganic redox couples with their standard potentials (vs standard hydrogen electrode (SHE))

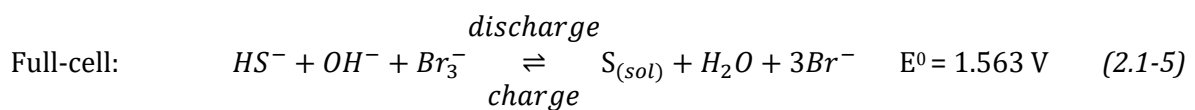
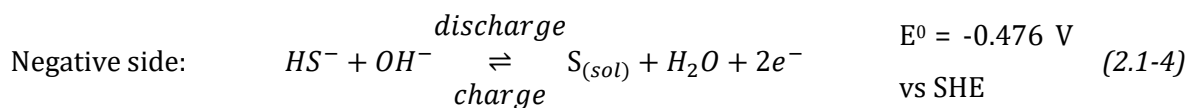
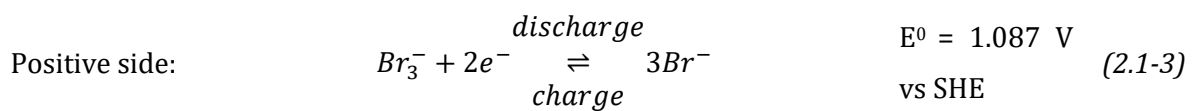
Inorganic redox couples are often formed by elements from one of the following few categories: **first-row transition metals**, **chalcogens** and **halogens**. Examples of the most common inorganic redox couples together with their corresponding standard potentials are shown in Figure 2.1-3, among which the aqueous S_x^{2-}/HS^- redox couple is highly attractive in RFB applications mainly due to the abundance in raw materials, low cost and high energy density of the aqueous polysulphide electrolyte.

To date, four RFB systems have been reported utilising aqueous polysulphide electrolyte, including the PSB [33, 34, 43-45], the polysulphide-iodide RFB [19, 46, 47], the polysulphide-ferrocyanide RFB [48] and the polysulphide-air RFB [21, 49, 50].

2.1.3.1 PSB

Aqueous polysulphide/halogen RFB systems were first proposed by Remick and Ang in 1984 employing near neutral or slightly basic aqueous electrolytes [43]. The anode side utilises an aqueous S_x^{2-}/HS^- redox couple and the cathode side utilises a Cl_2/Cl^- , Br_2/Br^- or I_3/I^- redox couple. A CEM is employed to separate the anolyte and catholyte, allowing sodium or potassium ions to pass through. Among the aforesaid three polysulphide/halogen RFB systems, the PSB system has been the most developed.

PSB systems employ aqueous alkaline sodium sulphide/polysulphide solution as anolyte and sodium bromide/bromine solution as catholyte. During discharge, sulphide ions are oxidized to polysulphide ions at the anode while the tribromide ions are reduced to bromide ions at the cathode; and vice versa for the charging process. Half-cell reactions and the overall reaction of PSB are described as below.

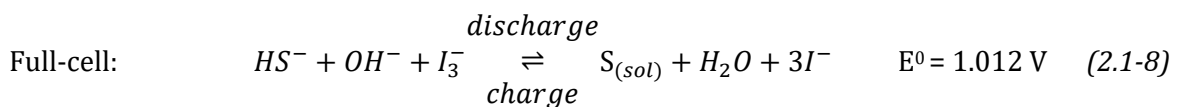
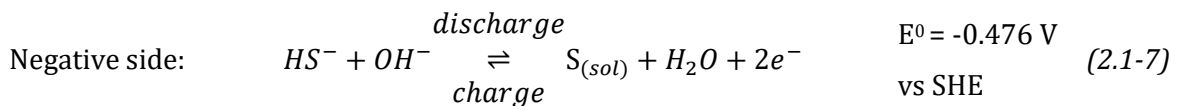
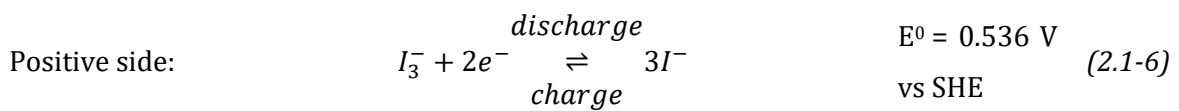


PSB technology was mostly developed by Innogy in the UK in the 1990s and 2000s, under the trademark 'Regenesys®'. A 15 MW/120 MWh Regenesys system was built at Little Barford, UK to facilitate the 'Black start' of Innogy's 680MW gas-fired combined cycle Power station and for arbitrage applications. However, development of Regenesys PSB technology was discontinued by RWE (parent company of Innogy) due to technical and funding issues in 2003 [51]. Regenesys PSB systems suffered from a series of problems including crossover and mixing of electrolytes, precipitation of sulphur species, and the formation of toxic H₂S gas and Br₂ vapour [52]. A second pilot plant of the Regenesys system (12 MW/120 MWh) constructed for Tennessee Valley Authority (TVA) to increase the grid reliability, which was to be in Mississippi, US, was subsequently abandoned due to this decision. In 2004, the global intellectual property of the PSB technology of RWE was acquired by VRB Power from Canada whose assets were later acquired by Prudent Energy from China in 2008.

In the 2000s (2002-2006), PSB technology was further developed by Dalian Institute of Chemical Physics, China (DICP) focusing on the improvement of electrodes for aqueous S_x²⁻/HS⁻ redox reaction [33, 34, 44, 45]. Since 2006, no further development of the PSB technology has been reported.

2.1.3.2 Polysulphide-iodide RFB

As a close variation of PSB, polysulphide-iodide RFB uses an aqueous alkali polysulphide solution and alkali iodide solution as the anolyte and catholyte respectively. Half-cell reactions and the overall reaction of the polysulphide-iodide RFB are described as below.



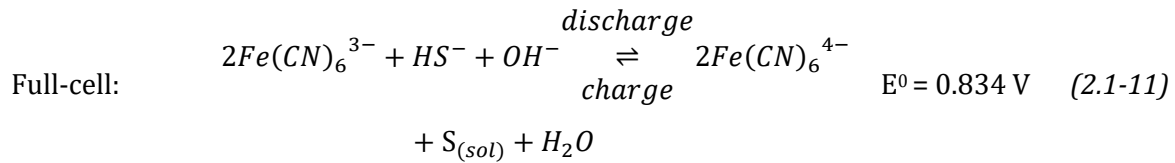
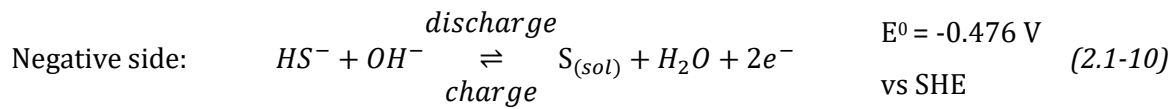
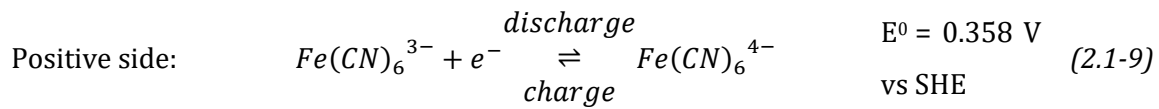
Although the polysulphide-iodide RFB was proposed as early as 1984, it was not until 2016 that this system was first demonstrated in a laboratory by Li et al. This system

achieved a high energy density of 43.1 Wh L⁻¹ and a significantly reduced electrolyte cost of \$85.4/kWh compared to VRB which is \$152.0-154.6/kWh [47].

Su et al also reported a similar system where the cation of the solutes used was sodium instead of potassium. A peak power of 65 mW cm⁻² was achieved in the demonstration; and crossover of polysulphide species was found to be the limiting factor of battery performance [19].

2.1.3.3 Polysulphide-ferrocyanide RFB

The Polysulphide-ferrocyanide RFB utilises neutral alkali metal polysulphides and alkali metal ferri/ferrocyanide as the redox species. Half-cell reactions and the overall reaction of the polysulphide-ferrocyanide RFB are described below.



Polysulphide-ferrocyanide RFB was first reported by Wei et al in 2016. With a Co/graphite felt cathode, a graphite felt anode and a Nafion® 117 CEM, Wei et al achieved a coulombic efficiency of 99%, an energy efficiency of ~74% and a capacity retention of 98% over 100 cycles [48]. This novel RFB was claimed to have a low electrolyte cost of around \$34/kWh at the redox material concentration of 1 mol l⁻¹.

2.1.3.4 Polysulphide-air RFB

The concept of polysulphide-air RFB [20] and the results of a previous demonstration of this system [21] have been discussed in Section 1.2.

A similar system was reported by Li et al in 2017, with an aqueous lithium or sodium polysulphide anolyte, an acidic or alkaline catholyte containing lithium or sodium ions and a ceramic membrane such as LiSICON and NaSICON [49]. With acidic electrolytes the polysulphide/air RFB gives an OCV of 1.68 V instead of 0.88 V in alkaline systems. A peak power density of 5.1 mW cm^{-2} at the current density of 7.1 mA cm^{-2} was achieved for the Li-based system at 55°C using a $50 \text{ }\mu\text{m}$ -thick LiSICON membrane [49]. According to the economic analysis of Li et al, polysulphide-air RFB system has an exceptionally low chemical cost of around $\$1/\text{kWh}$ using aqueous sodium polysulphide electrolyte which parallels those for PHS and CAES.

2.1.4 Evaluation of RFBs

Diagnosis and characterization of RFBs involves dozens of techniques including electrochemical, physical and spectroscopic measurements, which covers nearly all aspects of RFB technologies from material characterization, reaction mechanism study to performance evaluation. A comprehensive review on these diagnostic techniques used in RFB studies was recently published by Gandomi et al [36], among which the most commonly used techniques in RFB studies are the in-situ electrochemical characterization techniques.

This section mainly discusses the following three important electrochemical characterization techniques, charging-discharging test (battery cycling), polarization curve measurement, and EIS measurement. In addition, half-cell measurements as an important technique to decouple the performance of the full cell is also discussed.

2.1.4.1 Figures of Merit

The performance of a RFB can be evaluated by the following criteria: cell potential (E), current (I)/power (P)/energy densities and voltage/coulombic/energy efficiencies. Although sometimes expressed as linear equations, it is believed to be more precise to describe the deriving equations of these parameters in integration forms since potential and current are often volatile over time (t) in real electrochemical measurements. E, I and

t are the three direct output parameters from electrochemical measurements, which are the basis to derive other performance metrics.

Current density refers to the current per unit area as expressed in equation 2.1-12, where A is the active/geometric area of a RFB cell/reactor.

$$\text{Current Density} = \frac{I(t)}{A} \quad (2.1-12)$$

Power density (P) is defined as the product of cell potential and current density:

$$P(t) = \frac{E(t)I(t)}{A} \quad (2.1-13)$$

Energy density refers to the energy stored per unit mass or volume of the electrolyte, in the unit of Wh kg⁻¹ or Wh L⁻¹. It can be calculated via equation 2.1-14, where m and V refer to the mass and volume of the electrolyte respectively:

$$\text{Energy density} = \frac{\int_0^t E(t)I(t)dt}{m} \text{ or } \frac{\int_0^t E(t)I(t)dt}{V} \quad (2.1-14)$$

Capacity (Q) refers to the total available charge of the system, in the unit of ampere-hours (Ah), and can be calculated by equation 2.1-15:

$$Q = \int_0^t I(t)dt \quad (2.1-15)$$

For a given electrolyte, its theoretical capacity can be calculated via equation 2.1-16, where n is the number of electrons transferred per species, c is the concentration of the electrolyte, V is the volume of the electrolyte and F is the Faraday Constant (96485 C mol⁻¹).

$$Q = ncVF \quad (2.1-16)$$

As related to the capacity, **electrolyte utilisation** is another parameter that is sometimes used to evaluate an RFB system. Electrolyte utilisation is defined as the ratio between the actual capacity and the theoretical capacity of the system, which indicates the extent of utilisation of active species in the electrolyte [18]. Electrolyte utilisation can be calculated by the following equation:

$$\eta = \frac{\int_0^t I(t)dt}{ncVF} \times 100\% \quad (2.1-17)$$

Voltage efficiency (η_V) refers to the ratio between averaged discharge voltage and averaged charge voltage. It reflects the polarization properties of the system, which is related to the electrode material, manufacturing process and distribution of electrolyte within the system [18]. Voltage efficiency can be calculated via equation 2.1-18.

$$\eta_V = \frac{\int_0^{t_d} E_d dt / t_d}{\int_0^{t_c} E_c dt / t_c} \times 100\% \quad (2.1-18)$$

Coulombic efficiency (η_C), also called charge or current efficiency, refers to the charge ratio between fully discharging and charging. It reflects crossover, electrolyte osmotic rate and by-reactions of the system [18]. Coulombic efficiency can be calculated via equation 2.1-19:

$$\eta_C = \frac{\int_0^{t_d} I_d dt}{\int_0^{t_c} I_c dt} \times 100\% \quad (2.1-19)$$

Energy efficiency (η_E) refers to the ratio between discharge energy and charge energy, which can be calculated by the equation below:

$$\eta_E = \frac{\int_0^{t_d} E_d I_d dt}{\int_0^{t_c} E_c I_c dt} \times 100\% \quad (2.1-20)$$

The relationship between η_V , η_C and η_E in constant current mode is expressed as below:

$$\eta_E = \eta_V \times \eta_C \quad (2.1-21)$$

2.1.4.2 Charging-discharging Test

Charging-discharging test is the most common method used to evaluate RFBs, which determines the η_V , η_C and η_E of RFB systems. Charging-discharging test also shows the utilization of electrolyte and capacity decay over cycling [53]. It is often performed at constant current with charging and discharging processes being carried out alternatively and repetitively.

2.1.4.3 Polarization Curve Measurement

Polarization curves together with power density curves is another key technique to evaluate the performance of RFBs, which reveals the loss mechanisms of RFBs. It is often shown in a double-Y-axis plot where the left Y axis refers to the cell voltage and the right Y axis refers to the power density, as shown in figure 2.1-4.

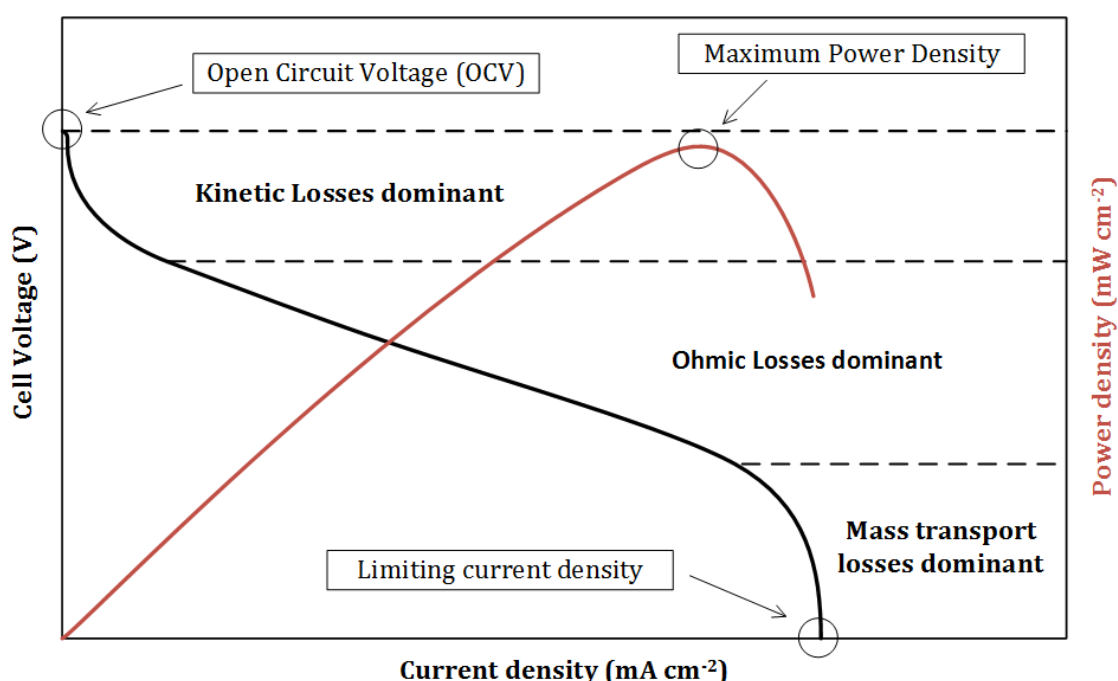


Figure 2.1-4 Generalized polarization curve and power density curve, with the indication of different sources of potential losses along the increasing current density

The polarization curve, often shown as the discharging polarization curve, is measured via steady state polarization of the RFB, which can be conducted under either constant potential (potentiostatic) mode or constant current (galvanostatic) mode. However, the galvanostatic polarization method is more commonly used. In each polarization step, a constant current/voltage is applied to the RFB for a certain period of time (i.e. 60s) to reach a steady state where the value of the corresponding voltage/current is taken as a data point for the polarization curve, after which the RFB is allowed to rest at its OCV for

a period of time (i.e. 2 min) to reach the steady state before the next polarization step [54].

It is worth noting that polarization curve analysis often assumes a constant state-of-charge (SoC) of the RFB, as is the case in fuel cells. This may induce substantial errors to the result where the concentrations of electroactive species are subject to significant changes over the course of the experiment, as can occur with low initial concentrations of electroactive species, high operating current densities and long testing periods. Various methods have been proposed and utilised to mitigate this issue, such as the cell-in series method, symmetric cell operation, single-phase polarization curve and alternating charge/discharge currents [36].

The primary losses for a RFB system include the kinetic losses, ohmic losses and mass transport losses, with different losses being dominant in different current density ranges, as shown in Figure 2.1-4.

Kinetic losses refer to the activation overpotentials resulting from the slow charge transfer reactions at the electrode/electrolyte interface, which is dominant at low current densities. It is often described as a charge-transfer limited kinetics using a Butler-Volmer model.

Ohmic losses mainly come from the electrical resistance of cell components, contact resistance between cell components and ionic resistance of the electrolyte (mainly from the IEM) [36, 54]. It is shown in the polarization curve as a straight line at intermediate current density regions.

Mass transport losses, sometimes called concentration polarization losses, usually become dominant at high current densities. Within this current region, the cell current largely depends on the diffusion speed of electroactive species towards the electrode surface from the bulk electrolyte. In fact, the mass transport effect may not reveal in the polarization curve under circumstances where the kinetics of electrochemical reaction is slow and internal ohmic resistance of the cell is high [36].

2.1.4.4 EIS Measurements

While it is useful to indicate the dominant losses of an RFB at certain current densities, quantitative comparison of the various losses are not provided by polarization curve measurement. EIS offers an opportunity to reveal the various sources of polarization of RFBs under different conditions.

EIS is conducted by applying an AC voltage/current signal with known amplitude and frequency (ω) to the system while measuring the corresponding current/voltage. Impedance ($\mathbf{Z}$) can be derived by dividing the voltage with corresponding current. EIS can be performed in potentiostatic or galvanostatic modes though the latter is more commonly used. The amplitude of the potential signal applied is normally very small (1-10 mV), such that the response of the studied system (I-V) can be regarded as pseudo-linear [55].

Impedance is a vector which can be described either as a complex number or in the polar form, as described below.

$$\mathbf{Z}_{(\omega)} = Z_{re} + jZ_{im} \quad (2.1-22)$$

$$\mathbf{Z} = Ze^{j\phi} \quad (2.1-23)$$

Where, Z , Z_{re} and Z_{im} represents the absolute value, real part and imaginary part of the impedance respectively, and ϕ represents the phase angle between the current and the potential [56]. Accordingly, the impedance can be displayed in two different ways, namely, the Nyquist plot and the Bode plot. In the Nyquist plot, Z_{re} is plotted on the X-axis and $-Z_{im}$ is plotted on the Y-axis. In the Bode plot, $\log |Z|$ and ϕ are plotted against $\log \omega$ independently. Figure 2.1-5 demonstrates the Nyquist plot and Bode plot for a parallel RC circuit with the resistance (R) of 100 Ω and the capacitance (C) of 1 μF respectively [57].

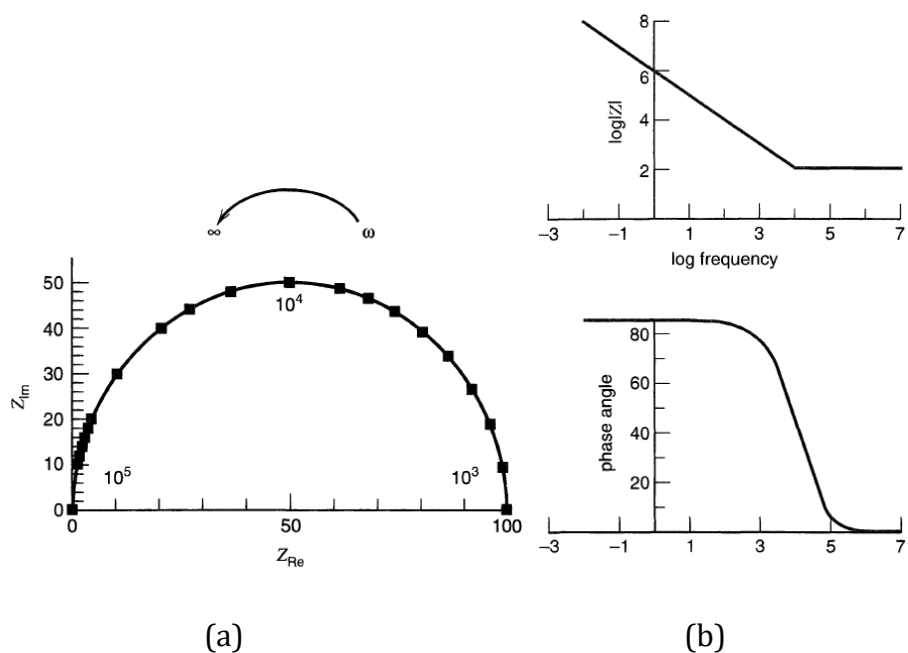


Figure 2.1-5 Nyquist plot (a) and Bode plot (b) for a parallel RC circuit with $R = 100 \Omega$ and $C = 1 \mu F$ [57]

EIS data is usually analysed by fitting with equivalent circuit models comprising a number of elements. There are three basic electrical elements, namely the resistor, capacitor, and inductor. These elements are linked to various physical components or processes within the RFB system, such as electrolyte resistance, double layer capacitance, polarization, charge transfer and diffusion. The non-ideality of real electrochemical systems can be compensated by replacing the ideal electrical elements with more sophisticated elements, such as constant phase elements (CPE), distributed elements and Warburg diffusion (W).

Impedance result of an electrochemical system involving electrode processes can often be fitted with the Randles circuit or a close variant [36]. As an example, Figure 2.1-6 shows the Randles circuit model for an electrochemical system with mixed kinetic and finite diffusion control.

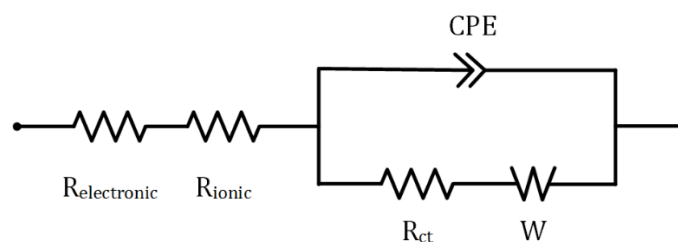


Figure 2.1-6 Randles circuit model with mixed kinetic and finite diffusion control

At high frequencies (5-30 kHz), the impedance of the RFB system is analogous to a resistor which represents the total ohmic resistance of the RFB including the ionic resistance of ion transport through the IEM, electrolyte resistance, electrode resistance and contact resistance, etc. [36]. This high frequency resistance (HFR) can be used to correct the cell potential with corresponding current density before plotting the polarization curve. The HFR is often measured with potentiostatic EIS with an amplitude of 10 mV and within the frequency range of 15-30 kHz [54]. However, due to the fact that HFR is nearly consistent under various current densities, it mainly contributes to a vertical shift of the polarization curve. As a result, polarization curve is often not adjusted with IR correction.

It is worth noting that for RFB systems using peristaltic pumps the impedance spectra can be distorted in the low frequency regions due to the pulsing nature of these pumps. This issue can be resolved by using constant syringe pumps or adding a pressurized intermediate electrolyte reservoir [36].

Additionally, equivalent circuit modelling of impedance spectra is not always straightforward as one impedance spectrum could be fitted perfectly with multiple equivalent circuits. Thus, effective and accurate fitting of impedance results for RFBs requires considerable knowledge in the understanding of the actual physical phenomena happening inside the RFB systems under various conditions.

2.1.4.5 Half-cell Measurements

During the operation of a single-cell RFB, voltage and current are measured for the whole battery whereas the voltage information of individual half-cells is unknown. However, by positioning a reference electrode (RE) between the negative and positive half-cells, it is possible to decouple the potentials of the two individual compartments. Electrochemical measurements of each half-cell are viable within a full-cell RFB setup using this method. With a second potentiostat, or by using a bipotentiostat, electrochemical measurements of individual half-cells are achievable during the full-cell operation of an RFB. Hence, the electrochemical behaviours of each half-cell under various operating conditions of an RFB can be obtained. With half-cell EIS measurements, the performance limiting side of an RFB could be more easily identified.

There are various methods of positioning the RE into RFB setups, such as the 'sandwich method' and 'edge method' [58]. In this work, due to the presence of an intermediate compartment between the AEM and CEM, it is convenient to position the RE by simply inserting the RE into the intermediate electrolyte reservoir.

2.2 Sulphur Chemistry in Aqueous Solutions

Sulphur (S) is an abundant, reactive and multivalent element, whose atomic number is 16 and atomic weight is 32. It is the 10th most abundant element in the universe and 5th most abundant element on earth by mass. Sulphur reacts with almost all other elements except for inert gases, gold and platinum [59]. Sulphur possesses a variety of chemical valences ranging from -2 to 6, which is the basis for the formation of various sulphur-containing species. Sulphur exists in nature as both pure element and compounds.

More than 30 molecular forms of elemental sulphur have been reported, with the most important allotrope being the yellow orthorhombic α -sulphur (α -S₈) and all other allotropes revert to this form at ambient temperature [60]. Elemental sulphur can be found in volcanic areas and hot springs. Sicily used to be a major source of sulphur production in the past, whereas today almost all elemental sulphur is produced as a by-product of processing natural gas, crude oil and other fossil fuels.

Elemental sulphur has long been used as fungicides and pesticides. It is also an essential part of gunpowder. Today, elemental sulphur is mainly used to produce sulphuric acid. Sulphur is also widely used in areas such as winemaking and food preservation, medical treatments, production of fertilizers and vulcanizing of natural rubber.

Sulphur compounds often exist in nature as sulphide minerals, such as pyrite (iron sulphide), cinnabar (mercury sulphide) and galena (lead sulphide) and sphalerite (zinc sulphide), and sulphates, such as gypsum (calcium sulphate), barite (barium sulphate) and mirabilite (sodium sulphate). Sulphur compounds also exist abundantly in organisms, in the form of organosulphur compounds or metal sulphides. It is an essential element in proteins and plays important roles in biochemical processes. Inorganic sulphides and polysulphides and their protonated forms, including H₂S, HS⁻, S²⁻, H₂S_n, HS_n⁻ and S_n²⁻, are found existing abundantly in natural aquatic systems, although concentrations are often low [61].

Elemental sulphur is hydrophobic, whose solubility in water at 25 °C was measured to be 30±10 nmol l⁻¹ [62]. However, elemental sulphur can dissolve in aqueous solutions in the presence of sulphide ions, the two of which would combine and form soluble

polysulphide ions in aqueous solutions. Aqueous polysulphide solutions exhibit colours from light yellow to orange and then deep red depending on concentration. As an example, the aqueous polysulphide solutions containing 1 mol kg⁻¹ of Na₂S₂ and 1 mol kg⁻¹ NaOH shows a deep red colour.

Inorganic polysulphides have long been used to increase the yields of the Kraft pulping process in the paper industry [63]. More recently, growing interests have been seen in utilising aqueous polysulphide solutions in energy conversion and storage applications, especially in photoelectrochemical solar cells (PECs) and RFBs. Aqueous polysulphide solutions were found capable of stabilizing cadmium chalcogenide photoelectrodes in PECs, because of which aqueous polysulphide solution has been widely used as electrolyte in Quantum Dot-Sensitized Solar Cells (QDSSCs) [64]. Due to the low cost, environmental benignity and high energy density of aqueous polysulphide electrolytes, the aqueous S_x²⁻/HS⁻ redox couple has attracted attention for application in RFBs [19, 21, 33, 34, 44, 47, 49, 50, 65, 66].

This section mainly discusses three aspects of the aqueous polysulphide electrolyte: (i) the equilibria within aqueous polysulphide electrolytes, (ii) a numerical model of aqueous polysulphide speciation, and (iii) properties of aqueous polysulphide electrolytes.

2.2.1 Equilibria within Aqueous Polysulphides Solutions

Aqueous S-H₂O system is highly complex, including various sulphides, polysulphides, oxy-sulphur anions and their protonated forms. The existence of aqueous polysulphide species, including H₂S_n, HS_n⁻ and S_n²⁻, with a maximum chain length of 8 have been reported in the literature [67]. Sulphur radicals such as supersulphides (S₂⁻), especially at elevated temperatures, were also reported [68-72].

Studies have shown that solubility and average chain length of aqueous polysulphides (S_n²⁻) is dependent on the solution alkalinity and temperature [72-74]. Arntson et al. investigated into the equilibrium composition of saturated S-Na₂S-H₂O system at 25°C and 50°C respectively, from which they derived an average polysulphide chain length of 4.77 ± 0.3 at 25°C [73]. Teder also investigated the equilibrium of polysulphides by

acidifying the polysulphide solutions until precipitation and dissolving elemental sulphur in polysulphide solutions until equilibrium among elemental sulphur and polysulphides are established. He concluded that the average chain length of polysulphides at equilibrium was 4.4 at 25 °C and 5.0 at 80 °C, and this value was highly dependent on the alkalinity of the solution [74]. Optical spectroscopic studies of aqueous polysulphide solutions also suggested that S_5^{2-} was the polysulphide species with the longest chain length that existed in aqueous alkaline polysulphide solutions [72, 75].

Hence, it is reasonable to assume that, in alkaline polysulphide solutions, only polysulphides with a maximum chain length of 5 (S_n^{2-} , $n=2-5$) exist in large quantities, apart from water, alkali-metal cations, OH^- and H^+ [72, 74-78]. The complex equilibria within aqueous polysulphide solutions include the water dissociation, hydrogen sulphide dissociation and equilibria among polysulphides [77].

2.2.1.1 Water Dissociation

Water dissociation into protons and hydroxide ions, as shown in equation 2.2-1, is fundamental for all aqueous systems. The equilibrium constant of this reaction, namely the ionic product of water (K_w), is dependent on the type of solute, ionic strength and temperature of the solution [79-84]. However, due to the complexity in composition of aqueous polysulphide solutions, the effect of solute type and ionic strength are often neglected.



$$K_w = a_{H^+}a_{OH^-}/a_w = a_{H^+}\gamma_{OH^-}[OH^-]/a_w \quad (2.2-2)$$

Licht et al adopted the pK_w value determined by Fisher and Barnes [80] in the numerical calculation of sulphur species concentrations in aqueous polysulphide solutions, which took into account the effect of temperature on pK_w [76, 77]. Lessner et al also reported the numerically calculated concentrations of sulphur species in aqueous polysulphide solutions, however, it was not mentioned in the work the pK_w used for the numerical calculation [68].

2.2.1.2 Hydrogen Sulphide Dissociation

Hydrogen sulphide dissociates in aqueous solutions in two steps, as shown in equation 2.2-3 and 2.2-5. While the first dissociation constant of H₂S ($K_{a,1}$) is fairly consistent among the reporting of various authors with a value close to 10^{-7} at room temperature, great debates have been seen on the second dissociation constant of H₂S ($K_{a,2}$) at room temperature, ranging from 10^{-12} to 10^{-19} [85]. However, in more recent studies, it was believed that a value of 10^{-17} to 10^{-19} should be appropriate [78, 86-95].



$$K_{a,1} = a_{H^+}a_{HS^-}/a_{H_2S} = a_{H^+}\gamma_{HS^-}[HS^-]/\gamma_{H_2S}[H_2S] \quad (2.2-4)$$



$$K_{a,2} = a_{H^+}a_{S^{2-}}/a_{HS^-} = a_{H^+}\gamma_{S^{2-}}[S^{2-}]/\gamma_{HS^-}[HS^-] \quad (2.2-6)$$

From spectroscopic measurements of highly alkaline sulphide solutions, Ellis and Giggenbach derived $pK_{a,2}$ values of >17 at 25°C, > 16 at 100°C, > 12.5 at 200°C and > 12 at 300°C [86]. They also indicated that the low values of previously reported $pK_{a,2}$ possibly came from oxygen contamination which converts sulphide ions into polysulphides and oxy-sulphur anions. Giggenbach reported a $pK_{a,2}$ value of 17.1 ± 0.2 at room temperature from a ultraviolet (UV) spectroscopic study of highly alkaline sulphide solutions [96]. The temperature dependence of $K_{a,2}$ from 10-70°C is shown in Figure 2.2-1 [96].

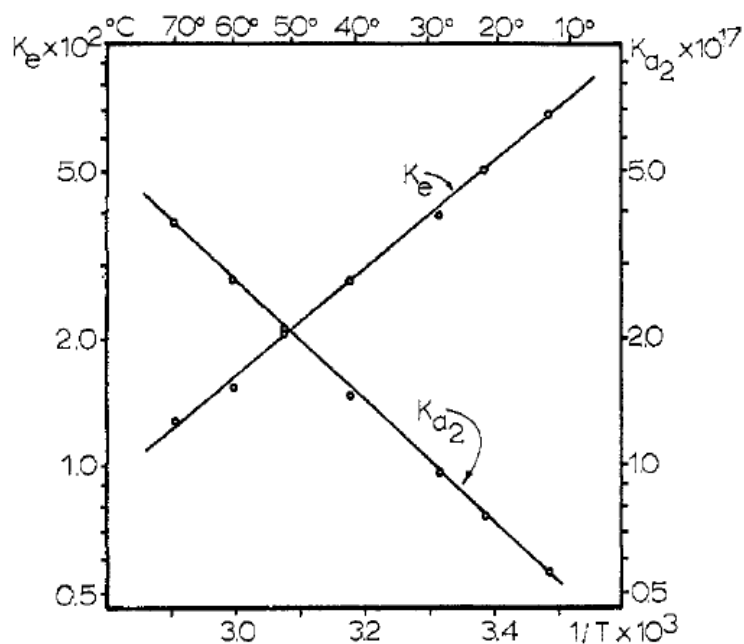


Figure 2.2-1 Temperature dependence of $K_{a,2}$ from 10-70 °C [96]

Meyer et al discovered a new absorption band at 2570 cm^{-1} in Raman spectroscopy referring to the H-S stretch of HS^- , based on which they had derived a $\text{p}K_{a,2}$ value of 17 ± 1 at room temperature [87].

Schoonen and Barnes derived a $\text{p}K_{a,2}$ value of 18.5 ± 0.56 at 20°C by extrapolation of the dissociation constants of polysulfanes (H_2S_n) as a function of their reciprocal chain length ($1/n$) [90]. This method was also adopted by Migdisov et al in the study of surface oxidation of crystalline sulphur from which they derived $\text{p}K_{a,2}$ values of 17.4 ± 0.3 at 25°C, 15.7 at 50°C and 14.5 at 75°C [95].

Licht and Manassen derived a $\text{p}K_{a,2}$ value of 17.6 ± 0.3 at 25°C by using a glass pH electrode to measure the liquid junction potential of highly concentrated sulphide solutions [89]. Licht et al also derived a $\text{p}K_{a,2}$ value of 17.1 ± 0.3 at room temperature by differential densometric analysis of highly alkaline potassium sulphide (K_2S) solutions [91]. From conductometric analysis of highly concentrated K_2S solutions, Licht et al derived a $\text{p}K_{a,2}$ value of 16.9 ± 0.2 at room temperature [92].

Myers suggested a $\text{p}K_{a,2}$ value of 19 ± 2 at room temperature, which is possibly the highest among reporting, after careful reviews of previously published data [88]. He also

suggested that a higher $pK_{a,2}$ value was more consistent with the periodic trends in the VIA acid (H_2O , H_2S , H_2Se and H_2Te) dissociation constants in water, that was $pK_{1,H_2O} > pK_{1,H_2S} > pK_{1,H_2Se} > pK_{1,H_2Te}$, $pK_{2,H_2O} > pK_{2,H_2S} > pK_{2,H_2Se} > pK_{2,H_2Te}$ and $pK_{1,H_2O} - pK_{2,H_2O} > pK_{1,H_2S} - pK_{2,H_2S} > pK_{1,H_2Se} - pK_{2,H_2Se} > pK_{1,H_2Te} - pK_{2,H_2Te}$.

From reviewing the published $pK_{a,2}$ values Kelsall and Thompson suggested a $pK_{a,2}$ value of 17-19, corresponding to standard Gibbs free energy of S^{2-} ($\Delta G_f^0(S^{2-})$) of 109.1-120.5 kJ mol⁻¹ [93].

Although most recent studies preferred a high value of $pK_{a,2}$ (>17), some have cast doubts on the appropriateness of these high values of $pK_{a,2}$. The major concern of obtaining these high $pK_{a,2}$ values is the adoption of highly concentrated alkaline solutions in the experiments in order to achieve sufficiently high concentrations of sulphide ions, however under certain conditions sulphide solutions can no longer be regarded as aqueous systems. Stephens and Cobble derived a value of around 13.8 at room temperature from calorimetric measurements of the heat of solution of adding KHS solution into basic solutions at 25 and 90 °C [97]. Temperature dependence of $pK_{a,2}$ was suggested following the following equation:

$$pK_{a,2} = \frac{4500}{T} + 12.6 \log\left(\frac{T}{298.15}\right) - 1.29 \quad (2.2-7)$$

The value given by Stephens and Cobble was adopted by Rao and Hepler in their review of the dissociation constants of hydrogen sulphide [98].

Vorobets et al also cast doubts on the high values of $pK_{a,2}$ by plotting $pK_{a,2}$ against the concentration of hydroxide ions [78]. As shown in Figure 2.2-22.2-1, the $pK_{a,2}$ value seems to increase steadily with increasing concentrations of OH^- , except for the data from Giggenbach [96].

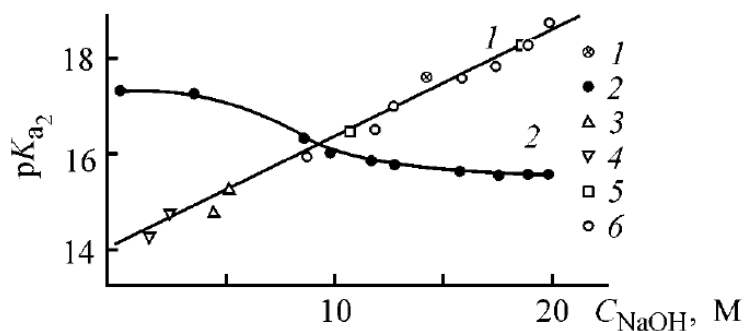
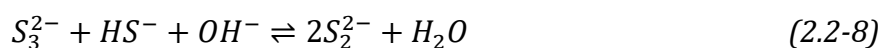


Figure 2.2-2 $pK_{a,2}$ vs NaOH concentration for data obtained in different studies [78]

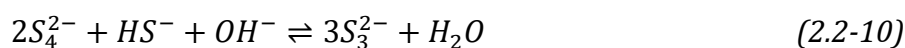
2.2.1.3 Equilibria among Polysulphides

Sulphide and polysulphide species have been detected and analysed by a variety of experimental techniques, such as UV-Vis absorption spectroscopy [70, 72, 75-78, 99-102], Raman spectroscopy [103-106], Nuclear magnetic resonance (NMR) spectroscopy [107, 108], Electrospray Ionization Mass Spectrometry (ESI MS) [109], Ion Chromatography (IC) [110] and a number of electroanalytical methods [111, 112]. Among which, UV spectroscopy had produced the most comprehensive and convincing information of aqueous polysulphide equilibria, as shown in equation 2.2-8, 2.2-10 and 2.2-12, over a wide range of concentrations, pH and temperatures.



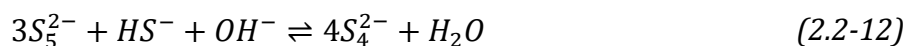
$$K_A = a_{S_2^{2-}}^2 a_w / a_{HS^-} a_{OH^-} a_{S_3^{2-}}$$

$$= (\gamma_{S_2^{2-}} [S_2^{2-}])^2 a_w / \gamma_{S_3^{2-}} [S_3^{2-}] \gamma_{HS^-} [HS^-] \gamma_{OH^-} [OH^-] \quad (2.2-9)$$



$$K_B = a_{S_3^{2-}}^3 a_w / a_{HS^-} a_{OH^-} a_{S_4^{2-}}^2$$

$$= (\gamma_{S_3^{2-}} [S_3^{2-}])^3 a_w / (\gamma_{S_4^{2-}} [S_4^{2-}])^2 \gamma_{HS^-} [HS^-] \gamma_{OH^-} [OH^-] \quad (2.2-11)$$



$$K_C = a_{S_4^{2-}}^4 a_w / a_{HS^-} a_{OH^-} a_{S_5^{2-}}^3$$

$$= (\gamma_{S_4^{2-}} [S_4^{2-}])^4 a_w / (\gamma_{S_5^{2-}} [S_5^{2-}])^3 \gamma_{HS^-} [HS^-] \gamma_{OH^-} [OH^-] \quad (2.2-13)$$

Equilibria among polysulphides in dilute aqueous polysulphide solutions ($< 0.1 \text{ mol l}^{-1}$) with moderate and high ionic strength ($\geq 2 \text{ mol l}^{-1}$) were extensively studied by Giggenbach and co-workers over a wide range of temperatures (up to 240°C) with UV absorption spectroscopy [72, 75]. It was suggested that the increase in the average chain length of polysulphides and equilibrium among polysulphides were little affected by the temperature.

Licht et al further improved the UV spectroscopic method with base-line correction of the HS^- and S^{2-} on polysulphide spectrum using computer analysis [77]. The resulting polysulphide absorption peak locations and widths and hence the derived equilibrium constants among various polysulphides are slightly different compared to that presented by Giggenbach.

Table 2.2-1 summarizes the equilibrium constants among polysulphides in aqueous solutions derived from UV spectroscopic studies by various authors.

Table 2.2-1 Equilibrium constants among polysulphides in aqueous solutions

K_i	pK_i	error	pH	I / mol l⁻¹	T / °C	Ref
K_A	3.70	± 0.15				Giggenbach [75]
K_B	1.75	± 0.15	6.8 - 17.5	≥ 2	20	
K_C	-5.60	± 0.30				
K_A	$4.2 + 0.35\sqrt{I}$	± 0.2				Giggenbach [72]
K_B	$1.75 + 0.35\sqrt{I}$	± 0.2	Near-neutral	0 - 2	20 - 140	
K_C	$-5.08 + 0.35\sqrt{I}$	± 0.3			20	
K_A	4.18	± 0.3				Licht et al [77]
K_B	0.35	± 0.3	≥ 6.4	≥ 2	20	
K_C	-5.6	± 0.6				

$$pK_i = a/T + b \times T + c + d \times \sqrt{I}, \text{ and } I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$$

2.2.2 Numerical Modelling of Aqueous Polysulphide Speciation

From knowledge of the mass constraints of total sulphur and sulphide, K_w , $K_{a,1}$, $K_{a,2}$, K_A , K_B , and K_C , it is possible to approximate the pH and concentrations of sulphur species in aqueous polysulphide solutions using an iterative method [68, 72, 75-77]. However, solution of the numerical model requires a number of assumptions [77]:

1. Only equilibria among adjacent polysulphides (S_x^{2-}/S_{x+1}^{2-}) are considered, as shown in reaction 2.2-8, 2.2-10 and 2.2-12.
2. The activity coefficient of OH^- (γ_{OH^-}) and the activity of water (a_w) are assumed equivalent to the known mean solution activity coefficients and the activity of water for an alkali-metal hydroxide (MOH) solution of the same cationic strength:

$$\gamma_{OH^-} = \gamma_{\pm, MOH}([M^+]) \quad (2.2-14)$$

$$\alpha_w = \alpha_{w, MOH}([M^+]) \quad (2.2-15)$$

3. Relative trends of the activity coefficients of various polysulphides and hydrosulphide tend to cancel:

$$(\gamma_{S_{x+1}^{2-}})^{x+1} / (\gamma_{S_x^{2-}})^x \gamma_{HS^-} = 1 \quad (2.2-16)$$

Previous studies suggested that S_4^{2-} was the dominant polysulphide species in polysulphide solutions over a wide range of solution compositions [75]. Thus, it is reasonable to assume that upon the addition of elemental sulphur into the aqueous alkali sulphide solutions the elemental sulphur combines with sulphide ions and forms tetra-sulphide ions, followed by rearrangements among polysulphide species according to equilibrium reaction 2.2-8, 2.2-10 and 2.2-12.

Hence, given the initial concentrations of NaOH, Na_2S and S, it is assumed that:

$$[S_4^{2-}]_i = 1/3 [S]_i \quad (2.2-17)$$

$$[HS^-]_i = [Na_2S]_i - [S_4^{2-}]_i \quad (2.2-18)$$

$$[OH^-]_i = [NaOH]_i + [HS^-]_i \quad (2.2-19)$$

Based on the equilibrium constants and the prior assumptions, the concentrations of H_2S , S^{2-} , S_2^{2-} , S_3^{2-} , S_5^{2-} can be derived:

$$a_{H^+} = K_w a_w / [OH^-] \gamma_{OH^-} \quad (2.2-20)$$

$$[H_2S] = a_{H^+} [HS^-] / K_{1,H_2S} \quad (2.2-21)$$

$$[S^{2-}] = K_2 [HS^-] / a_{H^+} \quad (2.2-22)$$

$$[S_5^{2-}] = ([S_4^{2-}]^4 a_{H^+} / K_C K_w [HS^-])^{1/3} \quad (2.2-23)$$

$$[S_3^{2-}] = (K_B K_w [HS^-] [S_4^{2-}]^2 / a_{H^+})^{1/3} \quad (2.2-24)$$

$$[S_2^{2-}] = (K_A K_w [HS^-] [S_3^{2-}] / a_{H^+})^{1/2} \quad (2.2-25)$$

The improved estimation of the concentrations of OH^- , HS^- , and S_4^{2-} can be calculated from the mass constraints of OH^- , total sulphides and total elemental sulphur:

$$[S_4^{2-}] = ([S]_i - [S_2^{2-}] - 2[S_3^{2-}] - 4[S_5^{2-}]) / 3 \quad (2.2-26)$$

$$[HS^-] = [Na_2S]_i - [H_2S] - \sum_{n=1}^5 [S_n^{2-}] \quad (2.2-27)$$

$$[OH^-] = [NaOH]_i + [Na_2S]_i + [H_2S] + [H^+] - \sum_{n=1}^5 [S_n^{2-}] \quad (2.2-28)$$

The process ends when the difference between S_4^{2-} input concentration and output concentration is smaller than 0.01%.

However, it is worth noting that this model is only soluble with low average polysulphide chain length (S_n^{2-} , $n < 4$). For higher average polysulphide chain length (S_n^{2-} , $n > 4$), estimates can be improved by assuming that both S_4^{2-} and S_5^{2-} exist at the initial stage.

2.2.3 Aqueous Polysulphide Electrolyte

2.2.3.1 Aqueous Solubility of Sulphides and Polysulphides

Studies have shown that the solubility and average chain length of aqueous polysulphides are dependent on the solution alkalinity and temperature [72-74]. Aqueous solubility of MOH , M_2S , M_2S_4 ($M=Na, K$) except for Na_2S_4 had been previously reported [113-115]. The dependence of the aqueous solubility of $NaOH$, KOH , Na_2S , K_2S and K_2S_4 on temperature are summarized in Figure 2.2-3 [114].

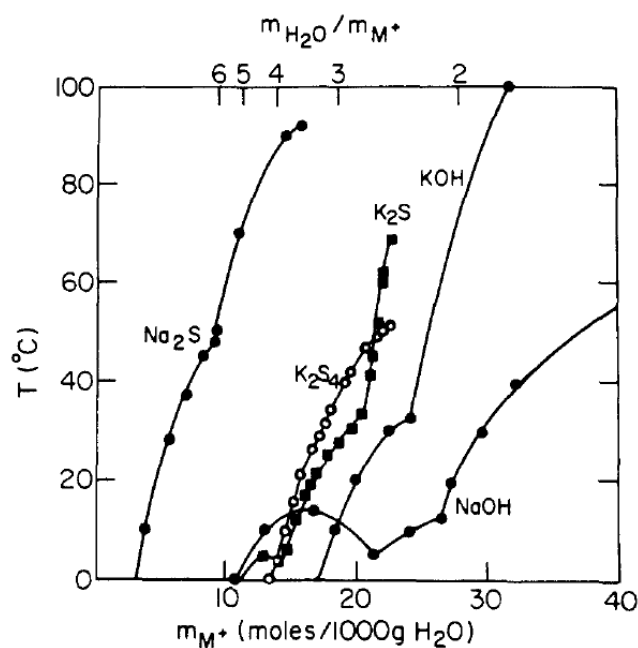


Figure 2.2-3 Aqueous solubilities of Na_2S , K_2S , NaOH and KOH as a function of temperature [114]

Table 2.2-2 gives the aqueous solubility of NaOH , Na_2S , KOH , K_2S , and K_2S_4 at 25 °C in both weight percentage and molality [113, 114, 116].

Table 2.2-2 Aqueous solubility of NaOH , KOH , Na_2S , K_2S and K_2S_4 at 25 °C

Solute	Solubility (% by wt.)	Solubility (mol kg^{-1})
NaOH	53	28.2
KOH	54	21.0
Na_2S	17	2.6
K_2S	49	8.9
K_2S_4	64	8.5

2.2.3.2 Preparation of Aqueous Polysulphide Electrolyte

Aqueous alkali (i.e. Na^+ , K^+) polysulphide solutions can be prepared by directly dissolving alkali polysulphides in water. Methods of synthesising alkali polysulphides with various

stoichiometries have been previously reported [117-123]. However, a more widely adopted method of preparing aqueous alkali polysulphide solutions is to dissolve elemental sulphur in corresponding alkali sulphide solutions, where alkali hydroxide can be added to adjust the pH of the solution [114].

Aqueous K_2S solutions, where K_2S is not commercially available, could be prepared with a general method for preparing alkali sulphide solutions which first saturates the alkali hydroxide solution with $H_2S_{(g)}$ then removes the excess H_2S by purging the saturated solution with purified nitrogen and finally adding equimolar identical alkali hydroxide into the solution [124]. However, H_2S gas is highly toxic thus its use should be avoided wherever possible.

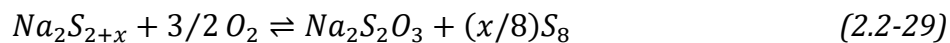
Since elemental sulphur, sodium hydroxide and sodium sulphide ($Na_2S \cdot 9H_2O$) are all commercially available, aqueous sodium polysulphide solutions are usually prepared by dissolving elemental sulphur in sodium sulphide solutions. Sodium hydroxide can be added to adjust the pH of the solution. Since sulphides and polysulphides can be oxidized by dissolved oxygen in the water [125-129], preparation of sodium polysulphide solution is usually kept under a nitrogen atmosphere and the deionised water used is usually boiled for at least 10 minutes to remove the dissolved oxygen [73].

2.2.3.3 Degradation of Aqueous Polysulphide Electrolytes

Degradation of aqueous polysulphide solutions mainly happens via the formation of oxy-sulphur anions. Formation of oxy-sulphur anions can not only block the membrane but also cause storage capacity decay for RFBs utilising aqueous polysulphide electrolyte due to the loss of electroactive species. Oxy-sulphur anions could be formed by three routes: chemical oxidation of sulphides/polysulphides by oxygen [125-129], disproportionation of polysulphides [72, 76, 77, 130, 131] and electrochemical oxidation of sulphides/polysulphides at high anodic overpotentials [132]. It was suggested that no appreciable oxy-sulphur anions were formed under anodic overpotentials of 200 mV [68].

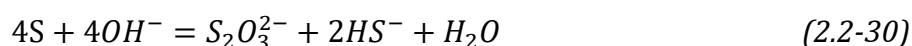
Various studies have shown that aqueous sulphide and polysulphide solutions are very sensitive to air (oxygen), and that polysulphides act as intermediates for the oxidation of sulphides by oxygen [125-129]. According to Steudel et al, for aqueous sodium

polysulphide solutions whose nominal composition is between Na_2S_2 to $\text{Na}_2\text{S}_{4.6}$, in the pH range of 9-13.5 and between 20-40 °C, the oxidation of polysulphides by O_2 happens in accordance to the reaction below [127]:

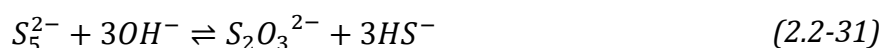


The results was confirmed by Kleinjan et al in the study of aqueous polysulphide solutions at pH 7-12, at temperatures between 20-40 °C and ionic strength between 0.05 – 0.5 mol l⁻¹ [129].

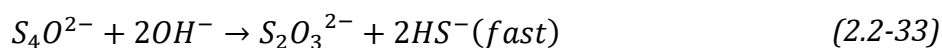
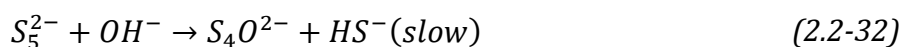
A phase diagram of the S-NaO-H₂O system at 25 °C was established by Arnston et al [130] who suggested that in alkaline aqueous solutions where sulphides are absent elemental sulphur reacts with OH^- to form $\text{S}_2\text{O}_3^{2-}$ and HS^- , according to the following reaction [130]:



Giggenbach extended the study of polysulphide disproportionation in aqueous solutions to a wide range of pH (5-13) and temperatures (up to 240 °C) [72, 131], suggesting that disproportionation of polysulphide ions in aqueous solutions becomes increasingly significant along with the rise in temperature and pH and decrease in sulphide concentration [77]. S_5^{2-} was the main active species which disproportionate according to the reaction below:



A corresponding mechanism for the disproportionation reaction above was also proposed by Giggenbach, as shown in equation 2.2-32 and 2.2-33.



The assumption of Giggenbach was adopted by Licht and Davis, who extended the study of polysulphide disproportionation to more concentrated aqueous polysulphide solutions (i.e. 2 mol kg⁻¹ KOH, 1.4 mol kg⁻¹ K₂S and 2.6 mol kg⁻¹ S) [76]. It was suggested that at up to 85 °C aqueous polysulphide solutions are extremely stable with high concentrations of polysulphides and low concentration of OH^- , and that at room temperatures these aqueous polysulphide solutions should be stable for several years.

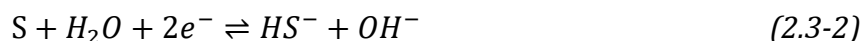
2.3 Electrochemistry of Aqueous Polysulphide Solutions

2.3.1 Aqueous S_x^{2-}/HS^- Redox Reaction

Due to the complex solution composition and lack of knowledge of the reaction mechanism, there has not been a universally agreed description of the aqueous S_x^{2-}/HS^- redox reaction. The most adopted representation of the aqueous S_x^{2-}/HS^- redox reaction is probably that described as equation 2.3-1 [133, 134]:



In aqueous alkaline polysulphide solutions, where sulphide species mainly exist as HS^- owing to the large value of $pK_{a,2}$, reaction 2.3-1 can be rewritten as [135]:



Reaction 2.3-2 is believed to be more appropriate as it was experimentally proven that the equilibrium potentials of an aqueous polysulphide solutions were highly dependent on the pH of the solutions [136].

Allen and Hickling indicated that the equilibrium potential of aqueous sodium polysulphide solution had a Nernstian dependence on the initial concentrations of S and Na_2S , as shown in equation 2.3-3 [132].

$$E = E_0 + \frac{RT}{2F} \ln \frac{[\sum S]}{[Na_2S]^2} \quad (2.3-3)$$

Lessner et al proposed the following expression to represent the aqueous S_x^{2-}/HS^- redox reaction, shown in equation 2.3-4, based on the facts that S_4^{2-} and HS^- are the most abundant polysulphide and sulphide species respectively for alkaline polysulphide solutions with a wide range of compositions [137]:



The equilibrium potential of reaction 2.3-4 can be calculated by:

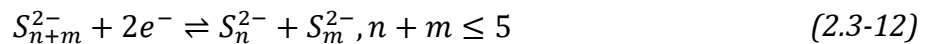
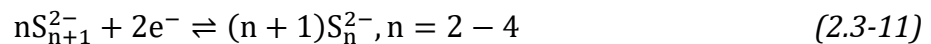
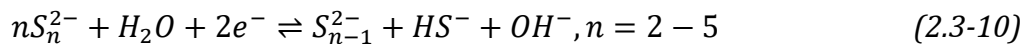
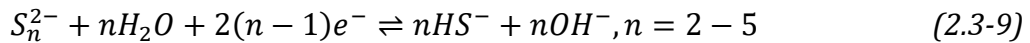
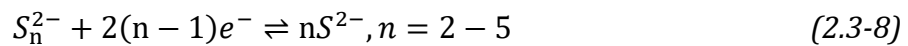
$$E = E^0 - \frac{RT}{6F} \ln \left(\frac{a_{HS^-}^4 a_{OH^-}^4}{a_{S_4^{2-}}} \right) \quad (2.3-5)$$

While activity coefficients of sulphur species are unknown, equation 2.3-6 could be approximated by replacing the activities with concentrations:

$$E = E^0 - \frac{RT}{6F} \ln \left(\frac{C_{HS^-}^4 C_{OH^-}^4}{C_{S_4^{2-}}} \right) \quad (2.3-6)$$

Equation 2.3-6 fits excellently (error < 2%) with the experimental data reported by Teder who measured the equilibrium potentials of aqueous polysulphide solutions over a wide range of compositions and temperatures ($0.1 < S/S^{2-} < 3.0$, $10.6 < \text{pH} < 13.8$, $25^\circ\text{C} < T < 90^\circ\text{C}$). The only exception was the polysulphide solution with $S/S^{2-} = 3$ at 80°C , for which the error was determined to be 6%.

However, there is no evidence suggesting that no other sulphides and polysulphides are involved in the aqueous S_x^{2-}/HS^- redox reaction apart from HS^- and S_4^{2-} . It is generalized below a few hypothetical redox reactions within aqueous polysulphide solutions:



Given their large number it is not possible to present all redox reactions, experimentally proven or hypothetical, within aqueous polysulphide solutions in this study. Table 2.3-1 summarizes those reported previously with their corresponding standard equilibrium potentials.

Table 2.3-1 Reported redox reactions within aqueous polysulphide solutions

Reactions	E ⁰ vs SHE / V	C/M	Reference
$2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828	-	[133, 135, 138]
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightleftharpoons 4\text{OH}^-$	0.401	-	[133, 135, 138]
$\text{S} + \text{H}_2\text{O} + 2\text{e} \rightleftharpoons \text{SH}^- + \text{OH}^-$	-0.478	-	[134]
	-0.476	C	[135, 138]
	-0.520	M	[135]
	-0.51	-	[139]
$\text{S} + 2\text{e} \rightleftharpoons \text{S}^{2-}$	-0.476	M	[133]
	-0.447	C	[135]
	-0.570	C	[138]
	-0.480	C	[140]
$2\text{S} + 2\text{e} \rightleftharpoons \text{S}_2^{2-}$	-0.428	M	[133]
	-0.500	C	[138]
$3\text{S} + 2\text{e} \rightleftharpoons \text{S}_3^{2-}$	-0.390	M	[133]
$4\text{S} + 2\text{e} \rightleftharpoons \text{S}_4^{2-}$	-0.360	M	[133]
$5\text{S} + 2\text{e} \rightleftharpoons \text{S}_5^{2-}$	-0.340	M	[133, 135]
$\text{S}_2^{2-} + 2\text{e} \rightleftharpoons 2\text{S}^{2-}$	-0.483	C	[135]
	-0.524	C	[141]
	-0.640	C	[138]
	-0.480	C	[140]
$2\text{S}_3^{2-} + 2\text{e} \rightleftharpoons 3\text{S}_2^{2-}$	-0.473	C	[135]
	-0.506	M/C	[133, 141]
$3\text{S}_4^{2-} + 2\text{e} \rightleftharpoons 4\text{S}_3^{2-}$	-0.453	C	[135]
	-0.478	M/C	[133, 141]
$4\text{S}_5^{2-} + 2\text{e} \rightleftharpoons 5\text{S}_4^{2-}$	-0.426	C	[135]
	-0.441	M/C	[133, 141]
$\text{S}_3^{2-} + 2\text{e} \rightleftharpoons \text{S}_2^{2-} + \text{S}^{2-}$	-0.490	C	[140]
$\text{S}_4^{2-} + 2\text{e} \rightleftharpoons \text{S}_3^{2-} + \text{S}^{2-}$	-0.520	C	[140]
$\text{S}_2^{2-} + 2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons 2\text{HS}^- + 2\text{OH}^-$	-0.541	C	[135]
	-0.530	C	[141]
	-0.45	C	[138]

$S_3^{2-} + 3H_2O + 4e \rightleftharpoons 3HS^- + 3OH^-$	-0.524	C	[135, 141]
	-0.516	C	[135]
$S_4^{2-} + 4H_2O + 6e \rightleftharpoons 4HS^- + 4OH^-$	-0.520	C	[141]
	-0.510	-	[139]
$S_5^{2-} + 5H_2O + 8e \rightleftharpoons 5HS^- + 5OH^-$	-0.511	C	[135]
	-0.515	C	[141]

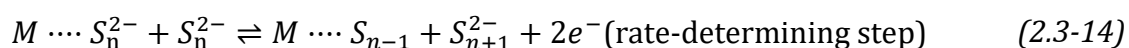
C – calculated, M - measured

2.3.2 Reaction Mechanisms

Due to the complex solution compositions, the reaction mechanism of aqueous S_x^{2-}/HS^- redox reaction has not yet been established [63, 142-159]. A number of mechanisms were proposed by various authors to explain the electrochemical behaviours of aqueous polysulphide solutions with various electrode materials [132].

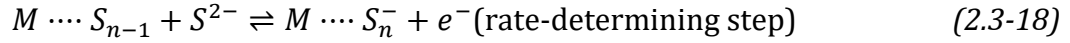
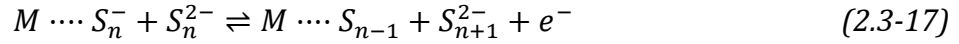
In 1957, Allen and Hickling investigated the electrochemical oxidation of aqueous alkaline polysulphide solutions at a variety of electrodes, including smooth platinum, platinized platinum, gold, tungsten, nickel and graphite [132]. All electrodes showed similar levels of activity except for platinized platinum which was significantly higher than other electrodes. This was explained, according to Allen and Hickling, by that the rate-determine step of the oxidation reaction of aqueous polysulphide solutions for the platinized Pt only involved one electron whereas for all other electrodes investigated two electrons were involved in the rate-determine step. As a result, two mechanisms were proposed for these two cases respectively.

The two-electron mechanism involved an initial absorption of a polysulphide ion on the metal surface followed by a charge transfer reaction (rate-determining step) between the absorbed polysulphide ion and a polysulphide ion in the solution and finished by the absorption of a sulphide ion on the remaining sulphur layer on the metal surface [132]:



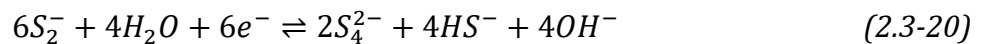


For the one-electron mechanism the initial absorption step and completion step also involves charge transfer:



Allen and Hickling claimed that the kinetics of alkaline polysulphide solution oxidation is independent of electrode material. However, it was suggested by Stephens that the appreciably higher Tafel slope of platinized Pt than the other electrodes indicated that electrode material was related to the reaction mechanism of aqueous S_x^{2-}/HS^- redox reaction [160]. The greater numbers of defects and under-coordinated Pt atoms on the surface of the platinized Pt led to its improved catalytic property compared to smooth Pt.

In 1986, Lessner et al carried out a kinetic study on the aqueous S_x^{2-}/HS^- redox reaction at low overpotentials (-20 to 20 mV) using a potential step technique with Co and Pt electrodes in 1.3 mol l⁻¹ Na₂S_{1.8} solution at pH=12 from 25 to 80 °C [68]. It was found out that S_2^{2-} was the actual kinetically active species since the temperature dependence of the reaction rate coincided with that of S_2^{2-} concentration. A hypothesis for the reaction mechanism was therefore proposed which included two rate-determining steps: a homogeneous dissociation-dimerization reaction between S_4^{2-} and S_2^{2-} occurring rapidly in the thin reaction boundary layer (1-3 μm) at the electrode followed by a heterogeneous charge transfer reaction [68, 161]:



In a later study, Lessner et al extended the kinetic study of the aforesaid aqueous polysulphide solution to a wider overpotential range (-200 to 200 mV) using a slow sweep potentiodynamic polarisation method with Co and Pt rotating disk electrodes (RDEs) [161]. Two more detailed mechanisms were elaborated for reaction 2.3-20:





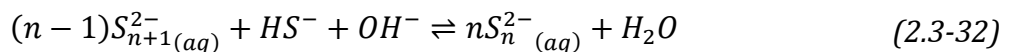
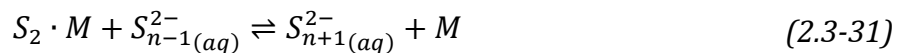
Or alternatively:



For both mechanisms, the initial reduction of S_2^- to S_2^{2-} was the rate-determining step (2.3-21 and 2.3-23), which however could be more complicated involving multistep processes.

For the cathodic reaction, Lessner et al claimed that a second reduction reaction was happening and became increasingly prominent at high current densities where the S_2^- was exhausted. This second reduction reaction could be suppressed by addition of DMF into the polysulphide electrolyte or by an increase in temperature, since both methods resulted in the increase of S_2^- concentration.

However, the exclusion of absorption of electroactive species on the electrode surface in Lessner's model was questioned by Licht [162, 163], who later on proposed a model for the photo-oxidation of polysulphides, considering the adsorptive processes and pH and temperature dependences of the photocurrent response, with S_2^- being the electroactive species, as described below [164]:



Licht claimed that the rate-determining step depended on the band bending of the photoelectrode: at maximum power output where the band bending is intermediate, the overall reaction is limited by the desorption step 2.3-31; at maximum photocurrents, the overall reaction is limited by the absorption step 2.3-29. Concentrations of OH^- and HS^- affected the reaction rate by participating in the equilibrium reaction among polysulphides, as shown in equation 2.3-32. At high pH (>14), where concentration of S_4^{2-} decreases, mass-transport limitation would occur at high photocurrents.

The assumption of S_2^- being the electroactive species during the photo-oxidation of polysulphides by Licht was disagreed by Winnick et al, who suggested that S_2^{2-} was the actual electroactive species in the photo-oxidation of polysulphides in PECs and that the oxidation of S_2^{2-} to S_2^- , which was intrinsically the reverse reaction of 2.3-21 and 2.3-23, was the rate-determining step [165].

Since then, there has been little development in the understanding of the mechanism for aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reaction.

2.3.3 Electrodes for Aqueous $\text{S}_x^{2-}/\text{HS}^-$ Redox Reactions

A variety of electrode materials have been investigated in aqueous polysulphide solutions, such as Pt [46, 63, 64, 68, 132, 144, 154, 155, 161, 166, 167], gold [142, 143, 146-148, 150, 152], glassy carbon [48], graphite [149, 157, 168], activated carbon [44, 158, 169], carbon felt [44], graphite felt [44], lead sulphide [64, 170], cadmium sulphide [171], tungsten monocarbide [167], conducting polymer [172] and transition metals and their sulphides [33, 34, 44, 46, 48, 64, 68, 153, 156, 159, 161, 166, 173-188]. However, the experimental conditions for these studies varied significantly in terms of electrolyte compositions, electrode morphologies and porosities and temperatures, etc. This makes it difficult to compare the activities of various electrode materials towards the electrocatalysis of aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reaction.

Little efforts were made in the past to normalise the activities of electrodes with their true surface area, except for Stephen et al who characterized the polarization performances of three WS_2 based electrodes, namely 2H- WS_2 , ball-milled WS_2 and IF- WS_2 , with the attempt of correlating the catalytic activities of electrodes with their

microstructures [188]. The catalytic activity of the three electrodes were found to be in the following order: IF-WS₂ < 2H-WS₂ < ball-milled WS₂. However, even the one with the highest catalytic activity, namely the ball-milled WS₂, did not provide satisfactory performance as an electrode for aqueous S_x²⁻/HS⁻ redox reaction, with its exchange current density being only ~0.012 mA cm⁻² which was far from the commercialization target of ~0.7 to 1 mA cm⁻².

Studies on aqueous polysulphide electrodes mainly lie in two research areas: PECs and PSBs utilising aqueous polysulphide electrolytes. Thin film and metallic mesh electrodes have been widely used as counter electrodes in PEC applications [64, 114, 167, 171-174, 176, 179-181, 184, 185, 189-200]. However, the low surface areas of these 2D materials often lead to insufficient catalytic activities of such electrodes for RFB applications. Hence, in RFB applications aqueous polysulphide catalysts are often incorporated with high surface area substrates, such as metallic foams [34, 46, 182] and high surface area carbons [16, 33, 34, 43-45, 48, 136, 158, 160, 166, 171, 186, 187, 201-219] to increase the surface areas of certain electrodes.

2.3.3.1 Counter Electrodes Developed for PECs

In 1977, Hodes et al characterized the catalytic activities of a number of Teflon-bonded high surface area carbon electrodes loaded with Pt, Ni or Co electrocatalysts towards aqueous S_x²⁻/HS⁻ redox reaction for the purpose of developing counter electrodes for PECs [166]. As shown in Figure 2.3-1, the catalytic activities of the various electrodes studied are in the sequence of Co/Vulcan > Co/B.H.D. carbon > Ni/B.H.D. carbon > Pt/B.H.D. carbon > B.H.D. carbon. The Co based electrode was found to have better catalytic activity towards aqueous polysulphide reduction and was more stable upon air exposure than the Ni based electrode. Stirring was found to give better current responses especially at higher current densities indicating an increasing role of mass transport control at higher current densities. Hodes et al also indicated that the actual electrocatalysts for Co and Ni based electrodes were their corresponding sulphides, namely CoS and NiS, which were formed upon immersing in sulphide electrolytes.

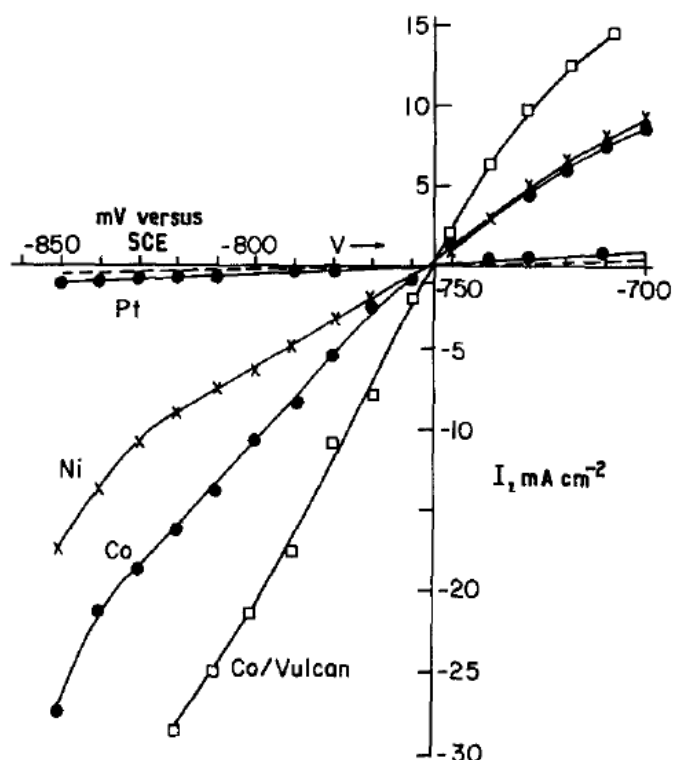


Figure 2.3-1 Polarization curves of various Teflon-bonded high surface area carbon electrodes in 1 mol l⁻¹ Na₂S, S and NaOH electrolyte at 27 °C with Ar atmosphere and no stirring. B.D.H. Carbon was used in each case except for the Co/Vulcan Carbon Black XC-72 electrode [166].

In a subsequent paper in 1980, Hodes et al studied the catalytic activities of a number of metallic mesh based electrodes with Cu₂S, CoS, PbS or RuS₂ electrocatalysts, as well as platinized Pt and high surface area carbon [64]. As shown in Figure 2.3-2, sulphidised brass (95% Cu and 5% Zn) was found to have the best electrocatalytic activity among all electrodes in aqueous polysulphide electrolytes. Increasing the Zn content of the Brass improved the stability of brass electrodes however at the expense of reduced catalytic activity. CoS/stainless steel mesh, PbS/stainless steel mesh and sulphidised Brass (70% Cu and 30% Zn) electrodes exhibited similar catalytic activities. RuS₂ was speculated to have similar catalytic activity to other metal sulphides. The lower catalytic activity of a RuS₂/stainless steel mesh electrode compared to other electrodes was attributed to the thinner RuS₂ catalyst layer. CoS/stainless steel mesh electrode was found to have the best electrochemical stability whereas PbS/stainless steel electrodes was the least stable among all the electrodes tested.

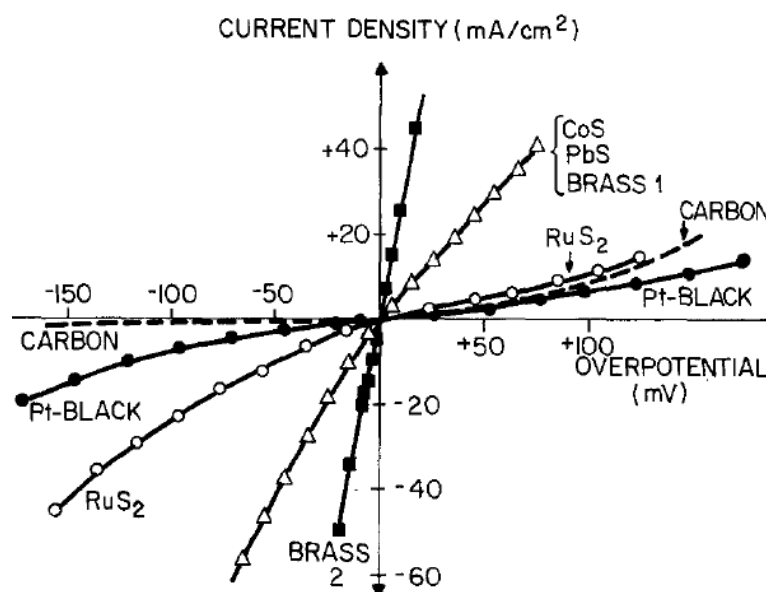


Figure 2.3-2 Polarization curves of various electrodes in 1 mol l⁻¹ Na₂S, S and KOH at 30 °C with Ar atmosphere and no stirring [64].

Cu₂S based electrodes were suggested by Hodes et al as suitable for relatively short-term experiments and were adopted by Licht et al in the study of the cation effect on the performance of PECs [220, 221]. The type of cation was shown to affect the equilibrium potential, cation activity, solution conductivity, and polarization losses of aqueous polysulphide solutions. Licht et al found out that with the increase of the atomic number of alkali metals, the equilibrium potentials of the polysulphide solution containing 1 mol l⁻¹ S, S²⁻ and OH⁻ decreased with a CdSe electrode. Using a brass-derived Cu₂S electrode, it was found out that the polarization losses of the same polysulphide electrolyte was reduced due to an overall effect of decreased cation activity and solution conductivity.

In 1987, Licht et al investigated a CoS/Brass foil thin film electrode as the counter electrode for PECs [114, 189, 190]. The thin film CoS/brass electrode was prepared by electroplating Co onto brass foil followed by alternating anodic and cathodic treatments in polysulfide solution. This method produced highly reproducible and durable electrodes which were not sensitive to air exposure, however the catalytic activity of this thin film CoS/brass electrodes was lower than previously reported CoS/stainless steel mesh electrode [64].

In 1992, Lessner et al prepared and assessed the catalytic activities of two mesh-type electrodes, namely Co/Ni mesh electrode and MoS₂/Mo mesh electrode, whose electrocatalytic performances are shown in Table 2.3-2 [181]. Both Co/Ni mesh and MoS₂/Mo mesh electrodes produced a current density of 10-20 mA cm⁻² at less than 50 mV overpotential. While varying the flow rate had only a small effect on the polarization behaviours of the two electrodes, increasing temperature and adding DMF to the electrolyte had positive effects on the catalytic activities of the electrodes.

Table 2.3-2 Current densities of Co/Ni mesh and MoS₂/Mo mesh electrodes at -50 mV overpotential [181]

Temperature / °C	2-Co/Ni mesh (no DMF) / mA cm ⁻²	2-MoS ₂ /Mo mesh (no DMF) / mA cm ⁻²	2-MoS ₂ /Mo mesh (13 mol% DMF) / mA cm ⁻²
25	-1.2	-0.8	-2.4
46	-5.0	-3.2	-14.6
65	-17	-9.2	-28.6
79	-	-20.5	-39

Recent studies of QDDSCs often adopt fluorine doped tin oxide (FTO) glass-based thin film counter electrodes. Apart from the transition metal sulphides [173, 174, 176, 179, 180, 184, 185, 191-200], PbS [200], CdS [171], WC [167] and conducting polymers [172] have also been demonstrated as catalysts for aqueous S_x²⁻/HS⁻ redox reactions.

Faber et al reported a series of pyrite-phase transition metal disulphides and their alloys as electrocatalysts for HER and polysulphide reduction reaction, including FeS₂, CoS₂, NiS₂ [173, 174, 176]. As shown in Figure 2.3-3, NiS₂ showed the best catalytic activity towards S_x²⁻/HS⁻ redox reaction among FeS₂, CoS₂ and NiS₂. PyS₂, where Py refers to permalloy which mostly consists of Ni and Fe, had shown improved catalytic activity compared to the single-metal pyrites likely due to the increased active sites introduced by the structure disorder of alloying different metals.

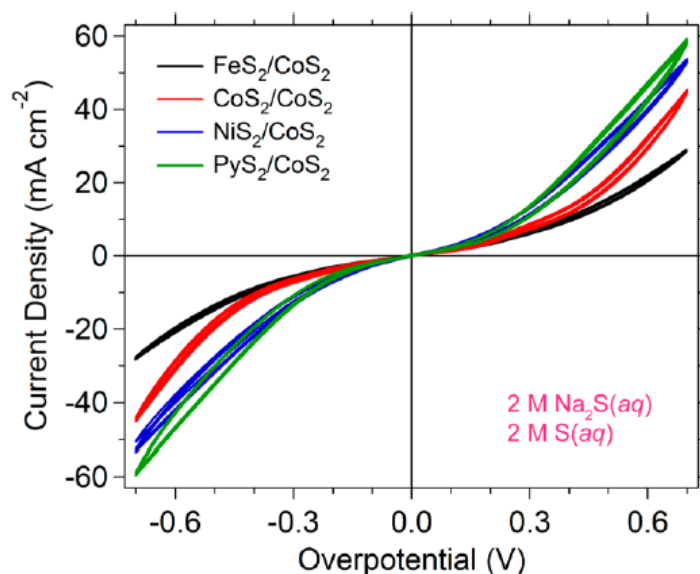


Figure 2.3-3 Polarization tests of pyrite-phase FeS_2 , CoS_2 , NiS_2 and PyS_2 thin film electrodes towards the aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reaction [174].

Kim and co-workers demonstrated two types of thin film electrodes for QDSSCs, namely a NiS thin film electrode prepared by hydrothermal deposition [184, 185] and a Mn-doped PbS thin film electrode prepared by successive ionic layer adsorption and reaction (SILAR) method [200]. NiS thin film electrodes lead to significantly improved power conversion efficiency for QDSSCs compared to Pt counter electrode. The improved catalytic activity of NiS thin film electrode compared to Pt electrode was also shown by EIS and polarization measurements of symmetrical PECs. The sulphur content in the NiS catalyst layer of the thin film electrodes, affected by hydrothermal deposition conditions such as pH of the solution, reactants concentrations, temperature and deposition time, was shown to have large effects on the photovoltaic performance of the QDSSCs. PbS and Mn-doped PbS electrodes also showed remarkable improvements in the performance of QDSSCs compared to a Pt electrode. In addition, Mn-doped PbS electrodes showed a $\sim 40\%$ higher power conversion efficiency compared to an unmodified PbS electrode for the CdS/CdSe QDSSC.

CdS nanomaterials were synthesized and loaded onto carbon cloth as electrodes for aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reaction by Li et al [171]. All CdS/carbon cloth electrodes showed better anodic catalytic performances than their cathodic catalytic performances, with single-phase CdS nanorods synthesized from CdCl_2 showing the best catalytic activity. At

the overpotential of 200 mV, a CdS nanorod/carbon cloth electrode achieved an anodic current density of 65 mA cm⁻² in a 2 mol l⁻¹ Na₂S_n/1.5 mol l⁻¹ KBr solution at 35 °C.

WC together with Pt was demonstrated as foil electrodes by Esposito et al in a concentrated aqueous polysulphide electrolyte [167]. X-ray photoelectron spectroscopy (XPS) measurement indicated that WC was stable in aqueous polysulphide electrolyte, with negligible formation of tungsten sulphides. The WC foil electrode also showed double the catalytic activity towards polysulphide reduction compared to a Pt foil electrode.

Poly(3,4-ethylenedioxythiophene) (PEDOT) was tested as the catalyst for aqueous S_x²⁻/HS⁻ redox reaction and loaded onto TiO₂ film as the counter electrode of QDSSCs [172]. TiO₂-PEDOT composite electrode showed better catalytic activity than bare PEDOT electrode, with a 20% higher power conversion efficiency gained during the demonstrations in QDSSC.

2.3.3.2 Anodes Developed for the Regenesys PSB System

In 1983, Remick and Camara assessed the electrocatalytic activity of a few sulphide wire electrodes including NiS, CoS and MoS₂, as well as a Pt wire electrode [136]. Experiments showed that MoS₂ was the preferred electrocatalyst for aqueous S_x²⁻/HS⁻ redox reaction, and a Teflon bonded MoS₂/Vulcan XC-72R carbon black composite electrode was prepared and characterized [136].

Remick and Ang patented the first RFB system in 1984 utilising aqueous polysulphide electrolyte coupled with a Cl₂/Cl⁻, Br₂/Br⁻ or I₃/I⁻ redox couple on the positive side. A number of transition metal sulphides including NiS, Ni₃S₂, CoS, PbS and CuS were suggested as electrocatalysts for aqueous S_x²⁻/HS⁻ redox reaction by Remick and Ang, who also emphasized the superiority of sulphidised nickel and cobalt over the other electrodes [43].

The PSB technology was then extensively developed by Regenesys Technologies Ltd. in the 1990s and 2000s in the UK. The Regenesys PSB system utilised mostly carbon-based electrodes [16, 158, 160, 201-211].

As early as 1994, Zito had patented a type of activated carbon-based composite electrode for application in aqueous polysulphide electrolyte based RFBs [201-204]. This activated carbon-based composite electrode was manufactured by hot pressing activated carbon powders onto a conductive substrate. The substrate was made by hot pressing a mixture of graphite flakes and plastic binders. Zito also described another method of embedding activated carbon on the conductive substrate [202]. A chemically resistant polymeric binder with a weight fraction of 15-20% was mixed with the activated carbon before being hot pressed onto the substrate. This method was widely adopted afterwards by other researchers from Regenesys Technologies Ltd in the development of negative electrodes for the PSB.

Calver et al further developed the aforesaid method in 1999 [205]. A variety of methods and raw materials were described for the preparation of activated carbon. Three polymeric binders, including polyethylene (PE), polypropylene (PP) and polyvinylidene fluoride (PVDF), were suggested to embed activated carbon onto the electrode core. Demonstration of such electrodes showed a 40 mV overpotential at the current density of -40 mA cm^{-2} with an electrode thickness of 3 mm in $1 \text{ mol l}^{-1} \text{ Na}_2\text{S}_4$ electrolyte. Further increase in the electrode thickness showed a negative effect on its catalytic performance. A nickel surfaced electrode was also characterized which showed much worse catalytic activities compared to activated carbon-based electrodes with the thickness over 2 mm.

In 2000, Clark et al patented a type of reticulated vitrified carbon with Cu, Sn, Zn, Pb, Ni and Fe based electrocatalysts [206]. However, no electrochemical performances of such electrodes in aqueous polysulphide electrolytes were presented in the patent.

In 2000, Cooley et al described a novel method of operating a redox flow cell by dispersing an amount of catalysts into the electrolytes [207]. The catalysts suggested included sulphides of Cu, Ni, Mo, Fe and Co. As an example, a CuS suspension was introduced to aqueous polysulphide electrolytes by adding precipitated copper powder or copper sulphate solution into the polysulphide electrolyte. With a rotating disk Pt electrode and a $1 \text{ mol l}^{-1} \text{ Na}_2\text{S}_3$ electrolyte, the total overpotential at current densities between 5-60 mA cm^{-2} was found to be significantly less in the electrolyte with CuSO_4 than in the electrolyte without CuSO_4 . At the current density of 20 mA cm^{-2} a total overpotential of 60 mV was achieved. For a single-cell PSB system with carbon composite electrodes on both sides,

the voltage efficiency of the PSB system increased remarkably with a CuS suspension in the electrolyte.

In 2000, Cranstone et al reported a process for preparing reticulated copper sulphide and/or nickel sulphide electrodes for the application of catalysing a number of redox reactions including aqueous S_x^{2-}/HS^- redox reactions [208]. Active materials included CoS, Cu_2S , PbSe, RuS_2 , MoS_2 , NiTe, Cu_2Se , Ni_3S_2 and CuS, with the latter two recommended. The reticulated metal sulphide electrodes were prepared by hot isostatic pressing a mixture of the active material and a salt followed by dissolving the salt in solvent. As an example, a reticulated CuS electrode was prepared (70% CuS and 30% NaCl in weight) and glued onto a brass backed graphite-PVDF composite electrode core and demonstrated in a single-cell PSB with 1 mol l^{-1} Na_2S_4 anolyte and 5 mol l^{-1} NaBr/ 1 mol Br_2 catholyte. The positive electrode utilised the same brass backed graphite-PVDF composite electrode without reticulated CuS catalyst. When operated at a current density of 40 mA cm^{-2} , the overpotential of the PSB was 100 mV for charging and 30 mV for discharging using a negative electrode with reticulated CuS catalyst and 400-600 mV for charging and 300 mV for discharging using a negative electrode without reticulated CuS catalyst. The mechanical stability of this reticulated CuS electrode was maintained over several hundred cycles.

In 2001, Morrissey presented a PSB system comprised of PE impregnated activated carbon electrode, Nafion® 115 CEM, 1.3 mol l^{-1} Na_2S_5 / 1 mol l^{-1} NaBr anolyte and 5 mol l^{-1} NaBr catholyte. The PSB system was cycled at the current density of 60 mA cm^{-2} with charging and discharging process of each cycle both lasting for 1.5 hr, from which an average cell efficiency of ~56% was achieved over 45 cycles [209].

In 2003, Fletcher and Van reported a number of transition metal organic complexes as catalysts for the aqueous S_x^{2-}/HS^- redox reaction [210]. Preferred transition metals include Mn, Fe, Co, Ni and Cu, where Co was preferred. Cobalt(II) phthalocyanine, cobalt(II) Bis(salicylaldehyde) or their mixtures were particularly preferred. Electrode substrates could be metals, activated carbon or other conducting materials. Catalytic performances of such electrodes were tested in a three-electrode cell with 1 mol l^{-1} $Na_2S_{3.4}$ / 1 mol l^{-1} NaBr electrolyte at $25\text{ }^\circ\text{C}$ using CV measurements. For all screen-printed electrodes with 4 wt% catalyst loading, Cobalt (II) Bis(salicylaldehyde) exhibited the best

catalytic activity with an overpotential of -144 mV at the current density of 2.25 mA cm⁻².

In 1999, Szanto reported a single-cell PSB system utilising activated carbon/polyolefin pressed electrodes with a Nafion® 115 CEM, a 5 mol l⁻¹ NaBr anolyte and a 1.2 mol l⁻¹ Na₂S catholyte [16]. The PSB system was cycled at a current density of 40 mA cm⁻² for 30 min charging and discharging cycles, and an energy efficiency of ~60% was achieved [160].

In 2007, Ponce-de-León et al reported an activated carbon based composite electrode for PSB applications [211]. The composite electrode was manufactured by mixing activated carbon with PVDF and then hot-pressed onto a carbon substrate made from graphite particles and high-density polyethylene (HDPE).

In 2009, Scamman reported the results of a pilot-scale demonstration of a Regenesys PSB system utilising the aforesaid composite electrode with a thickness of ~5.5 mm [222]. The stack of the PSB system consisted of 200 unit-cells constructed in a bipolar fashion. The membrane used was a 0.2 mm thick Nafion® 117 CEM. The initial anolyte was a 1 mol l⁻¹ Na₂S_{4.8} solution and the initial catholyte was a 4.5 mol l⁻¹ NaBr solution. The PSB was charged at 400 mA cm⁻² for 110 min and discharged at 600 mA cm⁻² for 65 min. Over 17 cycles, an energy efficiency of ~ 62% was achieved [160].

In 2008, Radford et al characterized a variety of activated carbon in aqueous polysulphide electrolyte with a specially designed flow-through packed bed cell [158]. Polarization tests clearly indicated that activated carbon performed significantly better than graphite in catalysing aqueous S_x²⁻/HS⁻ redox reaction, due to the high surface area. Comparison among various activated carbon materials suggested that electrochemical reactions mainly happened in meso/macropores (mesopores: pore size in the range of 2-50 nm; macropores: pore size > 50 nm).

2.3.3.3 Anodes Developed for PSB Systems at DICP

Researchers from the Dalian Institute of Chemical Physics, China (DICP) have developed a number of Ni foam and carbon/graphite felt based electrodes for application in PSBs [33, 34, 44, 45, 212-219].

Ge et al prepared a number of polyacrylonitrile (PAN)-based graphite felt electrodes with various catalyst loadings. Pt loaded graphite felt electrodes showed little difference compared to bare graphite felt electrode in terms of PSB performance, indicating that Pt is a poor aqueous polysulphide electrocatalyst [212]. Sulphidised Ni, Co, Mo and their alloys were incorporated with carbon black as catalysts for graphite felt based electrodes. The composite catalysts were prepared by impregnation of carbon black powders with catalyst precursors followed by H₂ reduction at elevated temperature and a final sulphidisation process in aqueous polysulphide solutions. Catalytic activities of the various composite electrodes were found in the order of Ni-Co/C > Ni-Mo/C > Ni/C > Mo/C [213]. Among all electrodes, the Ni-Co/C electrode showed the best catalytic activity, and Co seemed to stabilize the catalysts in aqueous polysulphide electrolytes. Whereas, electrodes with Mo and Ni-Mo catalysts had observed obvious catalyst fall-off issues, likely due to the formation of layer-structured MoS₂. XRD measurements detected a variety of nickel sulphides in the sulphidised Ni/C electrode, including NiS, NiS₂ and NiS_x (x≥3) [45, 213]. Ge et al suggested that Ni and NiS_x might undergo mutual transformations during the redox reactions in aqueous polysulphide electrolytes.

Ge et al also demonstrated a Ni foam anode in PSB, together with a Pt/graphite felt cathode a maximum power density of 450 mW cm⁻² was achieved at the current density of 500 mA cm⁻² [215].

Zhao, who is the co-worker of Ge at DICP, further developed Ni foam-based electrodes for PSB applications [34, 216-218]. In 2004, Zhao et al demonstrated a Ni-Co alloy coated Ni foam negative electrode in a single cell PSB. With a PAN-based graphite felt positive electrode, a coulombic efficiency of 96.1% and an energy efficiency of 69.4% were achieved at the current density of 30 mA cm⁻² [216].

In a subsequent study, Zhao et al reported a single cell PSB system using carbon felt positive electrode and sulphidised Ni foam negative electrode, whose performance improved remarkably compared to the previous system [34]. The improvement of PSB performance is largely attributed to the sulphidisation treatment of the Ni foam electrode which lead to the formation of NiS_x on the electrode surface. According to the energy-dispersive X-ray spectroscopy (EDX) analysis, the sulphur content on the surface of Ni foam increased from 0.02 wt.% to 16.88 wt.% compared to untreated Ni foam. Over 48 cycles, the single cell PSB exhibited a power density of 56 mW cm⁻² and an averaged

energy efficiency of 77.2% at the current density of 40 mA cm⁻². Half-cell measurements showed that, at the current density of 50 mA cm⁻², the overpotentials of sulphidised Ni foam for charging and discharging the PSB was only -27 and 15 mV respectively.

In 2005, Zhao et al coated the Ni foam with Co and Ni-Co alloy and used as the negative electrodes of PSB, where bare Ni foam showed the best catalytic activity and Co-coated Ni foam showed the worst catalytic activity among all three electrodes [218].

In the meantime, Zhao et al also demonstrated Ni and Co loaded carbon felts as the negative electrodes for PSB. At the current density of 30 mA cm⁻², Ni foam, Ni/carbon felt and Co/carbon felt electrodes had all enabled an energy efficiency of ~80% for the PSB [217]. In the same paper, Zhao et al also reported the polarization tests of Fe, Co, Ni, Pb and graphite in a 1.3 mol l⁻¹ Na₂S₄ electrolyte with a three-electrode cell setup, as shown in Figure 2.3-4. Exchange current densities of the aforesaid electrode materials were extrapolated from the Tafel plots of the polarization test, as summarized in Table 2.3-3. Ni, Co and Pb showed significantly better catalytic activities towards aqueous S_x²⁻/HS⁻ redox reaction compared to graphite and iron.

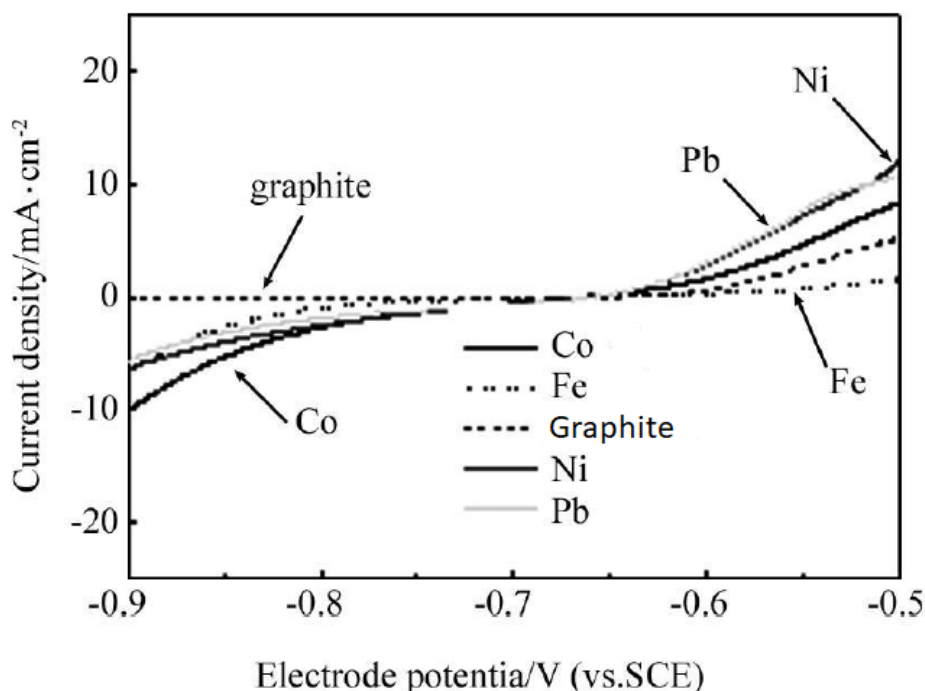


Figure 2.3-4 Steady-state polarization of Fe, Co, Ni, Pb, Graphite (ϕ 6 disk) in a 1.3 mol l⁻¹ Na₂S₄ electrolyte at 25 °C and a scan rate of 1 mV s⁻¹ [217].

Table 2.3-3 Exchange current density of different electrode materials in a 1.3 mol l⁻¹ Na₂S₄ electrolyte at 25 °C

Material	graphite	Fe	Co	Pb	Ni
Exchange current density / $\mu\text{A cm}^{-2}$	31.5	54.7	236	290	297

Zhou, who is the co-worker of Ge and Zhao at DICP, investigated into the catalytic activities of various porous carbon materials with/without catalyst loading towards the aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reaction [33, 44, 219]. Activated carbon/XC-72 carbon black/PVDF composite electrodes were prepared by hot isostatic pressing with various compositions and tested in a single cell PSB [219]. It showed that the performance of these carbon-based electrodes depended largely on its composition, particle size of activated carbon and weight portion of the pore precursor. The weight ratio of carbon black and activated carbon has an optimised value under the same amount of binder. At 80 °C, a maximum power density of 140 mW cm⁻² was achieved at the current density of 120 mA cm⁻² for a single cell PSB using the aforesaid carbon electrode for both positive and negative electrodes.

In 2006, Zhou et al prepared a Co-coated carbon felt electrode by electroless plating and demonstrated this Co/carbon felt electrode as the negative electrode for a single-cell PSB at room temperature [33]. At 40 mA cm⁻² the Co/carbon felt electrode exhibited an overpotential of -22 mV. With a carbon felt positive electrode, an energy efficiency of 83.4% was achieved for the single-cell PSB.

In another paper, Zhou et al assessed the catalytic activities of carbon felt and activated carbon-based electrodes with/without catalyst coating [44]. Figure 2.3-4 shows the polarization curves of different negative electrodes in a single-cell PSB. Activated carbon electrodes were found to suffer from sulphur deposition issues over the cycling of the PSB. Carbon and graphite felt electrodes, despite the low surface areas compared to activated carbon electrode, had shown similar polarization performances. With a catalyst coating, carbon and graphite felt electrodes provided even better cathodic polarization performances. With a Co/graphite felt negative electrode and a graphite felt positive electrode, the single-cell PSB achieved an average coulombic efficiency of 96.1%, voltage efficiency of 84.3% and energy efficiency of 81% at the current density of 40 mA cm⁻².

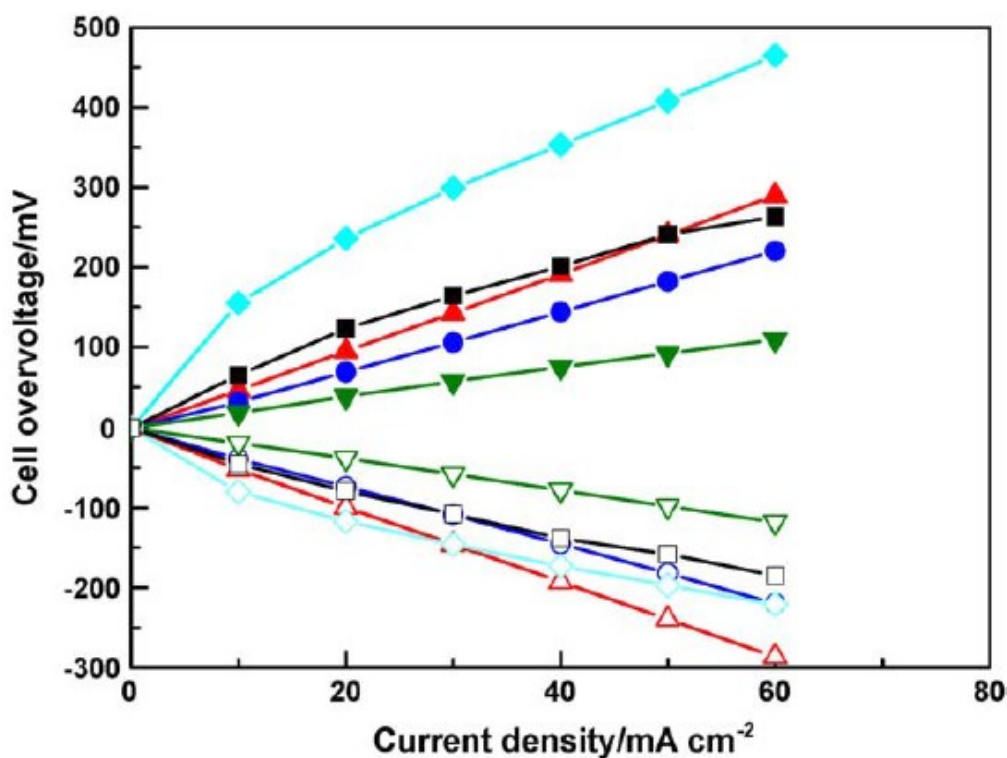


Figure 2.3-5 Polarization curves of different negative electrodes in PSB: ($\blacklozenge, \blacklozenge$) graphite felt; ($\blacksquare, \square$) carbon felt; ($\blacktriangle, \triangle$) activated carbon; ($\bullet, \circ$) Co-activated carbon; ($\blacktriangledown, \triangledown$) Co-graphite felt [44].

2.3.4 Electrochemical Characterization of Polysulphide Electrodes

A number of electroanalytical techniques can be used in the study of electrode processes, such as CV, LSV, chronoamperometry, chronopotentiometry and EIS. The later three have been introduced in detail in Section 2.1.4. This section mainly discusses CV and LSV methods.

2.3.4.1 CV

CV, which measures the current against a repetitively cycled range of electrode potentials, is often used to determine the reduction potential and reversibility of redox reactions [55]. Although it is a potential dynamic method rather than a potentiostatic method, the instantaneous current density corresponding to a certain overpotential as shown in a

voltammogram gives a relative comparison of the catalytic performance of different electrodes.

2.3.4.2 LSV

Slow scan linear scan voltammetry is often used to simulate a pseudo-steady state polarization condition, which greatly reduces the experimental time for the polarization test of an electrode compared to chronoamperometry or chronopotentiometry methods. The scan rates adopted, however, should be sufficiently slow, for example 1 mV s^{-1} , to achieve a satisfactory approximation of steady state polarization conditions.

2.3.4.3 Tafel Plot and Exchange Current Density

For a charge transfer controlled electrode reaction, by plotting the logarithm of the current against the corresponding overpotentials of the electrode, which is called a Tafel plot, the exchange current density (i_0) of a given redox reaction at a specific electrode in a specific electrolyte can be extrapolated. The exchange current density is directly proportional to the standard rate constant (k^0) which is an intrinsic parameter indicating the reaction rate between a particular reactant and a particular electrode material. The exchange current density can be used to compare the electrocatalytic activities of different electrode materials in a given electrolyte. However, it is worth noting that the surface area of the electrode, the reactant concentration and the electrode material all play an important role in the overall performance of a given electrode reaction [223].

2.4 Conclusions

Aqueous polysulphide electrolyte has been highly attractive in the applications of RFBs, due to its high energy density and low cost. However, the composition of aqueous polysulphide solutions is highly complex, where multiple electroactive species co-exist in chemical equilibria. This also makes it highly challenging to understand the aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reactions.

A computer-based iterative method was presented in the 1980s to calculate the equilibrium concentrations of the ionic species within aqueous polysulphide solutions, based on the various equilibrium constants among sulphides and polysulphides. However, due to the unknown of the activity coefficients of various sulphide and polysulphide species, the numerical model could only be approximated by assuming an activity coefficient of 1 for all sulphide and polysulphide species. Nevertheless, the numerical model remains a valuable way to approximate the equilibrium compositions of aqueous polysulphide solutions.

A large number of aqueous S_x^{2-}/HS^- redox reactions have been reported in previous studies. It is believed useful to summarize these reactions and re-evaluate their potentials according to the equilibrium ionic concentrations derived from the numerical modelling, to facilitate the interpretation of aqueous S_x^{2-}/HS^- redox reactions.

The reaction mechanism of aqueous S_x^{2-}/HS^- redox reactions have not yet been clearly understood. Although several mechanisms have been proposed by certain authors, based on the electrochemical measurements using a variety of electrode materials, electrolytes and potential ranges.

A variety of electrode materials have been characterized in aqueous sulphide/polysulphide electrolytes, such as noble metals, carbon materials, transition metals and their sulphides, among which the transition metal sulphides had exhibited the best catalytic performances towards aqueous S_x^{2-}/HS^- redox reactions, for instance, Cu_2S , NiS , CoS , MoS_2 . Nickel sulphides and cobalt sulphide have been the most widely used in the applications of RFBs utilising the aqueous S_x^{2-}/HS^- redox couple in the past.

It was decided to investigate into nickel and its sulphides as the electrocatalysts for aqueous S_x^{2-}/HS^- redox reaction in this study, based on the following three reasons: (i) much cheaper price of nickel (\$5.31/lb) compared to cobalt ((\$16.33/lb), (ii) readily available Ni foam as a high surface area 3D electrode, and (iii) the numerous methods available to prepare Ni-based 3D electrodes.

It was considered beneficial to study the aqueous S_x^{2-}/HS^- redox reactions under nickel electrode by CV measurements, since the reaction mechanism of aqueous S_x^{2-}/HS^- redox reactions is unclear. An inert electrode namely glassy carbon was also characterized, as a comparison.

NiS_x catalysts were embedded onto the carbon paper substrate with different methods to prepare high surface area 3D electrodes, whose catalytic performances were characterized by polarization tests in the aqueous polysulphide electrolyte. The best-performed electrode was then demonstrated in the polysulphide-air RFB.

Chapter 3 Experimental Methods

3.1 Experimental Setups

3.1.1 Three-electrode Cell

A three-electrode cell setup is used in this study to investigate the electrochemical behaviours and catalytic activities of various electrode materials in aqueous polysulphide electrolytes. The three-electrode cell mainly comprises of a ϕ 5 mm disk or 3 cm² rectangular sheet working electrode (WE), a saturated Ag|AgCl RE with salt bridge (Metrohm) and a platinum counter electrode (CE), as shown in Figure 3.1-1.

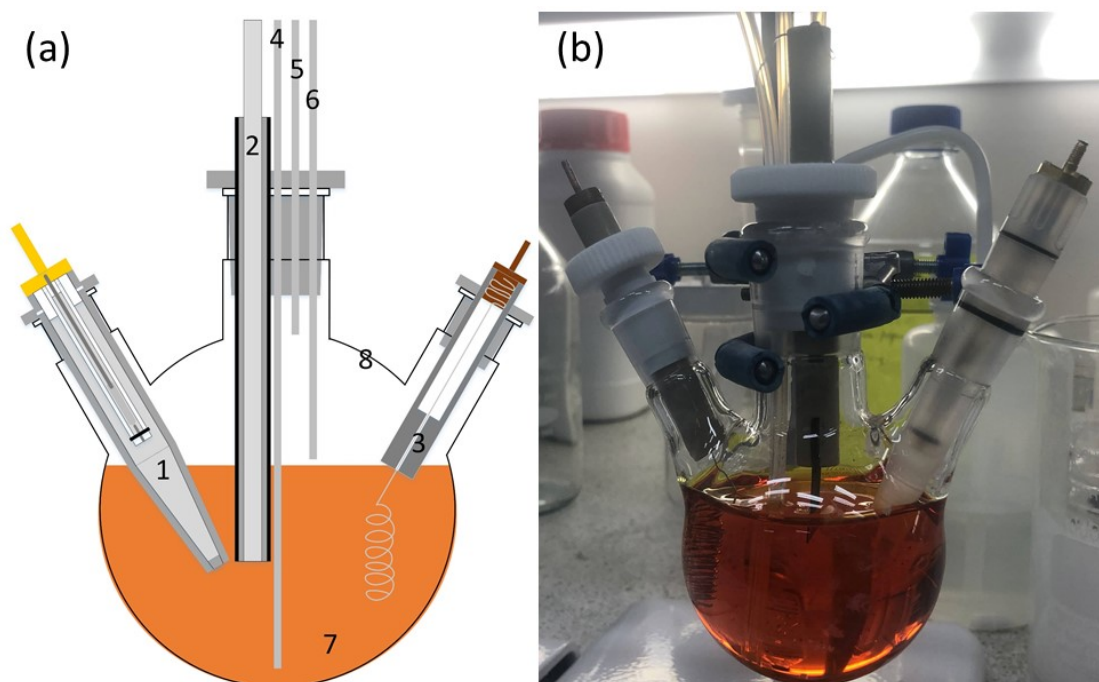


Figure 3.1-1 (a) Schematic view: (1) Ag|AgCl_(sat) RE, (2) WE, (3) Pt CE, (4, 6) gas inlets, (5) gas outlet, (7) electrolyte, (8) three-neck flask; and (b) laboratory setup of the three-electrode cell

Platinum CE is made from a strip of ϕ 0.5 mm platinum wire (99.99%, Advent Research Materials). The platinum wire is polished with P2500 silicon carbide abrasive paper and then rolled into a ϕ 5 mm coil. The Pt coil is then immersed in concentrated nitric acid for 10 min to remove surface impurities. Finally, it is rinsed with sufficient deionized water and absolute ethanol in turn and air dried before use.

The three-electrode cell has two gas inlets (one above the electrolyte surface and the other one deep inside the electrolyte) and one gas outlet to purge the electrolyte compartment with $N_{2(g)}$ for an oxygen-free experimental environment.

Three electrolytes had been investigated in the three-electrode cell experiments in this study, including the 1 mol kg⁻¹ NaOH electrolyte, the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte and the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte. Preparation of these three electrolytes are discussed in Section 3.2.

3.1.2 Single-cell Polysulphide-air RFB

A 5 cm² single-cell polysulphide/air RFB system is designed and set up in laboratory to demonstrate the performance of a variety of aqueous polysulphide electrodes, as shown in figure 3.1-2. The single-cell reactor consists of two aluminium end plates (1, 16), two PVC body plates (2, 15), two graphite flow channel plates (4, 13), a Nafion® 117 CEM (7), (9) a number of ethylenetetrafluoroethylene (ETFE)/ polyetheretherketone (PEEK) meshes, a Fumapem® FAA-3-PK-75 AEM (10), a sulphidised Ni foam negative electrode (6), a C/MnO_x/gold-plated Ni mesh positive electrode (11) and several ethylenepropylenedienemonomer (EPDM) gaskets (3, 5, 8, 12, 14), as listed in Table 3.1-1.

Aluminium end plates, PVC body plates and graphite flow channel plates were designed in SolidWorks and manufactured by CNC machine. EPDM gaskets were prepared by laser cutting from the bulk sheet. The air electrode was directly purchased from Gaskatel GmbH and cut into 5 cm² squares with a scalpel. Membranes pre-treatments are discussed in Section 3.3. All components except for the electrodes and membranes were cleaned with deionized water and absolute ethanol before assembly.

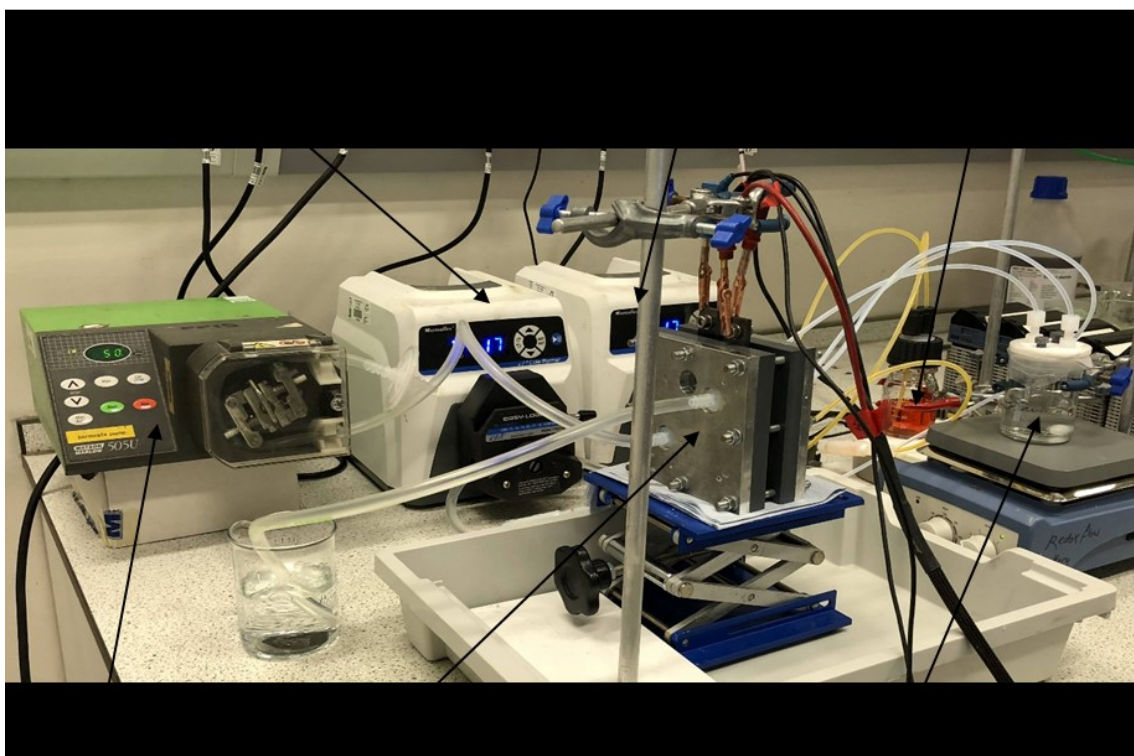
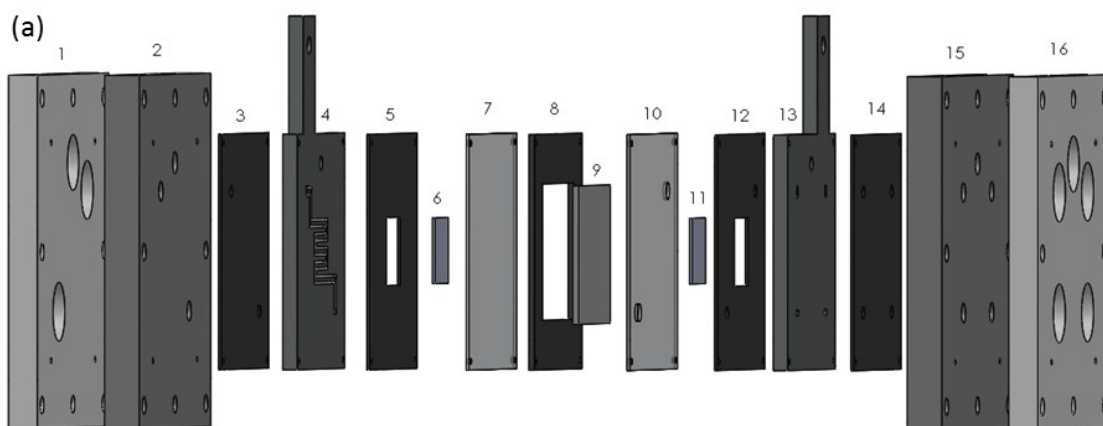


Figure 3.1-2 (a) Exploded view of the single cell design: (1, 16) end plates, (2, 15) body plates, (4, 13) flow channel plates, (7) CEM, (9) mesh flow channels (10) AEM, (6) negative electrode, (11) positive electrode and (3, 5, 8, 12, 14) gaskets; and (b) laboratory setup of the 5 cm² single-cell polysulphide/air RFB

Table 3.1-1 List of components for the polysulphide/air RFB single cell

Components	Specifications	Supplier
Cathode	C/MnO _x /gold-plated Ni mesh	Gaskatel GmbH
	C/MnO _x /gold-plated Ni mesh	
Anode	Sulphidised 0.9 mm thick Ni foam	GoodFellow
CEM	Nafion® 117	Fuel Cell Store
AEM	Fumapem® FAA-3-PK-75	Fumatech GmbH
Hg HgO RE	XR400	Radiometer Analytical
Flow channel plate	PPG 86 (Polypropylene)	SGL GROUP
Body plate	PVC	RS Components
End plate	Aluminium	RS Components
Gasket	EPDM	-
Mesh flow channels	ETFE/PEEK	GoodFellow

The single-cell polysulphide/air RFB uses a 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH solution as the anolyte, a 1 mol kg⁻¹ NaOH solution as the intermediate electrolyte and air catholyte. The flow rates of the electrolytes are summarized in Table 3.1-2. Preparation of the anolyte and the intermediate electrolyte are discussed in Section 3.2, and the catholyte(air) is pumped directly from the atmosphere.

Table 3.1-2 Compositions and flow rates of the electrolytes used in the single-cell polysulphide/air RFB tests

Electrolyte	Composition	Flow rate / ml min⁻¹
Anolyte	1 mol kg ⁻¹ Na ₂ S ₂ /1 mol kg ⁻¹ NaOH	50
Catholyte	air	100
Intermediate electrolyte	1 mol kg ⁻¹ NaOH	50

Table 3.1-3 lists the components of the auxiliary electrolyte pumping system. The catholyte (air) was pumped by a Waston-Marlow 505 U permeate pump. A PTFE filter

was attached to the air inlet in order to remove the impurities (i.e. dust) from the air before being pumped into the cathode compartment. Aqueous electrolytes, including the intermediate electrolyte and the anolyte, were pumped by MasterFlex® L/S® series peristaltic pumps provided by Cole-Parmer. Tubing and adapters were made from PTFE, perfluoroalkoxy alkanes (PFA) or Tygon® which all have good chemical resistances towards alkaline solutions. A stack of ETFE/PEEK meshes were used as the flow channels for the intermediate electrolyte. This also provided mechanical support for the CEM and AEM attached to it, preventing the two membranes from being compressed into the middle chamber of the cell during the assembly and operation. The laboratory setup of the single-cell polysulphide/air RFB system is shown in figure 3.1-2 (b).

Table 3.1-3 List of components for the electrolyte pumping system

Equipment	Model	Manufacture
Permeate pump	505U	Waston-Marlow
MasterFlex® L/S® series Precision Pump Drives	07528- 10	Cole - Parmer
Easy Load® II pump head	77200-60	Cole - Parmer
L/S® Tubing	#17	Cole - Parmer
PTFE Tubing	-	Cole - Parmer
PFA Adapters	-	Cole – Parmer

3.2 Preparation of Electrolytes

3.2.1 Sodium hydroxide solution

The stock sodium hydroxide solution with a concentration of 1 mol kg⁻¹ was prepared by directly dissolving 40.00 g of NaOH pellets (≥98%, Sigma Aldrich) into 1 litre of deionized water (Millipore). It is used as the baseline electrolyte for the three-electrode cell experiments, the cleaning solution for washing the electrodes after each three-electrode cell experiment, and the intermediate electrolyte for the single-cell polysulphide-air RFB tests.

3.2.2 Aqueous polysulphide Electrolytes

Polysulphide electrolytes were prepared by dissolving in sequence a quantity of NaOH ($\geq 98\%$, Sigma Aldrich), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ($\geq 98\%$, Sigma Aldrich) and powdered S ($\geq 99.5\%$, Sigma Aldrich) in deionized water with agitation and in a $\text{N}_{2(\text{g})}$ atmosphere. Under such conditions, complete dissolution of NaOH, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and S could be achieved within a few hours. NaOH was added to the aqueous polysulphide electrolytes as the supporting electrolyte to enhance their conductivities and hence to eliminate the effect of ion migrations and to maintain the ionic strength and pH of the electrolytes.

Two polysulphide electrolytes were prepared: a concentrated polysulphide solution containing $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2$ and $1 \text{ mol kg}^{-1} \text{ NaOH}$ and a dilute polysulphide solution containing $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2$ and $1 \text{ mol kg}^{-1} \text{ NaOH}$.

The $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ stock solution was prepared by dissolving 20.00 g of NaOH, 120.09 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 16.04 g of S into 418.91 ml of deionized water in sequence with agitation and in the $\text{N}_{2(\text{g})}$ atmosphere. It was used for the CV and polarization measurements of various disk/porous electrodes, the sulphidisation treatment of Ni-based electrodes and as the anolyte of the single-cell polysulphide-air RFB.

The $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ stock solution was prepared by diluting the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ solution with $1 \text{ mol kg}^{-1} \text{ NaOH}$ solution for 50 times. It was used as the main electrolyte for the CV experiments in this study. The dilute polysulphide electrolyte was employed in this study since the mass transport limitations and hence the peak currents of the electrochemical processes can be achieved more easily in a dilute electrolyte than in a concentrated electrolyte at a certain scan rate of potential.

3.3 Pre-treatment of Membranes

The single-cell reactor of the polysulphide/air RFB used two membranes, including a Nafion® 117 CEM and a Fumapem® FAA-3-PK-75 AEM. Both membranes need pre-

treatments before use. The physical and chemical properties of the two membranes are attached in the Appendix A and B.

3.3.1 Nafion® 117 CEM

The as-received Nafion® N-117 membrane is in the hydrogen ionic (H^+) form and dry state. However, the polysulphide-air RFB system requires a sodium ionic (Na^+) form CEM. In order to exchange the H^+ ions with Na^+ ions, the Nafion® membrane needs to be impregnated in 1 mol kg^{-1} NaOH solution for at least 4 hours at 18-30 °C.

Since the expansion rate of the Nafion® membrane depends on the pH of the alkaline bath, the same sodium hydroxide solution (1 mol kg^{-1}) as the intermediate electrolyte was used here for the pre-treatment so that the size of the Nafion® membrane would not change appreciably after being assembled into the cell. During impregnation, the Nafion® membrane must be completely immersed into the sodium hydroxide solution. Mesh separators between Nafion® membrane sheets are required if multiple membranes are impregnated at the same time and placed horizontally in the impregnation bath. The membrane should not be folded or wrinkled. Also, due to the expansion of the Nafion® membrane after impregnation, the positioning holes for easy assembly of the cell must be drilled after the impregnation treatment.

3.3.2 Fumapem® FAA-3-PK-75 AEM

The as-received Fumapem® FAA-3-PK-75 membrane is in the Br^- form and dry state. However, the system requires an OH^- form AEM. Hence, the Fumapem membrane also needs to be impregnated in 1 mol kg^{-1} NaOH solution for at least 12-20 hours to convert to OH^- form. The impregnation bath was replaced with fresh 1 mol kg^{-1} NaOH solution for several times over the entire process.

Unlike Nafion® membranes, the Fumapem® FAA-3-PK-75 membrane was likely to curl during the impregnation and hence needed to be stabilized between meshes/spacers. The wet form Fumapem® FAA-3-PK-75 membrane should never dry out as micro-cracks may occur due to shrinkage. Since the Fumapem® FAA-3-PK-75 membrane is PEEK

reinforced, its size does not change appreciably after the impregnation treatment. Hence the positioning holes could be drilled before the impregnation treatment.

3.4 Preparation of Electrodes

3.4.1 Nickel and Glassy Carbon Disk Electrodes

The disk electrodes were made from sealing a ϕ 5 mm glassy carbon (Alfa Aesar) or nickel (99.999%, Puratronic®, Alfa Aesar) rod inside a ϕ 10 mm hollow PVC/PEEK cylinder (RS Components) with Epoxy (EpoFix, Struers), as illustrated in Figure 3.4-1. After hardening of the Epoxy resin, the disk electrodes were cut with a diamond saw to produce a flat electrode surface.

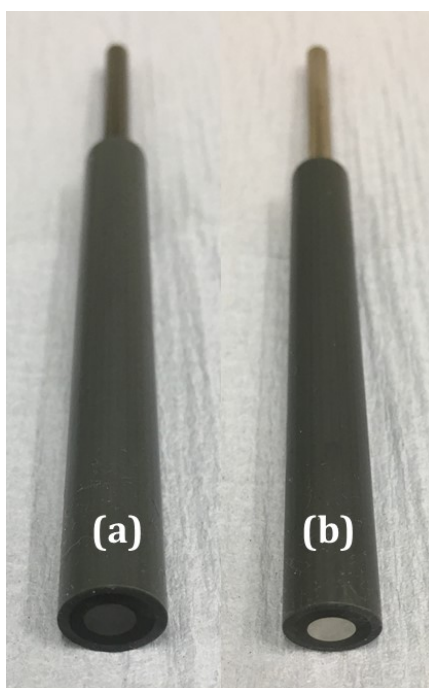


Figure 3.4-1 Glassy carbon (a) and nickel (b) disk electrodes with a diameter of 5 mm

3.4.2 Porous Electrodes

Porous sheet electrodes were tailored into $1 \times 3 \text{ cm}^2$ rectangular sheets and clamped onto a holder with Pt wire current collector for the electrochemical tests in the three-electrode cell, as shown in figure 3.4-2. The sheet electrodes were immersed into the polysulphide electrolyte for a depth of 1 or 2 cm during the electrochemical measurements.

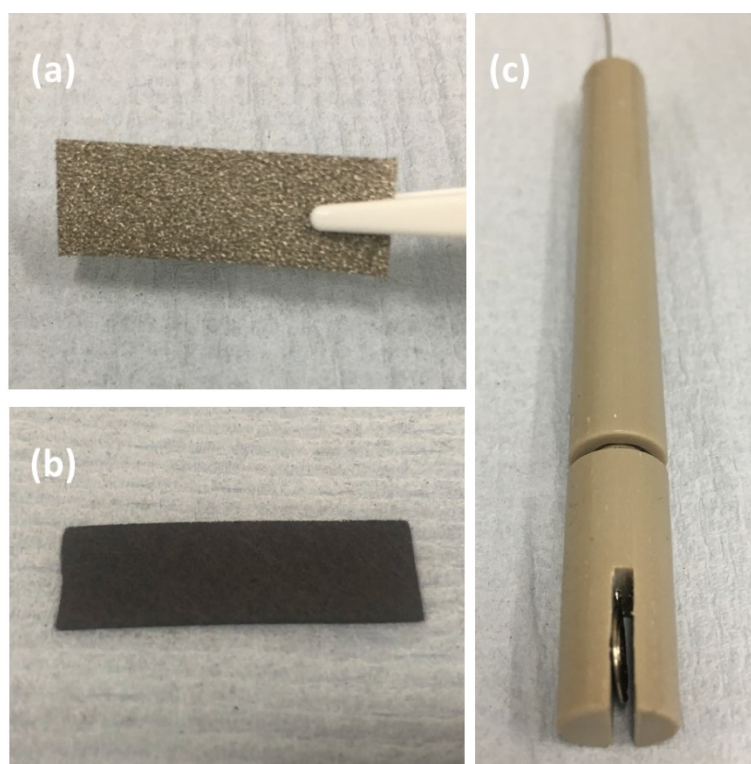


Figure 3.4-2 (a) $1 \times 3 \text{ cm}^2$ nickel foam electrode, (b) $1 \times 3 \text{ cm}^2$ carbon paper electrode and (c) sheet electrode holder

Ex-situ characterization of the porous electrodes was mainly carried out with scanning electron microscopy (SEM) which determines the micro-structure, surface morphology and distribution of catalysts on the electrodes. SEM images of the porous electrodes in this study were taken by a LEO Gemini 1525 field emission gun scanning electron microscope (FEG-SEM) at 5 kV.

3.4.2.1 Carbon Paper

The carbon paper used in this study was the SGL 10AA GDL (SGL Group) with a thickness of $\sim 390 \mu\text{m}$ and through-plane resistance of $< 6 \text{ m}\Omega \text{ cm}^2$. As indicated by previous studies, SGL 10AA carbon paper has a poor wetting in aqueous electrolytes hence necessitates pre-treatments to enhance its hydrophilicity before use. A variety of methods have been reported to increase the hydrophilicity of carbon materials [24-32]. Here, thermal treatment in the presence of oxygen was adopted due to the simplicity and effectiveness of this method, which introduced C-O-H and C=O functional groups on the surface of the carbon fibres hence enhanced the hydrophilicity of the carbon paper [26].

Thermal treatment of the SGL 10AA carbon paper was conducted by simply placing the carbon paper in a muffle furnace which was then heated to a set temperature for a period of time before cooling down to the room temperature. Conditions for thermal treatment are summarized in Table 3.4-1.

Table 3.4-1 Thermal treatment of SGL 10 AA carbon paper

Sample	Temperature / °C	Time / hr
#1	400	30
#2	450	6
#3	500	6

3.4.2.2 Ni Foam

A 0.9 mm thick nickel foam (GoodFellow) was used to study the sulphidisation conditions of nickel in aqueous polysulphide solutions. The physical properties of this nickel foam are shown in Table 3.4-2.

Table 3.4-2 Properties of the 0.9 mm thick Ni foams

Thickness / mm	Bulk density / g cm⁻³	Porosity	Pores/cm	Purity
0.9	0.62	93%	20	99.50%

Ni foam was sonicated in absolute ethanol and 6 mol l⁻¹ HCl solution for 30 min respectively to remove the organic impurities and oxide scale on its surface, after which it was rinsed with sufficient deionized water and absolute ethanol in turn and finally air dried before further sulphidisation treatment or electrochemical characterization [224].

3.4.2.3 NiS_x/carbon paper Composite Electrodes

NiS_x/carbon paper composite electrodes can be prepared using a variety of methods, such as (i) embedding pre-prepared NiS_x catalyst [225-232] onto the carbon paper, (ii) direct deposition of NiS_x onto the carbon paper from precursors of nickel salts and sulphur-containing chemicals [182, 233] and (iii) deposition of metallic nickel [234] onto the carbon paper followed by a sulphidisation treatment of the electrode. In this study, the last method was used. Sulphidisation of Ni-based electrodes are described in section 3.4.3.

Ni/carbon paper composite electrodes were prepared using three methods in this study, including electrodeposition, impregnation and electroless deposition. The latter two methods require successive reduction in H_{2(g)} at elevated temperatures of the as-deposited electrodes.

Electrodeposition of nickel is well documented [234]. In this study a simple plating bath consisting of only nickel sulfamate (Ni(OSO₂NH₂)₂) and boric acid (H₃BO₃) was adopted for the electrodeposition of nickel onto the carbon paper [235]. The electroplating was carried out in a classic two-electrode setup, with a Ni mesh (Advent, 99%) counter electrode. A 1 mol l⁻¹ Ni(OSO₂NH₂)₂ / 0.5 mol l⁻¹ H₃BO₃ solution was used as the plating bath. Electrodeposition was carried out with a galvanostatic method without stirring of the electrolyte at 55±2 °C. The effects of applied current density, current profile (continuous/pulse) and deposition time were investigated, as shown in Table 3.4-3.

Table 3.4-3 Experimental design for the electrodeposition of nickel onto carbon paper

Sample #	Weight of carbon paper / g	Designed wt% of nickel	Current density/ mA cm⁻²	Current profile	Duration / s
1	0.0957	10	10	Continuous	262
2	0.0960	20	10	Continuous	526.00
3	0.0969	20	100	Continuous	53
4	0.0987	20	10	Pulse (5s on/off)	541
5	0.1004	30	10	Continuous	825
6	0.0958	40	10	Continuous	1050

The impregnation method was conducted by first impregnating the carbon paper with nickel nitrate using a Ni(NO₃)₂/ethanol or Ni(NO₃)₂/isopropanol solution. The Ni(NO₃)₂ impregnated carbon paper was then dried in the oven followed by a reduction in the 100 ml min⁻¹ 10% H_{2(g)}/90% N_{2(g)} gas stream at 500 °C for 1 hr in the tube furnace to reduce the Ni(NO₃)₂ to metallic nickel [236]. In this study, both Ni(NO₃)₂/ethanol or Ni(NO₃)₂/isopropanol solution were in a concentration of 0.2 mol l⁻¹. Due to the low concentrations of nickel nitrate, the impregnation/drying process need to be repeated several times for samples to achieve the desired nickel loading. Ni/carbon paper electrodes with 10 wt%, 20 wt% and 30 wt% designed nickel loading (defined as the weight ratio of nickel and the carbon paper substrate) were prepared using both impregnation solutions, as shown in Table 3.4-4.

Table 3.4-4 Experimental design for the impregnation of Ni(NO₃)₂ onto carbon paper

Sample #	Weight of carbon paper / g	Designed wt% of nickel	Solvent	Volume of Ni(NO₃)₂(aq)/μl
1	0.0271	10	Ethanol	231
2	0.0257	20	Ethanol	438
3	0.0263	30	Ethanol	672
5	0.0266	10	Isopropanol	227
6	0.0257	20	Isopropanol	438
7	0.0256	30	Isopropanol	654

Electroless deposition method was carried out through an initial deposition of nickel oxyhydroxide (NiOOH) onto the carbon paper [237] followed by the reduction in a 100 ml min⁻¹ 10% H_{2(g)}/90% N_{2(g)} gas stream at 450 °C for 1 hr in the tube furnace to reduce the NiOOH to metallic nickel. NiOOH was deposited onto the carbon paper by placing the carbon paper in a deposition bath, prepared by mixing nickel sulphate solution (NiSO₄·6H₂O, 99%, Sigma Aldrich), ammonia water (28 wt%, Sigma Aldrich), ammonium persulphate solution ((NH₄)₂S₂O₈, ≥98%, Sigma Aldrich) and deionized water, for 1 hr under moderate stirring. The concentrations, volumes and sequences of addition of the prior solutions are summarized in Table 3.4-5. The sequence of mixing the three solutions was of crucial importance to the success of experiments. After being removed from the deposition bath the NiOOH deposited carbon paper sample was sonicated for a few seconds to remove excess deposits on the surface and then air dried in the oven.

Table 3.4-5 Solutions used to prepare the NiOOH deposition bath

Solution	Composition	Volume / ml	Adding sequence
1	1 mol l ⁻¹ NiSO ₄	4	#1
2	0.25 mol l ⁻¹ (NH ₄) ₂ S ₂ O ₈	3	#3
3	28 wt% NH ₃	1	#2
4	H ₂ O	2	#4

3.4.3 Sulphidisation of Ni-based Electrodes

Several methods were used by various authors to sulphidise Ni-based electrodes, such as reaction with $\text{H}_2\text{S}_{(\text{g})}$ at elevated temperature [187], electrochemical polarization in aqueous polysulphide solutions [166] and impregnation in aqueous polysulphide solutions [34, 46, 214]. However, H_2S is highly toxic, whose usage should be avoided to the greatest extent. The mechanism of how electrochemical polarization improves the activities of transition metal-based electrodes in catalysing aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reactions is not clear. In addition, impregnation with an aqueous polysulphide solution remains the most convenient among the aforesaid three methods. It is therefore decided to use the impregnation method to sulphidise Ni-based electrodes.

Various impregnation conditions have been reported by different authors to sulphidise Ni-based electrodes in aqueous polysulphide solutions, in terms of the composition of aqueous polysulphide solutions, temperature, impregnation time, etc. [34, 46, 214].

In this study the same polysulphide solution used in the three-electrode cell experiments and single-cell polysulphide-air RFB tests, namely the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2 / 1 \text{ mol kg}^{-1} \text{ NaOH}$ solution, was used for the sulphidisation process. Two conditions were investigated using the 0.9 mm thick Ni foam: (i) impregnation at room temperature for 72 hr and (ii) boiling for 30 min. Ni foam sulphidised under these two conditions were characterized with SEM and in the three-electrode cell for their electrocatalytic performances in aqueous polysulphide electrolytes.

3.5 Electrochemical Measurements

The electrochemical measurements carried out in this work include CV, LSV, chronoamperometry, chronopotentiometry and EIS. All experiments were carried out at $20 \pm 3^\circ \text{C}$, using an Autolab PGSTAT302N potentiostat/galvanostat (Metrohm). Anodic polarization and cathodic polarization experiments were allowed to carry out alternatively in order to minimize the effects of electrochemical measurements on the electrolyte compositions.

3.5.1 Three-electrode cell Experiments

Previous experiments showed that the electrode process taking place in aqueous polysulphide electrolytes under low overpotentials ($< \pm 200$ mV) were mainly charge transfer controlled [21]. The effect of mass transport on the experimental results is considered to be small under such conditions. As a result, electrochemical measurements in the three-electrode cell were carried out in static polysulphide electrolytes.

A variety of electrodes were characterized in the three-electrode cell setup, including glassy carbon and nickel disk electrodes, as-received and heat-treated carbon paper electrodes, Ni/NiS_x modified heat-treated carbon paper electrodes, and Ni foam electrodes. After successful setup of the three-electrode cell according to Figure 3.1-1, N_{2(g)} was purged through the electrolyte for 30 min in order to remove the dissolved oxygen in the electrolyte. A flow of N_{2(g)} was maintained over the electrolyte surface throughout the experiments to ensure an O₂-free atmosphere inside the electrolyte compartment.

3.5.1.1 CV measurements

CV measurements were conducted using glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ NaOH electrolyte, the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte and the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte within a variety of potential windows at the scan rate of 20 mV s⁻¹. This scan rate was widely adopted and was considered as appropriate here as it allowed sufficient electrochemical information to be revealed within acceptable experimental timing. The maximum cathodic and anodic potentials adopted in the CV experiments were -1.1 V and 0.3 V vs Ag|AgCl_(sat) respectively in order to avoid significant side reactions such as HER and oxygen evolution reaction (OER). All CV measurements were conducted in the positive potential sweep direction.

Before each experiment, the glassy carbon or nickel disk electrode was cleaned according to the procedures shown in Figure 3.5-1, to ensure complete removal of residues from previous experiments and produce a fresh electrode surface.

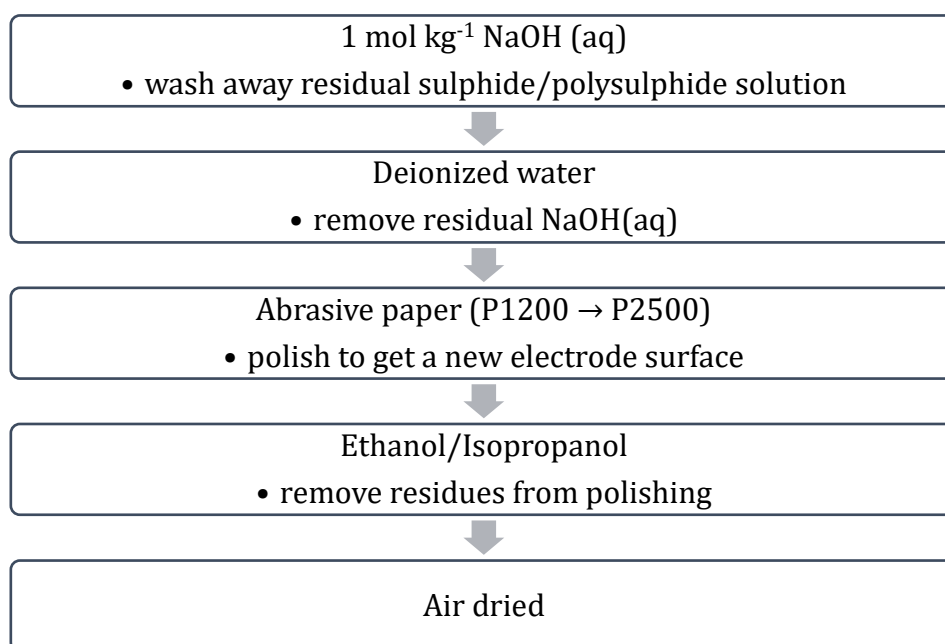


Figure 3.5-1 Procedures for cleaning disk electrodes

3.5.1.2 Polarization Tests

Polarization tests of the various disk and porous electrodes were performed in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte to characterize their catalytic activities towards aqueous S_x²⁻/HS⁻ redox reactions. Both potentiodynamic and potentiostatic polarization tests were performed, with the overpotentials of both experiments limited to ±200 mV to avoid significant side reactions.

The potentiodynamic polarization tests was conducted using the LSV method starting from the equilibrium potential to a maximum overpotential of ±200 mV, with a slow scan rate of 1 mV s⁻¹ to simulate a pseudo-steady-state polarization condition.

The potentiostatic polarization tests were performed with chronoamperometry method. A constant overpotential was applied to the working electrode for a period of time (i.e. 10 min) to reach the steady state current, which was recorded at the end of the measurement, afterwards the applied overpotential was stepped to the next higher or lower value with an increment of 20 mV.

Results of the polarization tests were presented in both linear plots and Tafel plots. Exchange current density of each electrode in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH

electrolyte was derived from the corresponding Tafel plot, enabling a quantitative comparison among the catalytic activities of various electrodes.

3.5.2 Single-cell Polysulphide-air RFB Tests

The 5 cm² single-cell polysulphide/air RFB system was built according to Figure 3.1-2, using the parts and equipment listed in Table 3.1-1 and 3.1-3. The compositions and flow rates of the electrolytes are summarized in Table 3.1-2. Once set up the single-cell polysulphide/air RFB was allowed to run without load for a period of time (i.e. 30 min). After a stable OCV was reached, the single-cell polysulphide/air RFB was characterized with polarization curve measurement and EIS measurements.

3.5.2.1 Polarization Curve Measurement

The polarization curve measurement of the single-cell polysulphide/air RFB was performed using the chronopotentiometry method. A constant current is applied to the RFB for 1 min where the steady state cell voltage at the end of the polarization process was recorded as a data point for the polarization curve, after which the RFB was allowed to rest at its OCV for 2 min to reach the steady state before the next polarization step. The applied constant current started from 5 mA which equalled to 1 mA cm⁻² and then increased with an increment of 1 mA cm⁻² for each polarization step until the corresponding cell voltage approached zero.

The polarization curve was then obtained by plotting the cell potentials against corresponding current densities. Power density curve was successively derived by plotting the power densities, which was virtually the product of cell voltage and the corresponding current density, against current densities.

3.5.2.2 EIS Measurements

EIS measurements of the single-cell polysulphide/air RFB were performed for both the full-cell and the two half-cells. It was performed using the potentiostatic method with an

amplitude of 10 mV and a frequency range of 0.01 ~ 100000 Hz. EIS measurements of the half-cells were achieved using an Hg|HgO RE which was placed inside the intermediate electrolyte.

Chapter 4 Fundamentals of Aqueous Polysulphide Electrolytes

4.1 Speciation of Aqueous Polysulphide Electrolyte

4.1.1 Results of the Numerical Modelling

Table 4.1-1 summarizes the equilibrium constants used in the numerical calculation of sulphur species concentrations in this work. K_w is obtained from the work of Fisher and Barnes [80]. $K_{a,1}$ is obtained from the work of Ellis and Giggenbach [86]. $K_{a,2}$ is obtained from the work of Giggenbach [96]. K_A , K_B , K_C are adopted from the work of Giggenbach [72]. γ_{OH^-} and a_w are adopted from the work of Akerlof and Kegeles [238].

Table 4.1-1 Equilibrium constants associated with aqueous polysulphide solutions

K_i	a	b	c	d	Ref
K_w	3927.1	0.01223	- 2.8334	-	[80]
K_1	2830.4	0.02083	- 8.7289	-	[86]
K_2	28646	0.2657	- 158.255	-	[96]
K_A	-	-	4.2	- 0.35	[72]
K_B	-	-	1.75	- 0.35	[72]
K_C	-	-	- 5.08	- 0.35	[72]

$$pK_i = a/T + b \times T + c + d \times \sqrt{I}, \text{ where } I \text{ is the ionic strength and } I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$$

Using the equilibrium constants listed in Table 4.1-1, the equilibrium concentrations of OH^- and various sulphur species within the following two aqueous polysulphide solutions, namely 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH and 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH, at 20 °C are calculated using the numerical model discussed in Section 2.2.2, as shown in Table 4.1-2.

Table 4.1-2 Calculated equilibrium concentrations of OH⁻ and major sulphur species in two aqueous polysulphide solutions at 20 °C

Species	Concentrations / mol kg ⁻¹	
S	0.02	1.00
Na ₂ S	0.02	1.00
NaOH	1.00	1.00
H ₂ S	1.36×10 ⁻⁹	3.27×10 ⁻⁸
HS ⁻	1.26×10 ⁻²	6.12×10 ⁻¹
S ²⁻	5.58×10 ⁻⁶	5.47×10 ⁻⁴
S ₂ ²⁻	5.23×10 ⁻⁵	6.10×10 ⁻³
S ₃ ²⁻	2.10×10 ⁻³	1.53×10 ⁻¹
S ₄ ²⁻	5.10×10 ⁻³	2.27×10 ⁻¹
S ₅ ²⁻	6.59×10 ⁻⁵	1.80×10 ⁻³
OH ⁻	1.01	1.61

As can be seen from Table 4.1-2, HS⁻ is the prominent sulphide species within the two aqueous polysulphide solutions, whose concentration is also higher than any individual polysulphide species within the solution. S₄²⁻ is the dominant polysulphide species within the two aqueous polysulphide solutions, followed by S₃²⁻. Other sulphide and polysulphide species do not exist in significant amounts in the two aqueous polysulphide solutions compared to HS⁻, S₃²⁻ and S₄²⁻.

4.1.1.1 Effects of Initial S/S²⁻

Variations in the equilibrium concentrations of sulphur species in aqueous polysulphide solutions according to the initial sulphur to sulphide ratio are investigated with aqueous

polysulphide solutions containing 1 mol kg⁻¹ Na₂S, 1 mol kg⁻¹ NaOH and various concentrations of S using the numerical model, are demonstrated in Figure 4.1-1.

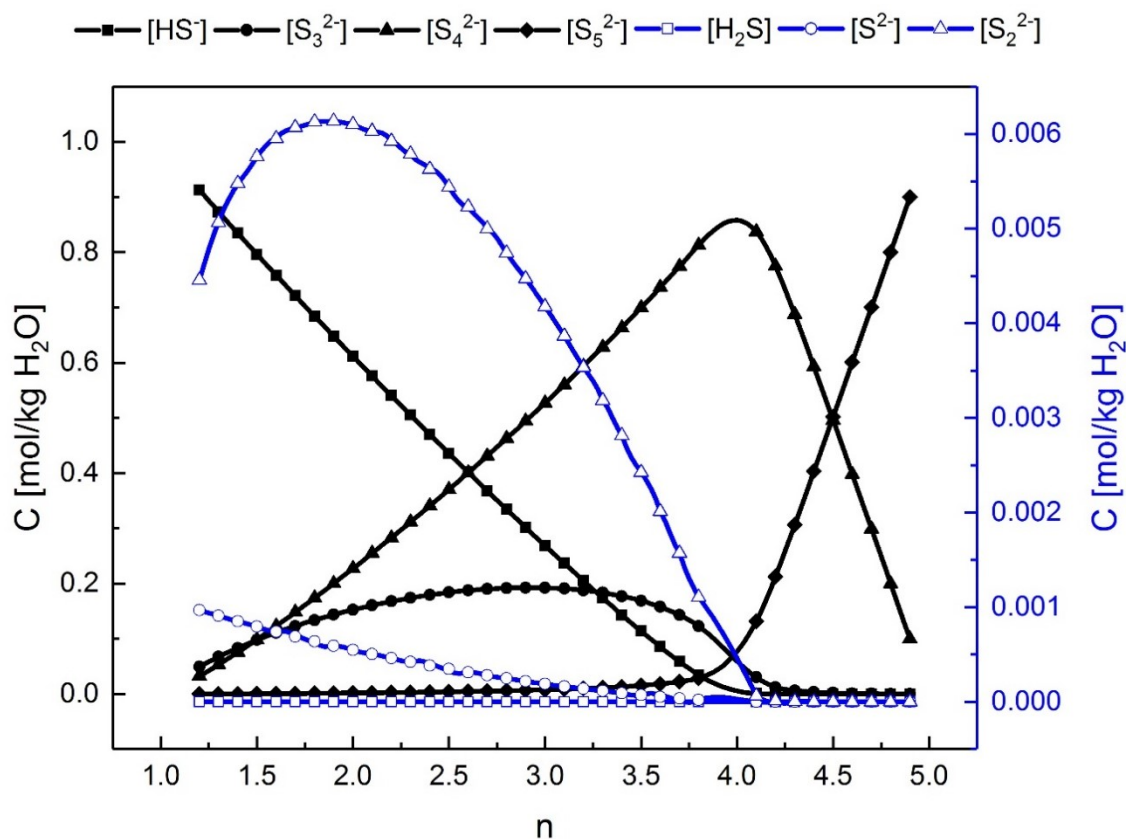


Figure 4.1-1 Effects of initial S/S^{2-} on the speciation of aqueous polysulphide solutions containing 1 mol kg⁻¹ Na₂S, 1 mol kg⁻¹ NaOH and various concentrations of S

At low S concentrations, S_3^{2-} and S_4^{2-} are the dominating polysulphide species. With the increase of S concentration, S_4^{2-} becomes increasingly predominant until the nominal solution composition reaches an average polysulphide chain length of around 4. In the meantime, S_3^{2-} concentration first increases and then decreases. The highest S_3^{2-} concentration is reached around the average polysulphide chain length of 3.

Before the nominal solution composition reaches an average polysulphide chain length of 4, S_5^{2-} does not exist in significant amounts. Further increase in S concentration will increase the S_5^{2-} concentration dramatically at the expenses of rapidly decreased S_4^{2-} .

concentration. This is apparent since the formation of S_5^{2-} mainly comes from the binding reaction of S_4^{2-} and S.

H_2S , S^{2-} and S_2^{2-} are the minor species that do not exist in significant amounts under any solution compositions. Over the whole S concentration range, concentrations of HS^- and S^{2-} decreases along with the increase in S concentration due to the formation of polysulphides via the binding reaction of S and sulphides. S_2^{2-} concentration increases first and then decreases after the nominal solution composition reaches an average polysulphide chain length of around 2.

4.1.1.2 Effects of NaOH Addition

Addition of NaOH is affecting the aqueous polysulphide speciation in two aspects: (i) changing the ionic strength of aqueous polysulphide solutions hence affecting the equilibrium constants among polysulphides and (ii) affecting the equilibria of hydrogen sulphide dissociation as higher pH favours the formation of S^{2-} .

Figure 4.1-2 shows the variations in sulphur species concentrations according to the initially added NaOH concentration for aqueous polysulphide electrolytes containing $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2$. As shown in Figure 4.1-2, with the increase in the concentration of initially added NaOH, concentrations of HS^- , S_4^{2-} and S_5^{2-} decrease whereas concentrations of S^{2-} , S_2^{2-} and S_3^{2-} increase. This result is expected since the increase of OH^- shifts the equilibria 2.2-8, 2.2-10 and 2.2-12 towards the left hand side favouring the formation of shorter-chain polysulphides. This result is in agreement with previous studies indicating that S_4^{2-} is predominant in solutions of intermediate alkalinity, followed by S_3^{2-} at higher pH and S_2^{2-} only predominates at extremely high alkalinities [75]. The concentration of H_2S is relatively unchanged due to the large value of $pK_{a,2}$.

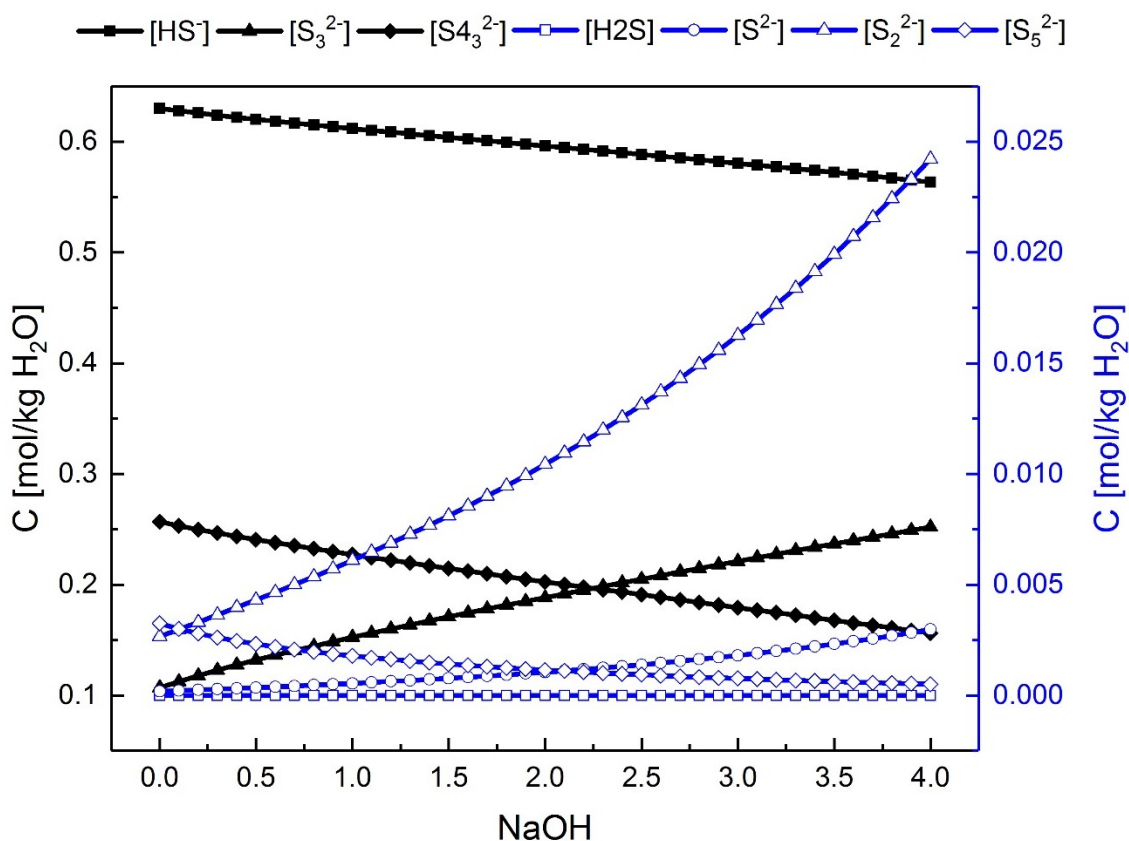


Figure 4.1-2 Effects of NaOH addition on the speciation of aqueous polysulphide electrolytes containing 1 mol kg⁻¹ Na₂S₂

4.1.1.3 Effect of Temperature

The effect of temperature on the speciation of aqueous polysulphide solutions mainly originates from the effect of temperature on the equilibrium constants of water dissociation and hydrogen sulphide dissociation, as indicated in Table 4.1-1. The temperature dependence of K_A , K_B and K_C was considered to be minor, based on the optical spectra studies by Giggenbach [72].

Operational temperatures for aqueous polysulphide based RFBs have been reported in the range of 20-70 °C [14, 66]. Hence, in this study the effect of temperature on the speciation of a 1 mol kg⁻¹ Na₂S₂ /1 mol kg⁻¹ NaOH solution was studied using the numerical modelling for the temperature range of 20-70 °C, as shown in Figure 4.1-3.

As shown in Figure 4.1-3, variations of polysulphide species concentrations within the aqueous polysulphide solution are small under various temperatures over the range 20-

70 °C. The sulphur species with the largest dependency on temperature is S^{2-} , which can be expected from the dependence of $K_{a,1}$ and $K_{a,2}$ on temperature. However, the accuracy of the numerical model is affected by various assumptions and relative errors of the numerical calculation for low-concentration species could be large. Hence, no effort is devoted here to analyse in detail the effects of temperature on the speciation of aqueous polysulphide solutions.

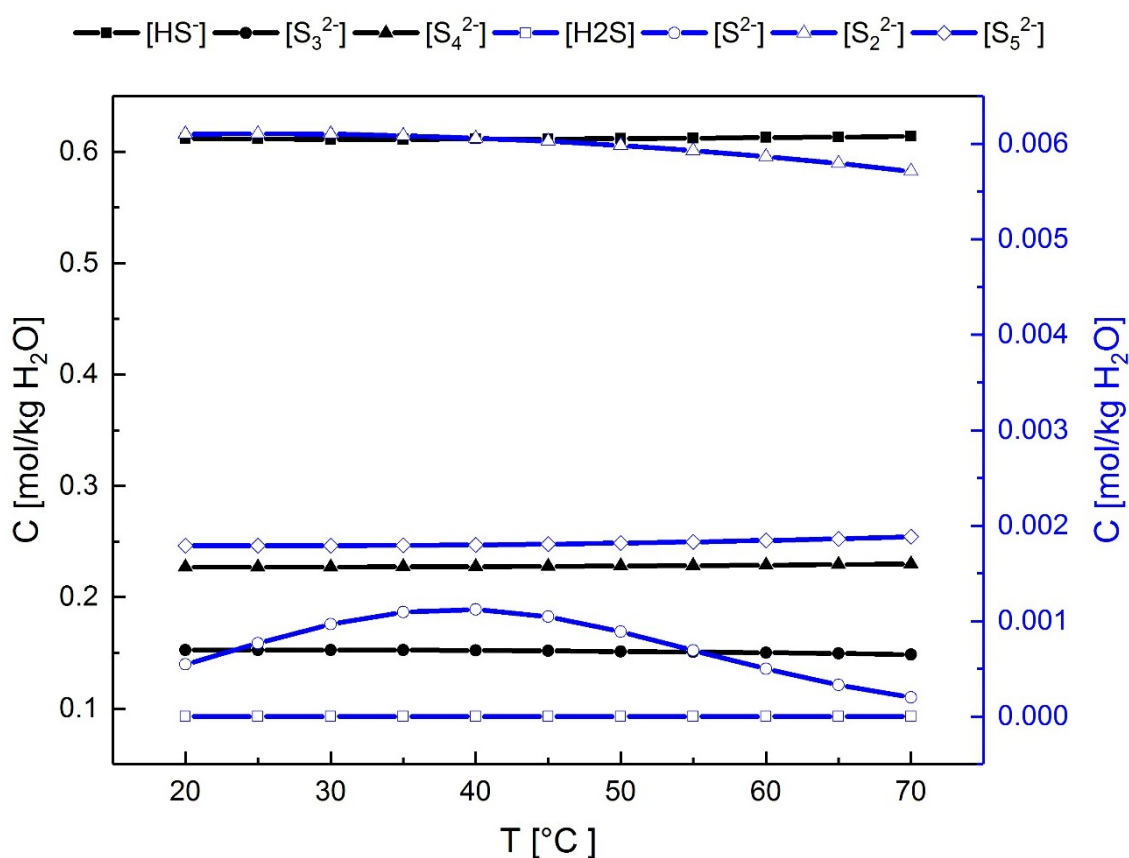


Figure 4.1-3 Effect of temperature on the speciation of 1 mol/kg Na_2S_2 / 1 mol/kg $NaOH$ solution

4.1.1.4 Variation in Speciation with SoC

It is assumed that 0% and 100% SoC of aqueous polysulphide electrolytes refer to nominal solution compositions of Na_2S_2 and Na_2S_4 respectively, despite the addition of $NaOH$ [49]. For an aqueous polysulphide electrolyte containing 1 mol/kg of Na_2S , S and

NaOH initially, 0% SoC of the electrolyte refers to a solution composition of 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH, and 100% SoC of the electrolyte refers to a solution composition of 0.5 mol kg⁻¹ Na₂S₄/1 mol kg⁻¹ NaOH. The effect of water transport on the concentrations of sulphur species and the ionic strength of the polysulphide electrolyte during the operation of the polysulphide-air RFB are ignored here.

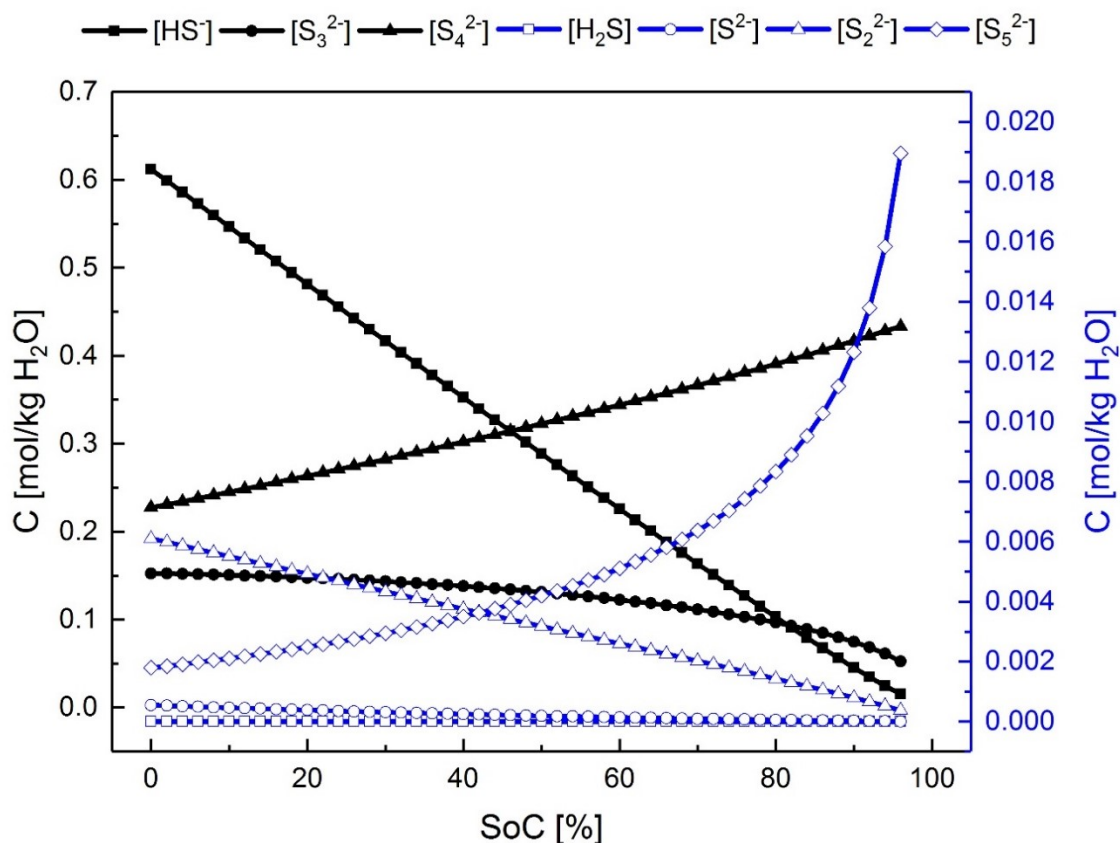


Figure 4.1-4 Speciation of sulphur species of an aqueous polysulphide electrolyte containing initially 1 mol kg⁻¹ of Na₂S, S and NaOH at various SoC

Figure 4.1-4 shows the speciation results of an aqueous polysulphide electrolyte containing initially 1 mol kg⁻¹ of Na₂S, S and NaOH respectively at various SoC. From Figure 4.1-4, it is clear that as the polysulphide electrolyte is charged, concentrations of HS⁻, S²⁻, S₂²⁻ and S₃²⁻ are decreasing, whereas concentrations of S₄²⁻ and S₅²⁻ are increasing, and the concentration of H₂S is relatively unchanged. This result is expected since sulphide species and polysulphide species with lower chain length are electrochemically

oxidized into polysulphide species with high chain length during the charging of the polysulphide electrolyte.

At low SoC, where the sulphur to sulphide ratio is small, the dominant polysulphide species are S_3^{2-} and S_4^{2-} . At high SoC, where the sulphur to sulphide ratio is large, the dominant species are S_4^{2-} . H_2S , S^{2-} , S_2^{2-} and S_5^{2-} never exist in significant quantities at any SoC of the polysulphide electrolyte.

4.1.2 Discussion of the Numerical Modelling

The accuracy of the numerical model is limited by several factors:

There is a lack of knowledge of the activity coefficients of sulphide and polysulphide ions. Hence the activities of ions within aqueous polysulphide solutions are often approximated by their concentrations [68, 76]. However, this simplification is not convincing for the case of highly concentrated solutions as the ionic strength has greater effects upon the activities of ionic species under such conditions. As a result, deviations would be expected for using concentrations instead of activities in the numerical calculation of sulphur species concentrations in highly concentrated polysulphide solutions. This issue could be partly solved by accounting for the activities of OH^- and H_2O in the numerical calculations, as was adopted in this work.

Deviations in the results of the numerical calculations with and without considerations of the activities of OH^- and H_2O were assessed. The numerical model was adjusted by replacing the activity terms with their corresponding concentrations. The new calculated concentrations of sulphur species in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte and their deviations from the results calculated by the original model of this work are summarized in Table 4.1-3.

Table 4.1-3 shows that deviations of the predominant sulphur species, including HS^- , S_3^{2-} and S_4^{2-} , in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte are less than 6.56%. Even for the minor sulphur species, such as S^{2-} and H_2S , the deviations are less than 12%.

Table 4.1-3 Calculated equilibrium concentrations of OH⁻ and major sulphur species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at 20 °C with the modified numerical model replacing activities of OH⁻ and H₂O by their concentrations

Species	Concentration / mol kg⁻¹	Deviation / %
H ₂ S	2.90×10 ⁻⁸	11.32
HS ⁻	6.10×10 ⁻¹	0.29
S ²⁻	6.13×10 ⁻⁴	11.97
S ₂ ²⁻	6.50×10 ⁻³	6.56
S ₃ ²⁻	1.57×10 ⁻¹	2.88
S ₄ ²⁻	2.24×10 ⁻¹	1.41
S ₅ ²⁻	1.70×10 ⁻³	5.56
OH ⁻	1.61	0.00

K_A and K_B were measured in highly alkaline solutions whereas K_C was measured in less alkaline solutions [78]. The appropriateness of using K_A , K_B and K_C in a single solution had been doubted by several authors [77, 78]. Licht improved the UV spectroscopic method of analysing aqueous polysulphide solutions and derived a set of new equilibrium constants among polysulphide species, however without correcting for the ionic strength [77].

Deviations of using different equilibrium constants among polysulphides in the numerical model are assessed by replacing the equilibrium constants given by Giggenbach [72] with those given by Licht [77], whose results are shown in Table 4.1-4 . As clearly indicated in Table 4.1-4 , deviations in the results of the numerical modelling introduced by use of different equilibrium constants among polysulphides are much more significant than those introduced by the activity coefficients of OH⁻ and H₂O.

Table 4.1-4 Calculated equilibrium concentrations of OH⁻ and major sulphur species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at 20 °C with the modified numerical model using K_A , K_B and K_C from [77]

Species	Concentration / mol kg ⁻¹	Deviation / %
H ₂ S	2.83×10 ⁻⁸	13.46
HS ⁻	5.86×10 ⁻¹	4.22
S ²⁻	5.80×10 ⁻⁴	5.95
S ₂ ²⁻	3.80×10 ⁻³	37.70
S ₃ ²⁻	2.33×10 ⁻¹	52.69
S ₄ ²⁻	1.75×10 ⁻¹	22.98
S ₅ ²⁻	1.40×10 ⁻³	22.22
OH ⁻	1.59	1.24

This is a lack of agreement in the value of pK_{a,2}. Deviations of the results for the numerical model introduced by the uncertainty in pK_{a,2} were studied using different pK_{a,2} values of in the model. Results have shown that only the S²⁻ concentration is affected by the use of different pK_{a,2} values, whose effects on the concentrations of other sulphur species are negligible.

The proton concentration used to derive improved estimations of S₄²⁻ concentrations in the iterative procedures, as shown in equation 2.2-28, is approximated by its activity. However, the error introduced by this assumption is considered negligible since the proton concentration in highly alkaline solutions is very small ($\sim 10^{-15}$ mol kg⁻¹).

Evidence from UV/ATR and Raman spectroscopy suggest the existence of oxy-sulphur anions even in freshly prepared polysulphide solutions due to the reaction of S with OH⁻ [99]. However, the extent of oxy-sulphur formation was not presented in the paper.

Nevertheless, despite the uncertainties introduced by various assumptions, the numerical model provides a valuable method to approximate the concentrations of

various sulphur species within aqueous polysulphide solutions under a wide range of conditions.

4.2 Electrochemistry of Aqueous Polysulphide Electrolyte

4.2.1 Potentials of Aqueous S_x^{2-}/HS^- Redox Reactions

Equilibrium potentials of aqueous polysulphide electrolytes had been modelled by Lessner et al with the reaction 2.3-4 [137]. The standard reduction potential of reaction 2.3-4 has been reported between -0.510 V and -0.520 V vs SHE. The actual redox potential of reaction 2.3-4 within the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte could therefore be calculated from equation 2.3-5 using the reported standard reduction potential and the calculated concentrations of HS⁻, S₄²⁻ and OH⁻ shown in Table 4.1-2. The calculated redox potential of reaction 2.3-4 is between -0.718 and -0.728 V vs Ag|AgCl_(sat) at 20 °C, which agrees reasonably well with experimental value of -0.714 V vs Ag|AgCl_(sat) at 20 °C. The actual equilibrium potential of the aqueous polysulphide electrolyte was determined by measuring the potential difference between the working electrode and the Ag|AgCl_(sat) reference electrode of the three-electrode cell and was found little in differences among various electrodes. Deviation of the two values was likely attributed to the approximation of ionic activities by concentrations.

Since S₃²⁻ is the other dominating polysulphide species within the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte according to Table 4.1-2, the equilibrium potential of reaction 4.2-1 is also calculated, which is -0.737 V vs Ag|AgCl_(sat),



This value is also not far from the measured potential of the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte.

The actual redox potentials of other reported aqueous S_x^{2-}/HS^- redox reactions can also be calculated by Nernst equations using the calculated concentrations of corresponding species, as shown in Table 4.2-1.

Table 4.2-1 Calculated potentials of the reported aqueous S_x^{2-}/HS^- redox reactions

Reactions	E^0 vs SHE / V	E vs SHE / V (at 20 °C)	E vs Ag AgCl _(sat) / V (at 20 °C)
$S + H_2O + 2e \rightleftharpoons SH^- + OH^-$	-0.478	-0.478	-0.680
	-0.476	-0.476	-0.678
	-0.520	-0.520	-0.722
	-0.510	-0.510	-0.712
$S + 2e \rightleftharpoons S^{2-}$	-0.476	-0.381	-0.583
	-0.447	-0.352	-0.554
	-0.570	-0.475	-0.677
	-0.480	-0.385	-0.587
$2S + 2e \rightleftharpoons S_2^{2-}$	-0.428	-0.364	-0.566
	-0.500	-0.436	-0.638
$3S + 2e \rightleftharpoons S_3^{2-}$	-0.390	-0.366	-0.568
$4S + 2e \rightleftharpoons S_4^{2-}$	-0.360	-0.341	-0.543
$5S + 2e \rightleftharpoons S_5^{2-}$	-0.340	-0.260	-0.462
$S_2^{2-} + 2e \rightleftharpoons 2S^{2-}$	-0.483	-0.358	-0.560
	-0.524	-0.399	-0.601
	-0.640	-0.515	-0.717
	-0.480	-0.355	-0.557
$2S_3^{2-} + 2e \rightleftharpoons 3S_2^{2-}$	-0.473	-0.327	-0.529
	-0.506	-0.360	-0.562
$3S_4^{2-} + 2e \rightleftharpoons 4S_3^{2-}$	-0.453	-0.414	-0.616
	-0.478	-0.439	-0.641
$4S_5^{2-} + 2e \rightleftharpoons 5S_4^{2-}$	-0.426	-0.652	-0.854
	-0.441	-0.667	-0.869
$S_3^{2-} + 2e \rightleftharpoons S_2^{2-} + S^{2-}$	-0.490	-0.354	-0.556
$S_4^{2-} + 2e \rightleftharpoons S_3^{2-} + S^{2-}$	-0.520	-0.420	-0.622
$S_2^{2-} + 2H_2O + 2e \rightleftharpoons 2HS^- + 2OH^-$	-0.541	-0.605	-0.807
	-0.530	-0.594	-0.796
	-0.45	-0.514	-0.716

$S_3^{2-} + 3H_2O + 4e \rightleftharpoons 3HS^- + 3OH^-$	-0.524	-0.536	-0.738
	-0.516	-0.522	-0.724
$S_4^{2-} + 4H_2O + 6e \rightleftharpoons 4HS^- + 4OH^-$	-0.520	-0.526	-0.728
	-0.510	-0.516	-0.718
$S_5^{2-} + 5H_2O + 8e \rightleftharpoons 5HS^- + 5OH^-$	-0.511	-0.531	-0.733
	-0.515	-0.535	-0.737

4.2.2 Eh-pH Diagram of Metastable S-H₂O System at 25 °C

Standard Gibbs energies of formation (ΔG_f^0) of species existing in aqueous polysulphide solutions at 25 °C are summarized in Table 4.2-2. The higher values of $pK_{a,2}$ (17-19) reported recently lead to higher values of $\Delta G_f^0(S^{2-})$ (109.1-120.5 kJ mol⁻¹). A $\Delta G_f^0(S^{2-})$ of 120.5 kJ mol⁻¹ was adopted in the calculations of standard reduction potentials of reactions listed in Table 2.3-1.

A metastable Eh-pH diagram of S-H₂O system at 25°C with a total dissolved sulphur concentration of 2 mol kg⁻¹, which agrees with the total sulphur concentration of the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, was built with the HSC software (Qutotec) using the standard Gibbs energies of formation, as shown in Figure 4.2-1.

Table 4.2-2 Standard Gibbs energies of formation of species in aqueous polysulphide solutions at 25 °C [93]

Species	$\Delta G^0/\text{kJ mol}^{-1}$
H ₂ O	-237.178
OH ⁻	-157.293
H ₂ S	-27.87
HS ⁻	12.05
S ²⁻	120.5 (pK _{a,2} =19)
S ₂ ²⁻	79.5
S ₃ ²⁻	73.6
S ₄ ²⁻	69
S ₅ ²⁻	65.7
S _{rhombic}	0

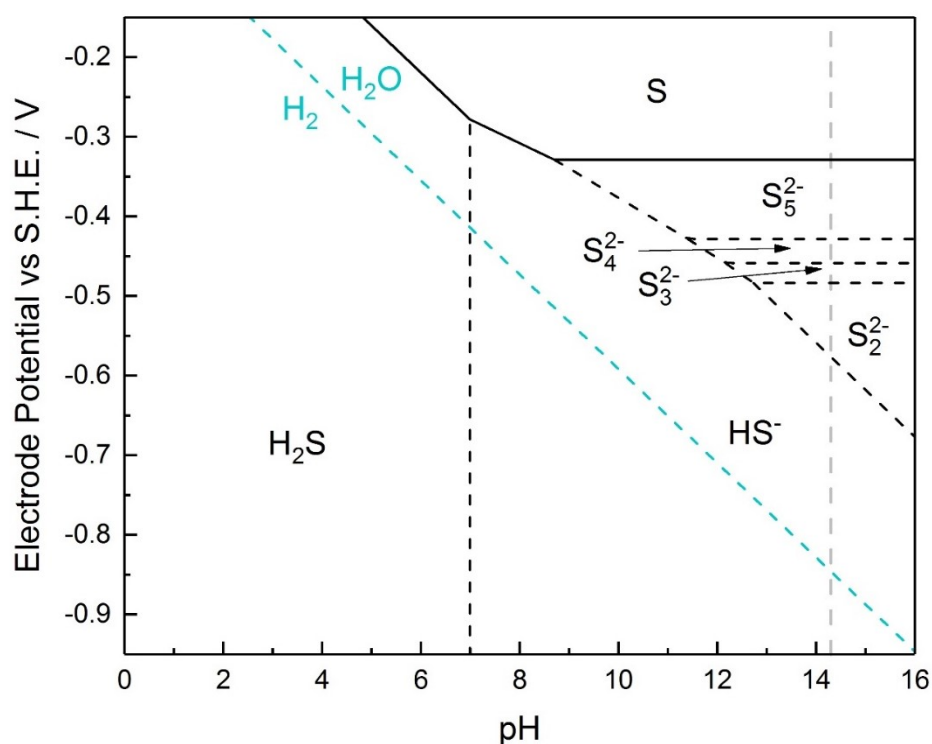


Fig. 4.2-1 Calculated metastable Eh-pH Diagram of S-H₂O system excluding all oxy-sulphur anions at 25°C with a dissolved total sulphur concentration of 2 mol kg⁻¹

The pH of the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte was approximated as 14.3 using the numerical model. According to Figure 4.2-1, the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH polysulphide electrolyte remains metastable within the potential window of -0.33 V - -0.58 V vs SHE. At the rest potential of such an electrolyte (~-0.518 V vs SHE), S₂²⁻ is shown to be the most stable polysulphide species. At potentials above -0.33 V vs SHE, elemental sulphur is likely to form. At potentials below -0.85 V vs SHE, H₂ is likely to form.

4.3 Conclusions

The numerical model has provided a valuable way of approximating the concentrations of sulphur species in aqueous polysulphide solutions. S₃²⁻ and S₄²⁻ are shown to be the predominant polysulphide species in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte. Upon charging of the electrolyte, concentrations of polysulphides with larger chain length increase. After reaching a nominal solution composition with an average polysulphide chain length of 4, continuous charging of the electrolyte will dramatically increase the concentration of S₅²⁻ at the expenses of a rapidly decreasing S₄²⁻ concentration. Addition of NaOH into the aqueous polysulphide electrolyte will shift the polysulphides equilibria towards the formation of shorter-chain polysulphides, such as S₂²⁻ and S₃²⁻. Temperature was shown to have little effect on the speciation of aqueous polysulphide solutions.

Effects of accounting for the activities of OH⁻ and H₂O in the numerical model shows a small deviation (≤ 6.56%) in the resulting concentrations of predominant sulphur species. Values of K_A, K_B and K_C were shown to have much more significant effects on the calculated concentrations of sulphur species, especially for polysulphides whose deviations were between 22.22% and 52.69%.

The numerical model is useful in predicting the sulphur species concentrations at various SoC of the polysulphide electrolyte. The derived sulphur species concentrations can be subsequently used to calculate the reversible potentials of aqueous S_x²⁻/HS⁻ redox reactions, which is useful for the interpretation of the results of electrochemical measurements.

The metastable Eh-pH diagram of S-H₂O system at 25°C with a total dissolved sulphur concentration of 2 mol kg⁻¹ was built. It is useful in predicting the potential window

within which the polysulphide electrolyte is stable, and the starting potentials where S and H₂ is likely to form.

Chapter 5 Study of Glassy Carbon and Nickel in Aqueous Polysulphide Electrolytes

This chapter mainly discusses the extensive CV measurements of glassy carbon and nickel disk electrodes in aqueous polysulphide electrolytes, conducted in a variety of potential windows. Polarization tests of the glassy carbon and nickel disk electrodes in a concentrated aqueous polysulphide electrolyte were performed with both potentiodynamic and potentiostatic methods, from which the exchange current densities of each electrode were derived from their corresponding Tafel plots.

5.1 CV Measurements

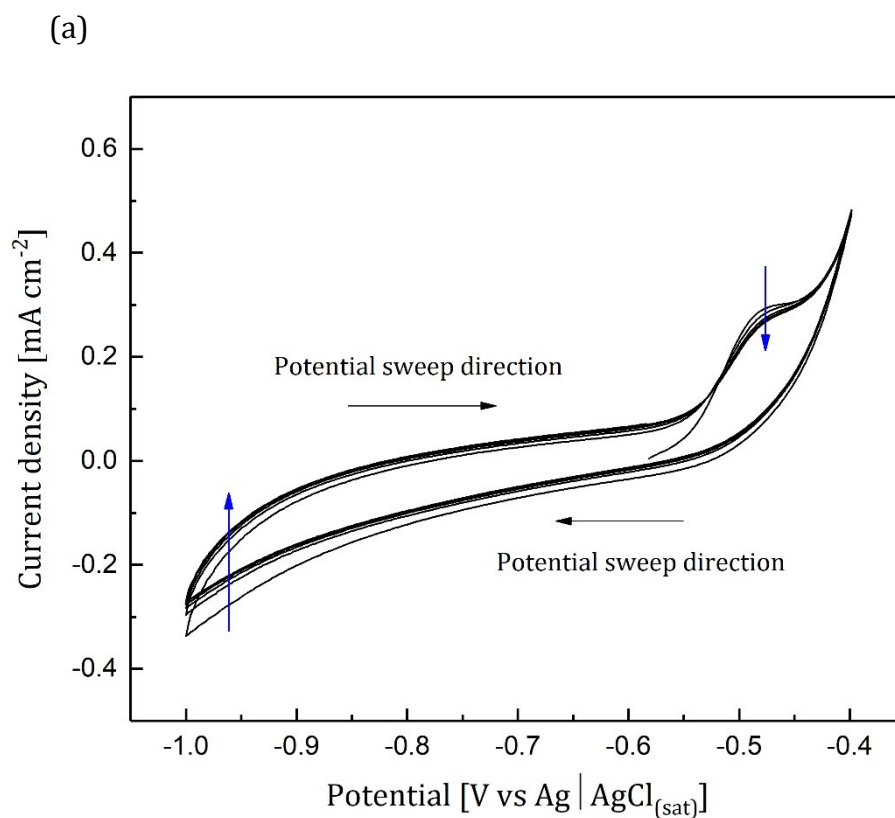
CV measurements of glassy carbon and nickel disk electrodes in aqueous polysulphide electrolytes were performed with a scan rate of 20 mV s^{-1} at 20°C , to investigate the complex and multi-process-involved aqueous $\text{S}_x^{2-}/\text{HS}^-$ redox reactions. The maximum cathodic and anodic potentials adopted in the CV experiments were -1.1 V and 0.3 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$ respectively. Within this potential range, no significant side reactions such as HER and OER were observed.

CV experiments of glassy carbon and nickel were mainly performed in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, which enabled the various current peaks to display at a relatively high scan rate (20 mV s^{-1}) in this study. CV measurements were also performed with the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, which was identical to the anolyte of the single-cell polysulphide-air RFB, as a comparison. Blank experiments in the $1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte were also conducted, since $1 \text{ mol kg}^{-1} \text{ NaOH}$ was used as the supporting electrolyte for both the dilute and the concentrated polysulphide electrolytes.

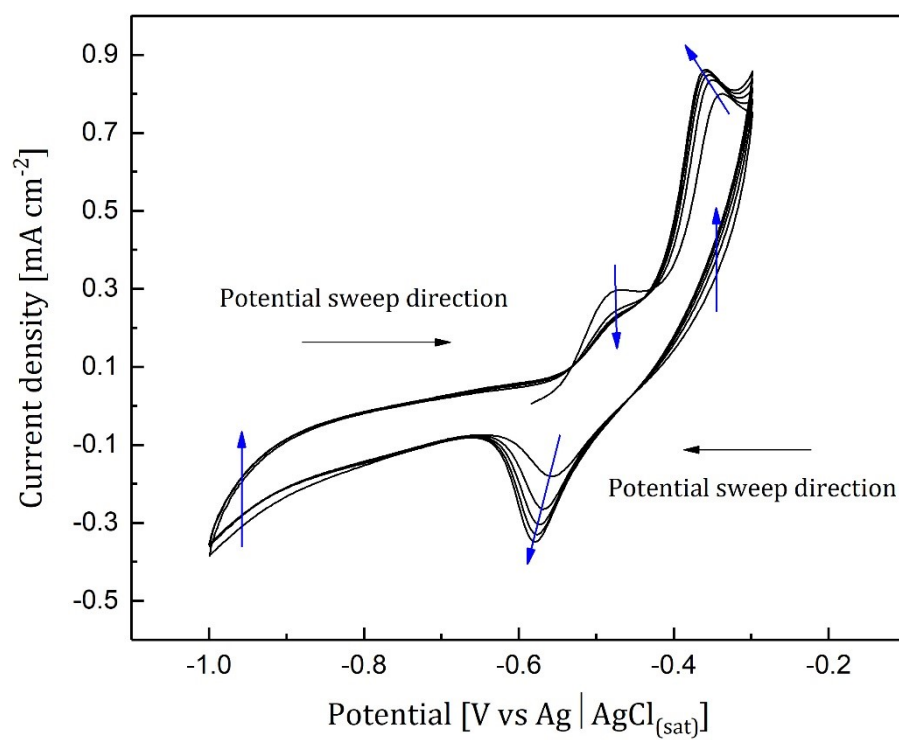
5.1.1 Glassy Carbon

5.1.1.1 In the Dilute Polysulphide Electrolyte

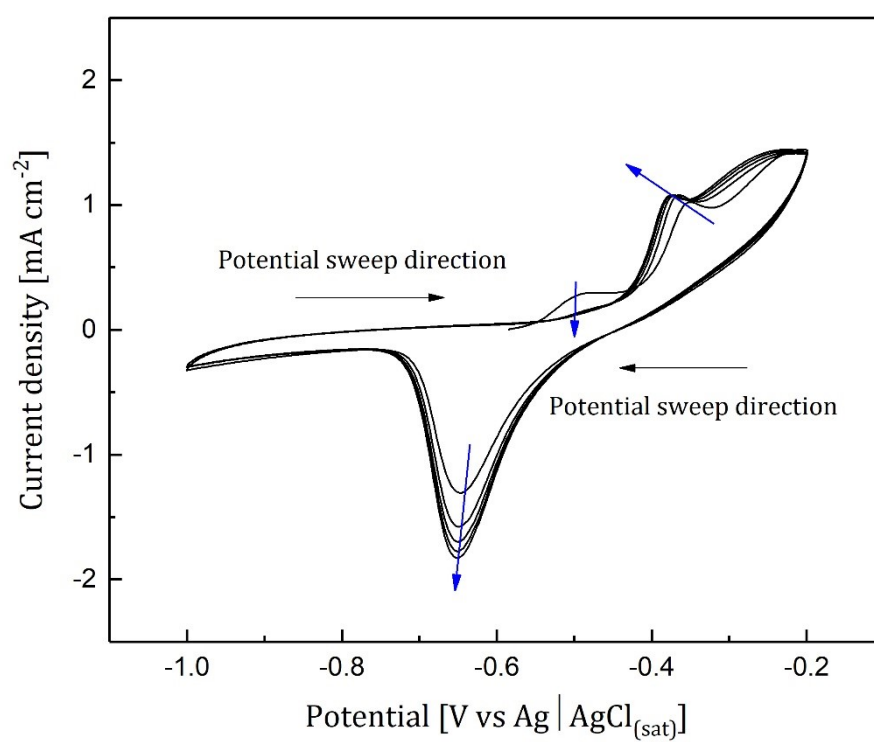
Figure 5.1-1 shows the cyclic voltammograms of the glassy carbon disk electrode in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, performed at a scan rate of 20 mV s^{-1} and within a variety of potential windows. All CV measurements in Figure 5.1-1 had a maximum cathodic potential of $-1.0 \text{ V vs Ag|AgCl}_{(\text{sat})}$ while the maximum anodic potential increased from -0.4 V to $0.3 \text{ V vs Ag|AgCl}_{(\text{sat})}$ with a step change of 100 mV .



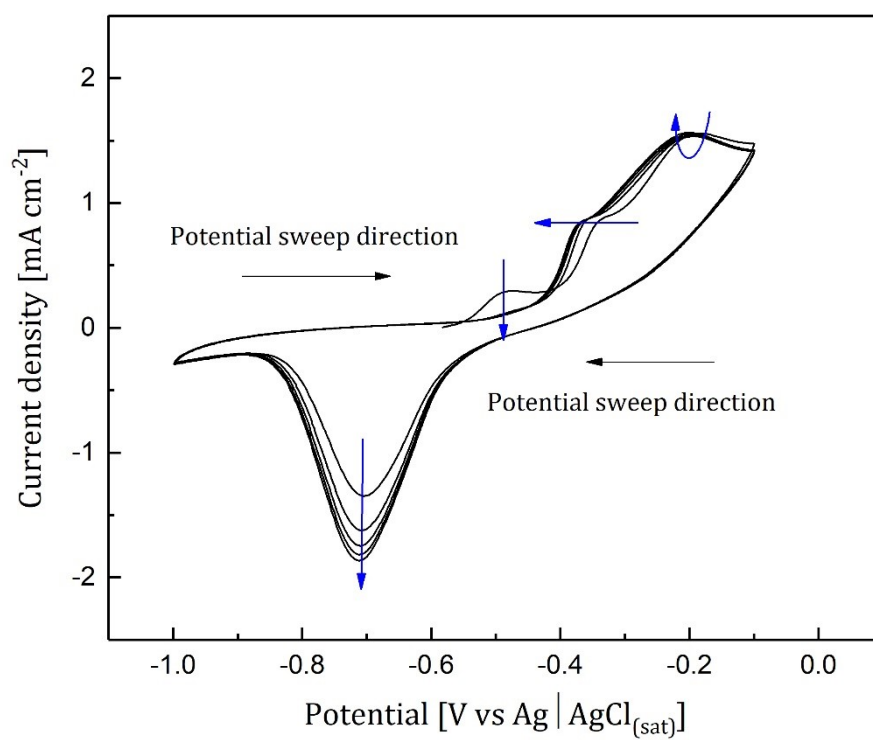
(b)



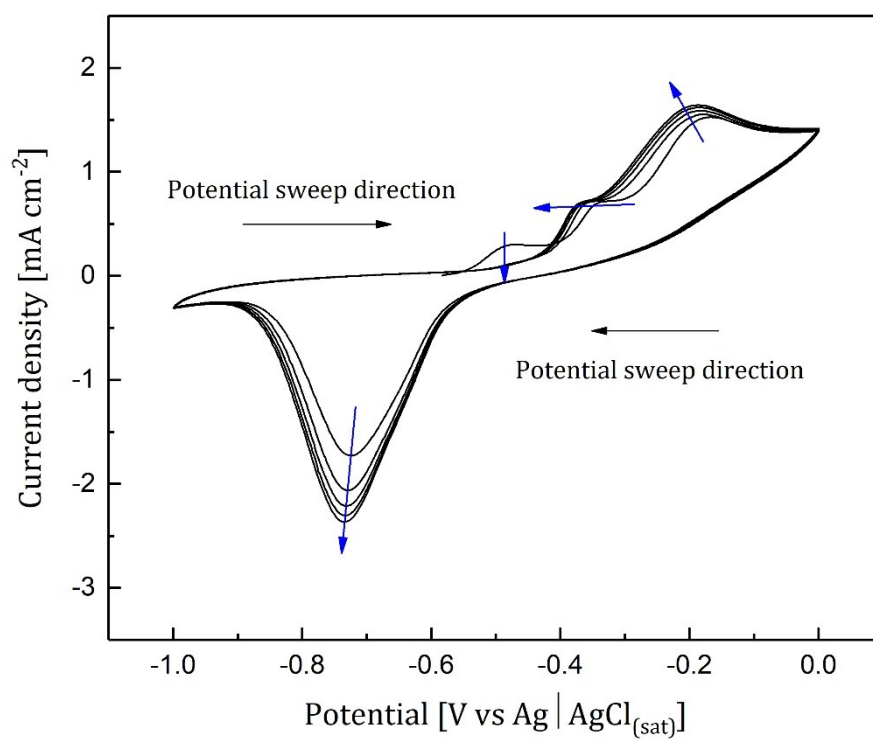
(c)



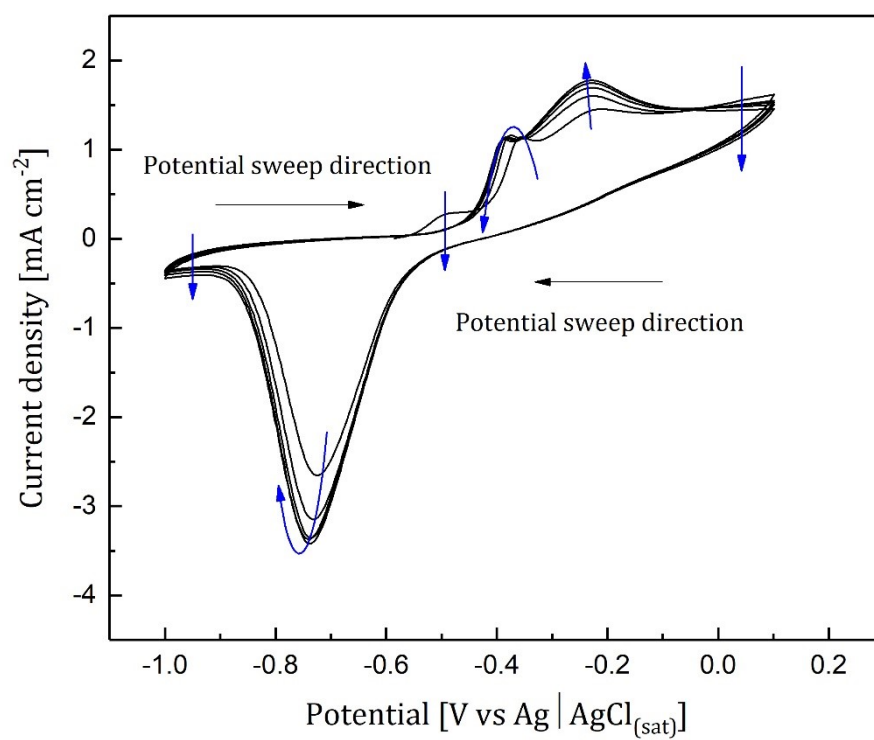
(d)



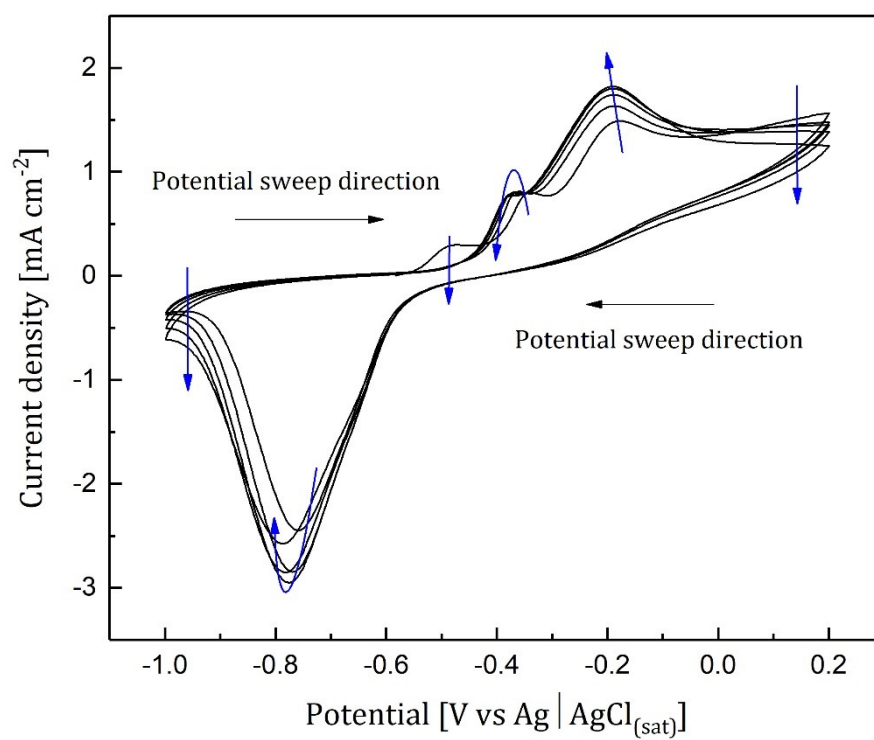
(e)



(f)



(g)



(h)

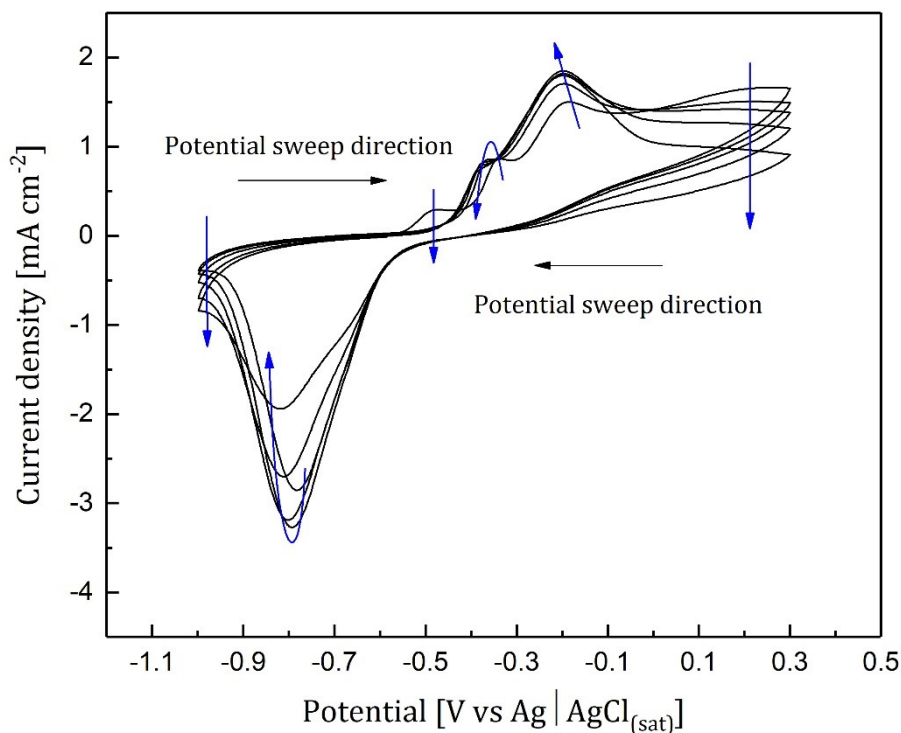


Figure 5.1-1 Cyclic voltammograms (5 cycles) of the glassy carbon disk electrode in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, performed at the scan rate of 20 mV s^{-1} and within the potential window of: (a) $-1.0 \text{ V} \sim -0.4 \text{ V}$, (b) $-1.0 \text{ V} \sim -0.3 \text{ V}$, (c) $-1.0 \text{ V} \sim -0.2 \text{ V}$, (d) $-1.0 \text{ V} \sim -0.1 \text{ V}$, (e) $-1.0 \text{ V} \sim 0 \text{ V}$, (f) $-1.0 \text{ V} \sim 0.1 \text{ V}$, (g) $-1.0 \text{ V} \sim 0.2 \text{ V}$, (h) $-1.0 \text{ V} \sim 0.3 \text{ V}$.

Figure 5.1-1 (a) shows the cyclic voltammogram obtained within the potential range of $-1.0 \text{ V} \sim -0.4 \text{ V}$ vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$. Only an anodic peak at around -0.45 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$ was observed in Figure 5.1-1 (a), which decreased along the scans. This initial anodic peak likely corresponded to the deposition of a thin layer of sulphur onto the surface of the glassy carbon disk electrode. A similar peak has been reported in the voltammograms of gold in an aqueous polysulphide solution [152].

As the maximum anodic potential increased to -0.3 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$, as shown in Figure 5.1-1 (b), a second anodic peak at around -0.35 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$ and a cathodic peak at around -0.58 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$ appeared. This obviously indicated that the species produced during the anodic polarization process within $-0.4 \text{ V} \sim -0.3 \text{ V}$ vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$ were subsequently reduced in the cathodic polarization process. And it is reasonable to

speculate that the species produced in the anodic polarization process should not be any prominent and free sulphide or polysulphide ions within the aqueous polysulphide electrolyte, otherwise the cathodic peak should also be observed in Figure 5.1-1 (a). Instead, the second anodic peak was more likely attributed to the electrochemical formation of polysulphide species on the thin sulphur layer on the surface of the glassy carbon disk electrode [153]. The cathodic peak was attributed to the reduction of absorbed polysulphide species on the surface of the glassy carbon disk electrode [153]. Both the second anodic peak and the cathodic peak increased and shifted negatively along the scans, which was also found true in Figure 5.1-1(c), indicating an increased catalytic activity of the glassy carbon disk electrode due to the formation of the absorbed polysulphide layer on the surface of the glassy carbon disk electrode over the potential cycling.

As the maximum anodic potential increased to -0.2 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (c), a third anodic peak appeared close to the maximum anodic potential, likely corresponding to the electrochemical formation of sulphur species on the surface of the glassy carbon disk electrode [153]. This speculation was supported by Szynekarczuk et al who confirmed the formation of elemental sulphur via the intermediate of polysulphides on the Pt electrode during the electrolysis of a Na₂S solution [154, 155]. The first anodic peak disappeared after the first scan, which was also observed in Figure 5.1-1 (d, e, f, g, h). This finding was identical to the study of gold in aqueous polysulphide solutions by Kelsall and Thompson, who suggested that the disappearance of this anodic peak after prolonged potential cycling was likely due to the presence of an absorbed sulphur layer[152]. Compared to other voltammograms in Figure 5.1-1, it shows that the deposition process corresponding to the first anodic peak could be accelerated by anodic polarization, which was also indicated by the CV study of Cu in a dilute Na₂S solution [159]. The cathodic peak shifted negatively to around -0.65 V vs Ag|AgCl_(sat) and increased significantly compared to that in Figure 5.1-1 (b), from ~ 0.3 mA cm⁻² to ~ 1.8 mA cm⁻². This indicated that more oxidized species had been produced during the anodic polarization process and were subsequently reduced in the cathodic polarization process.

As the maximum anodic potential increased to -0.1 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (d), the third anodic peak fully appeared at around -0.2 V vs Ag|AgCl_(sat). The second anodic peak was lower than that in Figure 5.1-1 (b, c) and shifted negatively along the

scans. The cathodic peak again shifted further negatively to around -0.7 V vs Ag|AgCl_(sat) and increased along the scans. It also became broader compared to that in Figure 5.1-1 (c), which indicated that multiple processes were likely happening during the cathodic polarization.

As the maximum anodic potential increased to 0 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (e), the second anodic peak further decreased compared to that in Figure 5.1-1 (b, c, d). The third anodic peak shifted slightly positively to around -0.18 V vs Ag|AgCl_(sat). The cathodic peak again shifted negatively to around -0.73 V vs Ag|AgCl_(sat) and became broader and larger compared to that in Figure 5.1-1 (d). The second and third anodic peaks and the cathodic peak all shifted negatively along the scans; the third anodic peak and the cathodic peak increased with scans whereas the second anodic peak remained constant along the scans. This was also found true in Figure 5.1-1 (f).

As the maximum anodic potential increased to 0.1 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (f), the second and third anodic peaks and the cathodic peak all increased compared to that in Figure (b, c, d, e). The positions of the second anodic peak and the cathodic peak did not change considerably compared to that in Figure 5.1-1 (e), whereas the third anodic peak shifted slightly negatively to around -0.23 V vs Ag|AgCl_(sat). A distinct difference of Figure 5.1-1 (f) compared to previous voltammograms was that the cathodic peak increased along the scans and then decreased after a few scans. This phenomenon was found to be more evident with increased maximum anodic potential, as shown in Figure 5.1-1 (g, h), and over extensive cycling, as shown in Figure 5.1-2 (c, d) and 5.1-3 (c, d), indicating a passivation of the glassy carbon disk electrode towards the reduction of aqueous polysulphide electrolytes at higher potentials (≥ 0.1 V vs Ag|AgCl_(sat)).

As the maximum anodic potential increased to 0.2 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (g), the second anodic peak decreased compared to that in Figure 5.1-1 (f). The third anodic peak shifted slightly positively to around -0.18 V vs Ag|AgCl_(sat), which was the same as in Figure 5.1-1 (e). The cathodic peak again shifted more negatively to around -0.78 V vs Ag|AgCl_(sat). Another cathodic peak appeared as a shoulder on the major cathodic peak, at around -0.65 V vs Ag|AgCl_(sat). This second cathodic peak supported the prior speculation that the cathodic polarization of aqueous polysulphide electrolyte involved multiple processes. Szynekarczuk et al suggested that the cathodic process of CV measurements of Pt in Na₂S solutions involved reduction of both elemental sulphur and

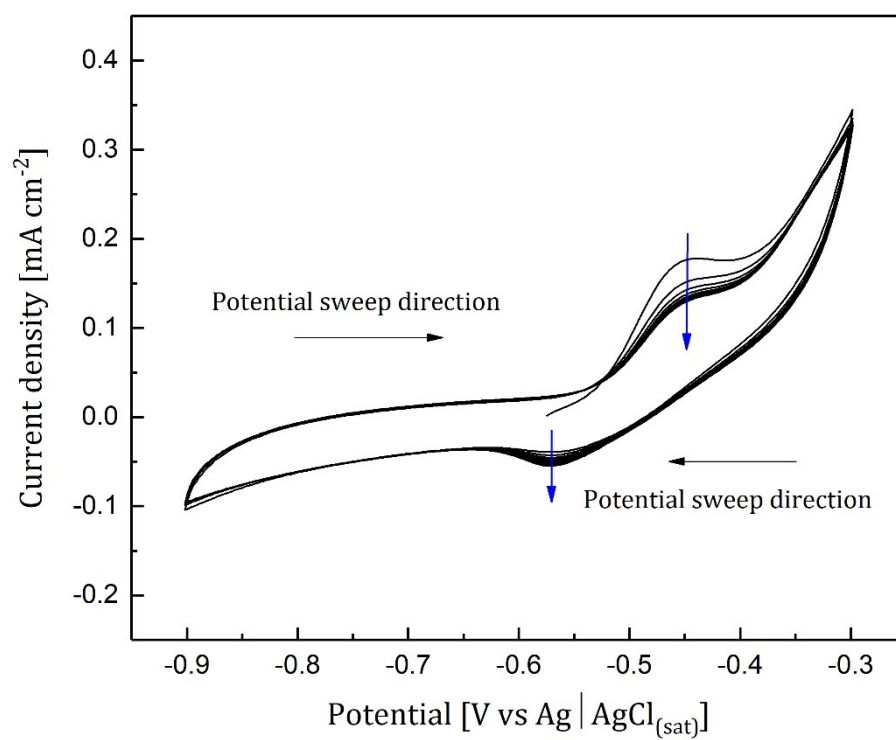
polysulphides [154]. Similarly, the second and third anodic peaks and the cathodic peak all shifted negatively along the scans; the second anodic peak stayed relatively constant along the scans and the third anodic peak increased along the scans. In addition, the considerable decrease of the anodic currents at the maximum anodic potentials suggested an evident passivation of the glassy carbon disk electrode, correlating to the deactivation of the glassy carbon disk electrode during the cathodic polarization process.

As the maximum anodic potential increased to 0.3 V vs Ag|AgCl_(sat), as shown in Figure 5.1-1 (h), the shoulder cathodic peak at around -0.65 V vs Ag|AgCl_(sat) became slightly clearer compared to that in Figure 5.1-1 (g). A slower scan rate might help to resolve the cathodic peaks more clearly. The major cathodic peak shifted further negatively to around -0.81 V vs Ag|AgCl_(sat) and grew even broader. The changes of the cathodic peaks and the anodic current at maximum anodic potential along the scans were found more evident in Figure 5.1-1 (h), suggesting that higher anodic potentials enhanced the passivation of glassy carbon disk electrode.

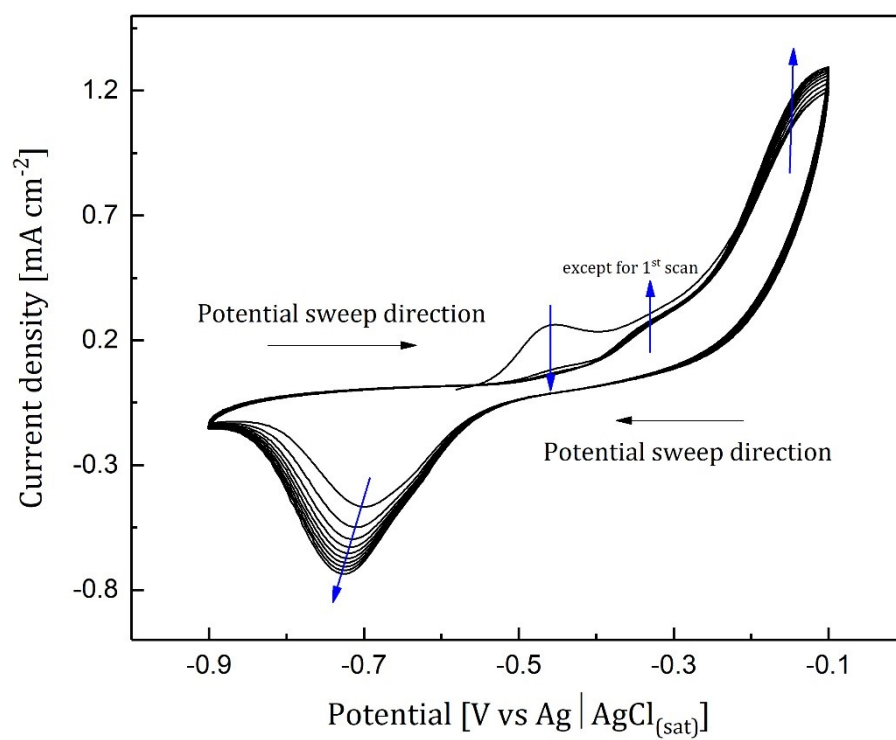
CV experiments of the glassy carbon disk electrode in the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte were also conducted for 10 cycles in potential windows with the maximum cathodic potential of -0.9 V or -1.1 V vs Ag|AgCl_(sat), as shown in Figure 5.1-2 and 5.1-3. Similar anodic and cathodic peaks as in Figure 5.1-1 had also been observed in Figure 5.1-2 and 5.1-3, whose variation trends in height and position also revealed more clearly in Figure 5.1-2 and 5.1-3 than in Figure 5.1-2. As an example, the shoulder cathodic peak at around -0.65 V vs Ag|AgCl_(sat) appeared more clearly in the cyclic voltammograms after the 5th cycle, as shown in Figure 5.1-2 (d) and 5.1-3 (d).

In addition, the passivation effect of the glassy carbon disk electrode at high anodic potentials also appeared on the third anodic peak which first increased along the scans but then started decreasing along the scans after a few cycles, as shown in Figure 5.1-2 (d) and 5.1-3 (d).

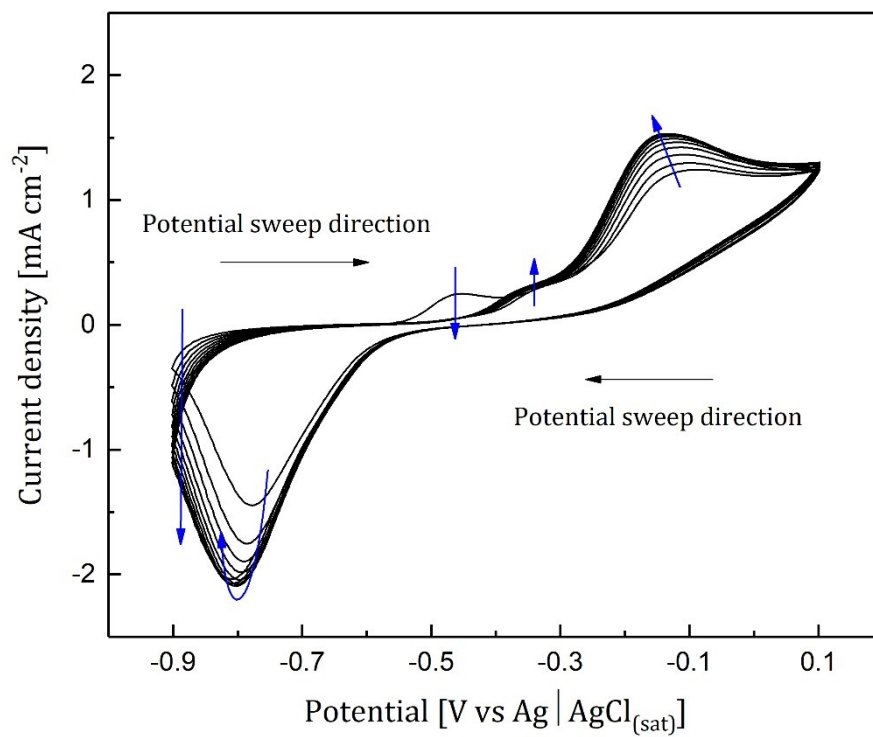
(a)



(b)



(c)



(d)

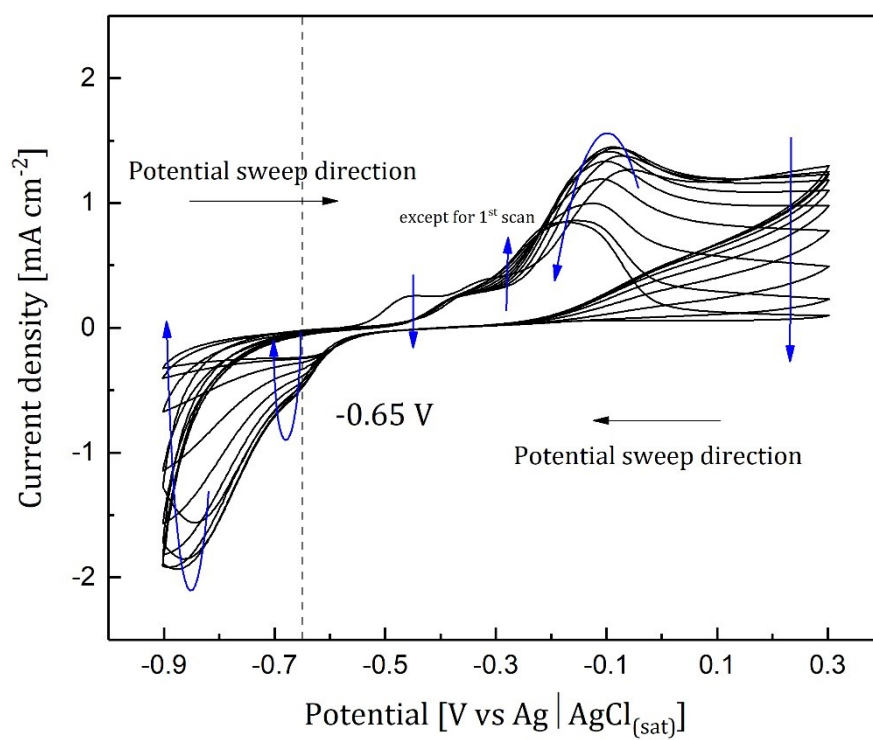
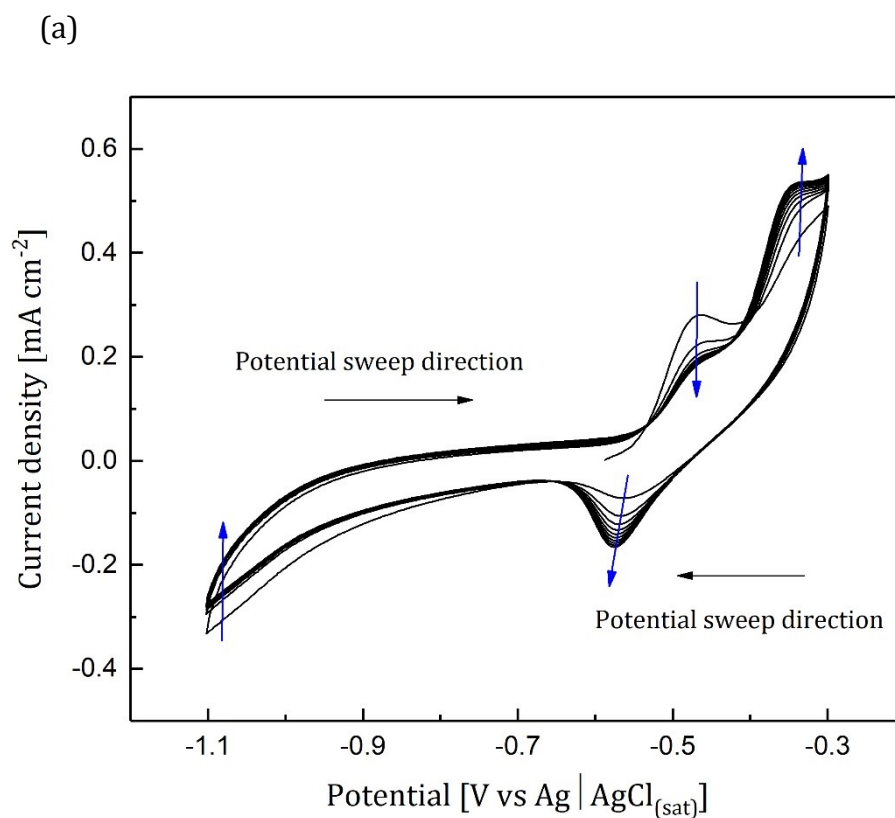
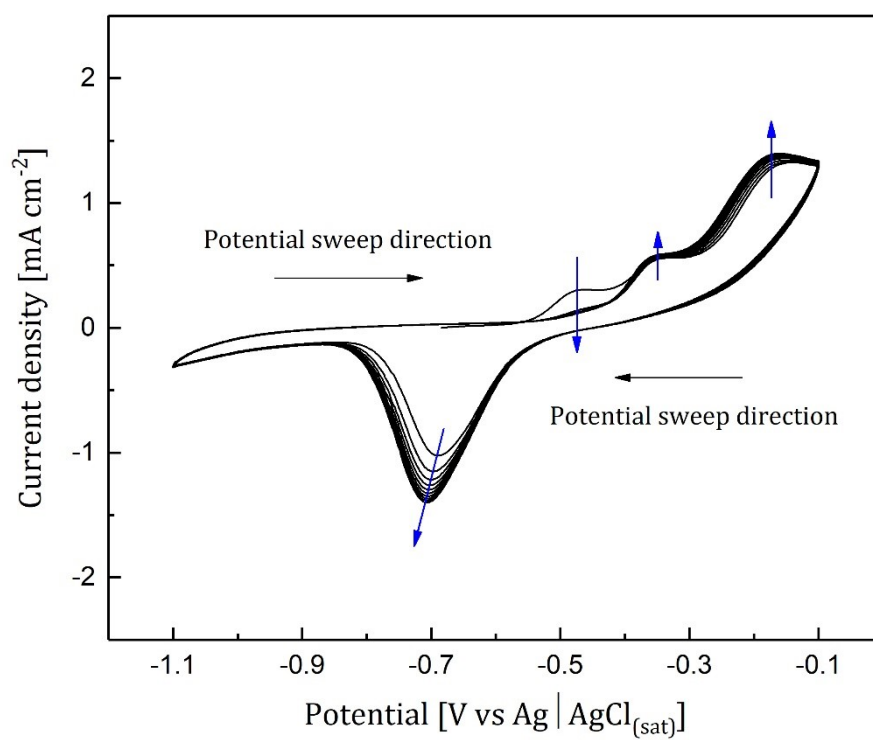


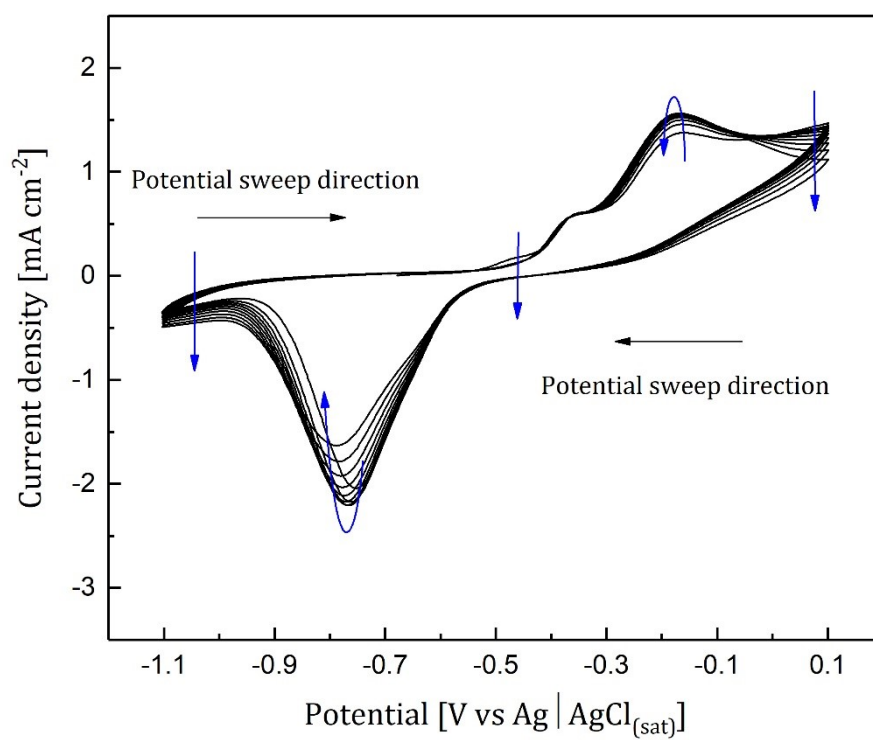
Figure 5.1-2 Cyclic voltammograms (10 cycles) of the glassy carbon disk electrode in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, performed at the scan rate of 20 mV s^{-1} and within the potential window of: (a) $-0.9 \text{ V} \sim -0.3 \text{ V}$, (b) $-0.9 \text{ V} \sim -0.1 \text{ V}$, (c) $-0.9 \text{ V} \sim 0.1 \text{ V}$, (d) $-0.9 \text{ V} \sim -0.3 \text{ V}$.



(b)



(c)



(d)

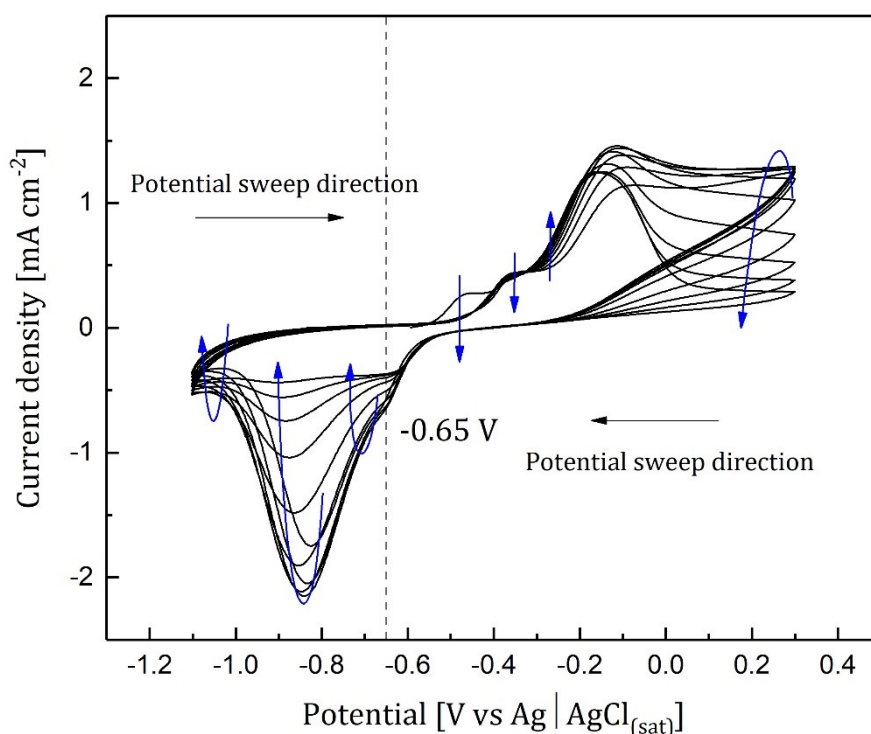


Figure 5.1-3 Cyclic voltammograms (10 cycles) of the glassy carbon disk electrode in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte, performed at the scan rate of 20 mV s^{-1} and within the potential window of : (a) $-1.1 \text{ V} \sim -0.3 \text{ V}$, (b) $-1.1 \text{ V} \sim -0.1 \text{ V}$, (c) $-1.1 \text{ V} \sim 0.1 \text{ V}$, (d) $-1.1 \text{ V} \sim -0.3 \text{ V}$.

5.1.1.2 In the Concentrated Polysulphide Electrolyte

Figure 5.1-4 shows the cyclic voltammogram of the glassy carbon disk electrode in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte at the scan rate of 20 mV s^{-1} and within the potential window of $-0.9 \text{ V} \sim 0.3 \text{ V}$ vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$.

Compared to the cyclic voltammograms of glassy carbon disk electrode in the dilute polysulphide electrolyte, as shown in Figure 5.1-1 to 5.1-3, the first anodic peak and the cathodic peaks disappeared in Figure 5.1-4. The cathodic current ($< 0.2 \text{ mA cm}^{-2}$ at -0.9 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$) became negligible compared to the anodic current, which was even less than in the dilute polysulphide electrolyte at corresponding potentials. In addition, the decrease in anodic current after the third anodic peak was more evident in the

concentrated polysulphide electrolyte than in the dilute polysulphide electrolytes. These phenomena are likely attributed to the enhanced passivation process in the concentrated polysulphide electrolyte due to the remarkably higher concentrations of sulphide and polysulphide species, as shown in Table 4.1-2. The high concentrations of sulphur species also led to the considerable increase of the second and third anodic peaks of the cyclic voltammogram of glassy carbon disk electrode in the concentrated polysulphide electrolyte.

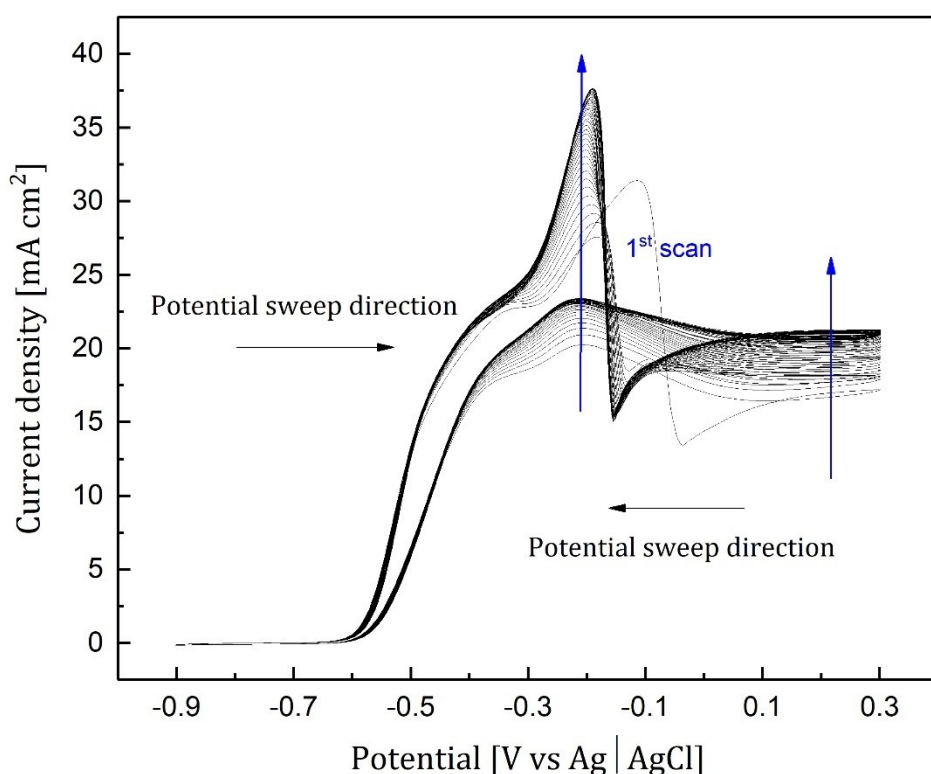


Figure 5.1-4 Cyclic voltammogram of the glassy carbon disk electrode in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s⁻¹ and within the potential window of -0.9 V ~ 0.3 V vs Ag/AgCl_(sat).

5.1.1.3 In the Supporting Electrolyte

CV experiments of the glassy carbon disk electrode in the 1 mol kg⁻¹ NaOH electrolyte, as shown in Figure 5.1-5, did not observe any of the peaks revealed in the cyclic

voltammograms in polysulphide electrolytes. Hence, it can be concluded that all the anodic and cathodic peaks in Figure 5.1-1 to 5.1-4 were related to reactions involving sulphide and polysulphide species.

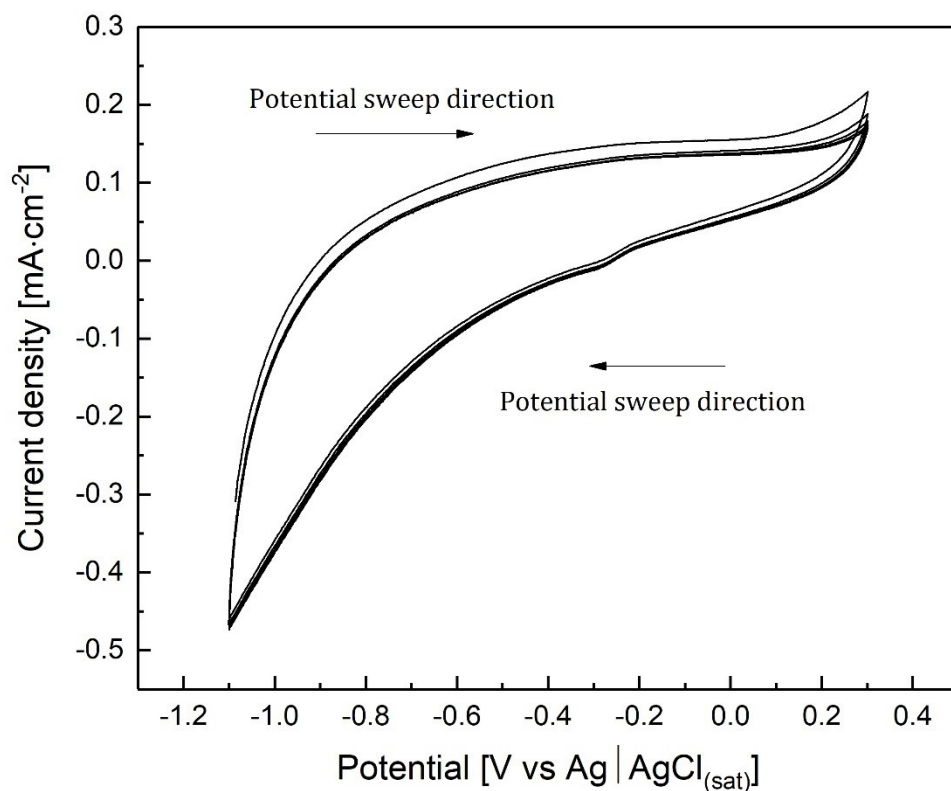


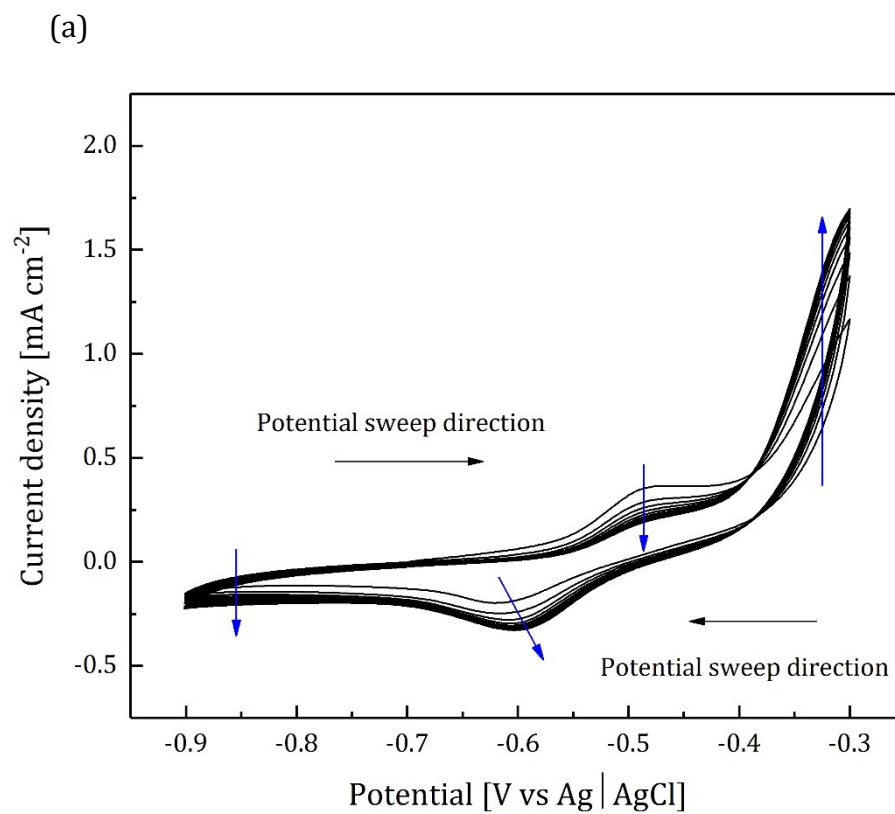
Figure 5.1-5 Cyclic voltammograms (5 cycles) of glassy carbon disk electrode in the 1 mol kg⁻¹ NaOH electrolyte, at the scan rate of 20 mV s⁻¹ and within the potential window of -1.1 ~ 0.3 V vs Ag/AgCl_(sat)

5.1.2 Nickel

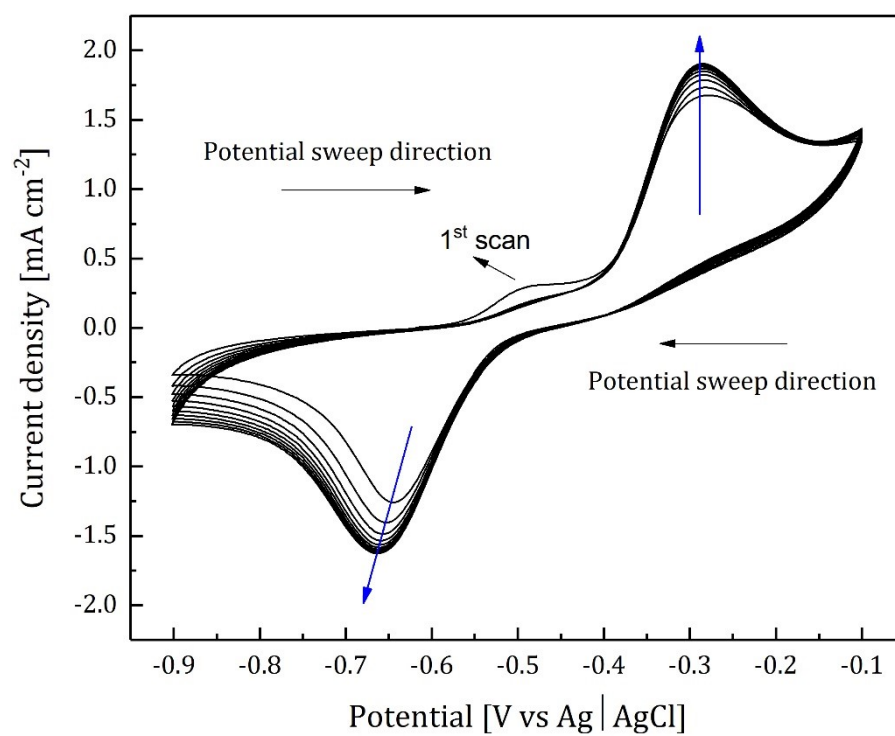
5.1.2.1 In the Dilute Polysulphide Electrolyte

Figure 5.1-6 shows the cyclic voltammograms (10 cycles) of the nickel disk electrode in the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s⁻¹ and within a variety of potential windows. All CV measurements in Figure 5.1-6 had a

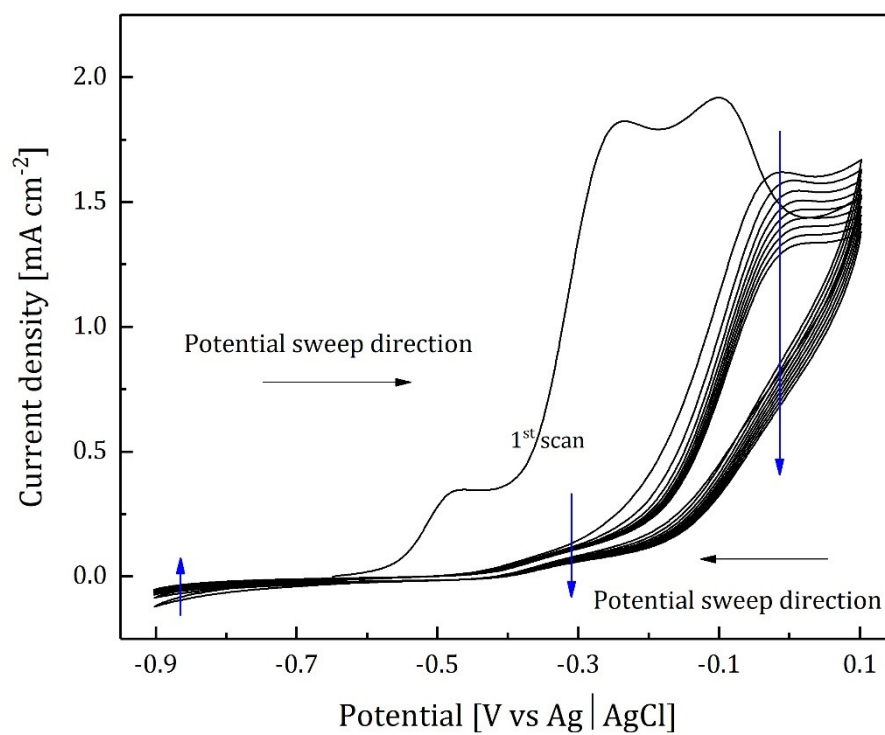
maximum cathodic potential of $-0.9\text{ V vs Ag|AgCl}_{(\text{sat})}$ with the maximum anodic potential increased from -0.3 to $0.3\text{ V vs Ag|AgCl}_{(\text{sat})}$ with a step change of 200 mV .



(b)



(c)



(d)

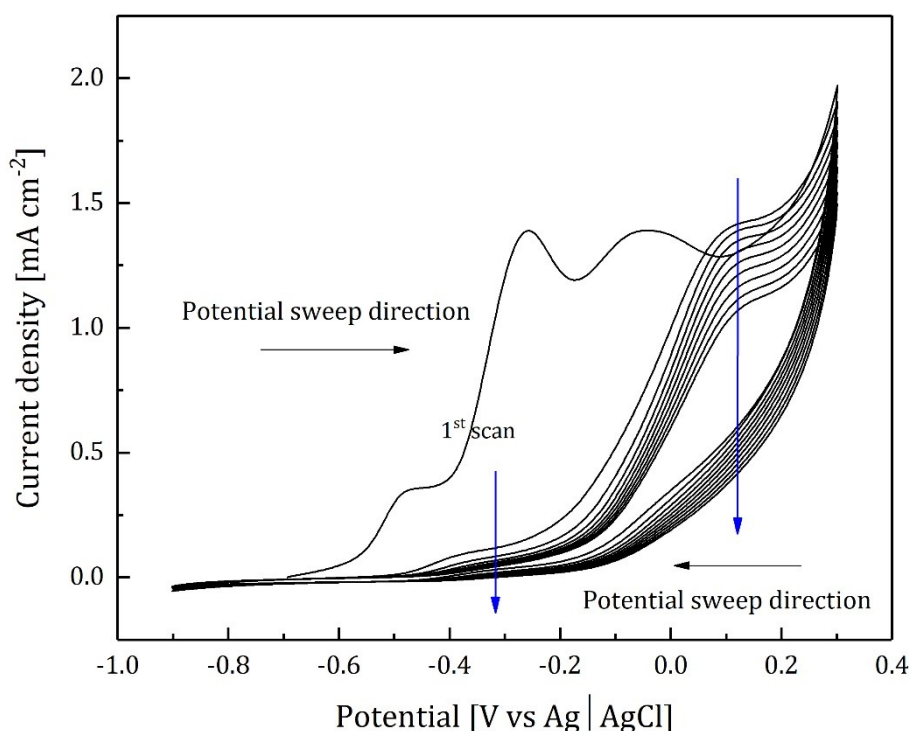


Figure 5.1-6 Cyclic voltammograms (10 cycles) of the nickel disk electrode in the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s⁻¹ and within the potential window of: (a) -0.9 V ~ -0.3 V, (b) -0.9 V ~ -0.1 V, (c) -0.9 V ~ 0.1 V, (d) -0.9 V ~ 0.3 V.

In Figure 5.1-6 (a), where the nickel disk electrode is cycled between -0.9 V ~ -0.3 V vs Ag|AgCl_(sat), an anodic peak and a cathodic peak were observed. The anodic peak appeared at around -0.5 V vs Ag|AgCl_(sat) and decreased along the scans. This anodic peak, similar to the first anodic peak observed for the glassy carbon disk electrode in the same electrolyte, was ascribed to the growth of a NiS 3D layer [153]. The cathodic peak, appeared at around -0.61 V vs Ag|AgCl_(sat), shifted positively and increased along the scans. The cathodic peak likely corresponded to the reduction of absorbed polysulphide species on the surface of the NiS-coated nickel disk electrode [153]. The anodic current at maximum anodic potential also increased along the scans. Both phenomena likely suggested an increased catalytic activity of the nickel disk electrode over the potential cycling. This result was not surprising since nickel sulphides, recognized as better

catalysts than the metallic nickel towards aqueous S_x^{2-}/HS^- redox reactions, were formed and aggregated on the surface of the nickel disk electrode over the CV measurements.

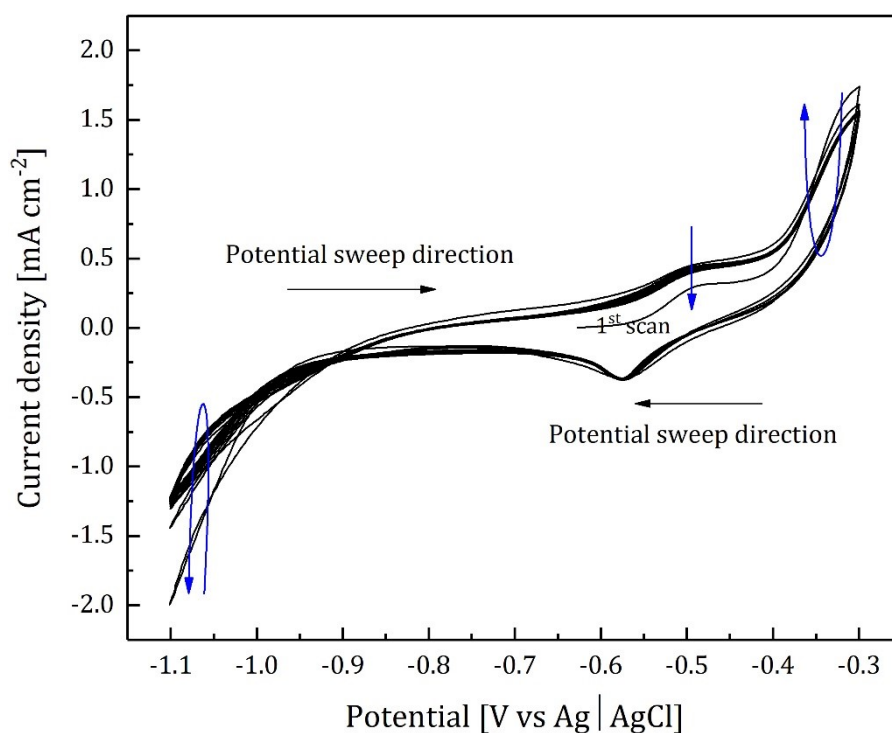
As the maximum anodic potential increased to -0.1 V vs $Ag|AgCl_{(sat)}$, as shown in Figure 5.1-6 (b), a second anodic peak appeared at around -0.28 V vs $Ag|AgCl_{(sat)}$ which increased along the scans, corresponding to the electrochemical formation of polysulphide species on the NiS-coated surface of the nickel disk electrode [153]. The cathodic peak shifted negatively to around -0.65 V vs $Ag|AgCl_{(sat)}$. Identical to the CV measurements of the glassy carbon disk electrode under the same conditions, the first anodic peak disappeared after the first scan, and the cathodic peak increased and shifted negatively along the scans.

As the maximum anodic potential increased to 0.1 V vs $Ag|AgCl_{(sat)}$, as shown in Figure 5.1-6 (c), a third anodic peak appeared at around -0.1 V vs $Ag|AgCl_{(sat)}$. However, after the first scan, the voltammogram in Figure 5.1-6 (c) underwent significant changes, where the second and third anodic peaks decreased and shifted to more positive potentials. In addition, the cathodic peak completely disappeared and the cathodic current decreased dramatically ($\sim 0.12 \text{ mA cm}^{-2}$ at -0.9 V vs $Ag|AgCl_{(sat)}$). Passivation of the nickel disk electrode was therefore speculated within the potential range of -0.1 V $\sim$ 0.1 V vs $Ag|AgCl_{(sat)}$. Both the anodic and the cathodic current decreased along the scans, suggesting a continuous passivation of the nickel disk electrode over the CV scans. Comparing the cyclic voltammograms of glassy carbon and nickel disk electrodes performed within -0.9 V $\sim$ 0.1 V vs $Ag|AgCl_{(sat)}$, as shown in Figure 5.1-2 (c) and Figure 5.1-6 (c), it can be suggested that passivation of the nickel disk electrode was more prominent than that of the glassy carbon disk electrode under the same anodic polarization conditions.

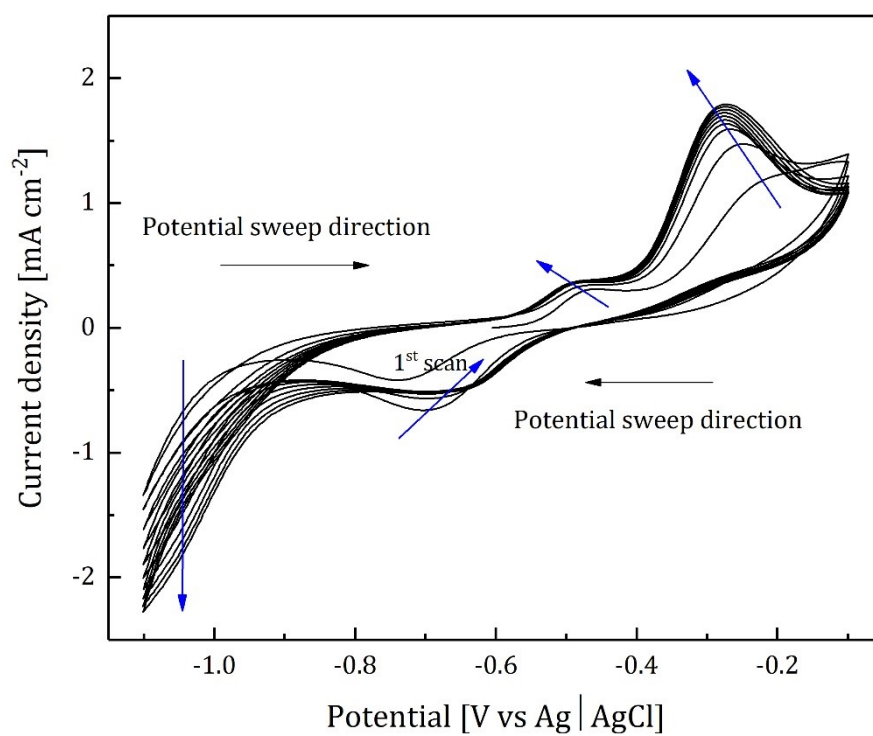
Further increase of the maximum anodic potential seemed to intensify the passivation of nickel disk electrode, as shown in Figure 5.1-6 (c, d). Similar changes of the anodic peaks were observed in Figure 5.1-6 (c) and Figure 5.1-6 (d). Both anodic and cathodic current reduced in Figure 5.1-6 (d), as compared to that in Figure 5.1-6 (c), indicating a more significant passivation of the nickel disk electrode at higher anodic potentials ($\geq 0.1 \text{ V vs } Ag|AgCl_{(sat)}$).

CV measurements of nickel disk electrode in the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte were also performed with the maximum cathodic potential of -1.1 V vs $\text{Ag}|\text{AgCl}_{(\text{sat})}$, as shown in Figure 5.1-7. Variations in the maximum cathodic potential applied seemed to have much large effect on the cyclic voltammograms of the nickel disk electrode than that of the glassy carbon disk electrode.

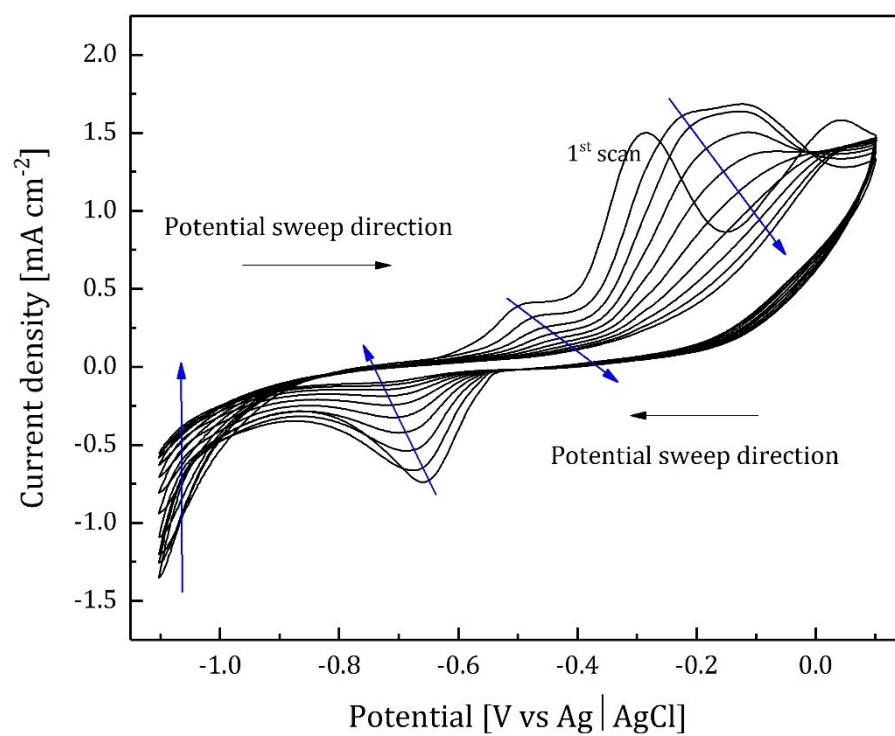
(a)



(b)



(c)



(d)

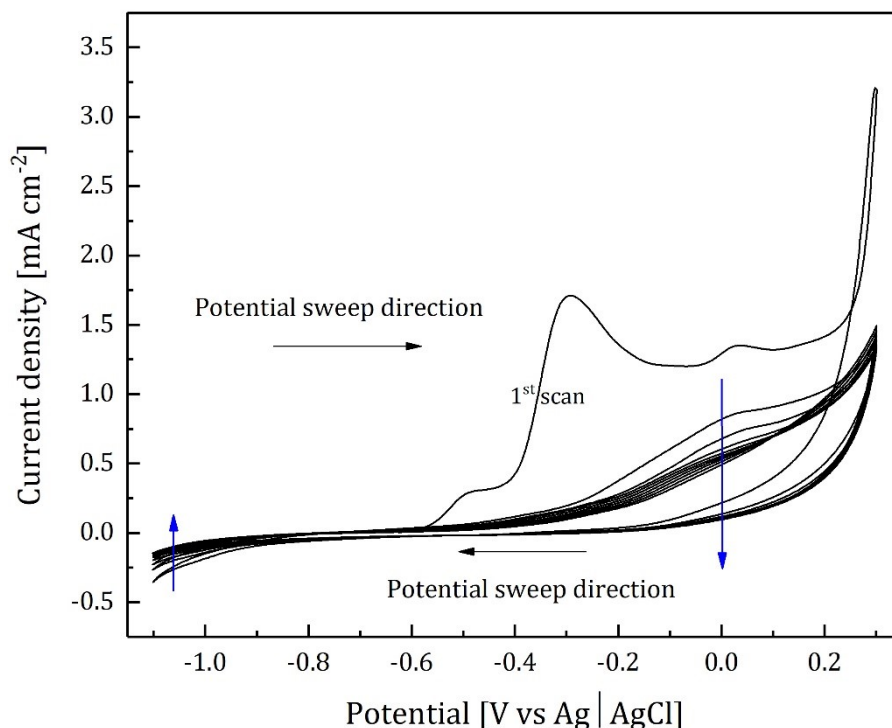


Figure 5.1-7 Cyclic voltammograms of nickel disk electrode in the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at the scan rate of 20 mV s⁻¹ within a variety of potential windows: (a) -1.1 V ~ -0.3 V, (b) -1.1 V ~ -0.1 V, (c) -1.1 V ~ 0.1 V, (d) -1.1 V ~ -0.3 V.

The first anodic peak did not disappear in the first two cyclic voltammograms, as shown in Figure 5.1-7 (a, b). Instead, the first anodic peak increased during the second scan and remained relatively consistent in the later scans, as shown in Figure 5.1-7 (a); the first anodic peak increased along the scans, as shown in Figure 5.1-7 (b). This suggested that at sufficiently negative potentials (-1.1 V ~ -0.9 V vs Ag|AgCl_(sat)), the initially formed NiS 3D layer would likely be reduced. The different observations of the first anodic peak in Figure 5.1-7 (a) and 5.1-7 (b) due to the increased maximum anodic potential suggested that either the NiS layer was continuously formed at higher anodic potentials (-0.45 V ~ -0.1 V vs Ag|AgCl_(sat)) or the species formed at higher anodic potentials, corresponding to the second anodic peak, were easier to reduce than NiS.

Comparison of Figure 5.1-6 (c) and Figure 5.1-7 (c) clearly showed that higher cathodic overpotentials (< -0.9 V vs Ag|AgCl_(sat)) were able to eliminate the passivation of the

nickel disk electrode. As can be seen from Figure 5.1-7 (c), increasing the maximum cathodic potential to -1.1 V vs Ag|AgCl_(sat) only delayed the passivation process however could not eliminate the passivation of the disk electrode. This suggested that sufficient polarization time or higher cathodic overpotentials would be required in order to fully reactivate the passivated nickel disk electrode. Figure 5.1-7 (d) further demonstrated the prior speculation, as the cathodic polarization process up to a maximum cathodic potential of -1.1 V vs Ag|AgCl_(sat), was not enough to reactivate the passivated surface layer of the nickel disk electrode formed during the anodic polarization process up to 0.3 V vs Ag|AgCl_(sat).

5.1.2.2 In the Concentrated Polysulphide Electrolyte

Figure 5.1-8 shows the cyclic voltammogram of the nickel disk electrode in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, performed at the scan rate of 20 mV s⁻¹ and within the potential window of -0.9 V ~ 0.3 V vs Ag|AgCl_(sat).

The anodic processes taking place within the potential window of -0.5 V ~ 0.05 V vs Ag|AgCl_(sat) were ascribed to the electrochemical formation of polysulphide and sulphur species on the NiS-covered nickel disk electrode [153]. Therefore, the transformation between the two anodic peaks, at around -0.35 V and 0 V vs Ag|AgCl_(sat) respectively, suggest that formation of sulphur species on the surface of the nickel disk electrode was more favoured than the formation of polysulphide species over the potential cycling.

A reactivation of nickel disk electrode at high anodic overpotentials (>0.1 V vs Ag|AgCl_(sat)) was observed after a few cycles. This reactivation phenomenon was suggested corresponding to the pitting corrosion of Ni as the composite surface layer grows thicker [153].

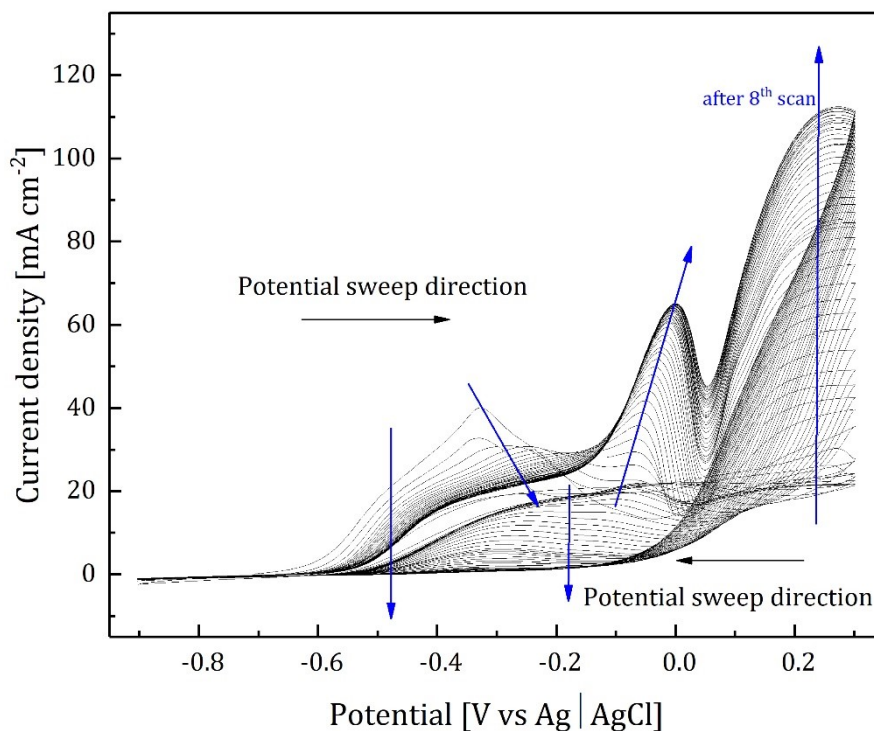


Figure 5.1-8 Cyclic voltammogram of nickel disk electrode in 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte at the scan rate of 20 mV s⁻¹ within the potential window of -0.9 V ~ 0.3 V vs Ag/AgCl_(sat).

5.1.2.3 In the Supporting Electrolyte

CV measurements of the nickel disk electrode in the 1 mol kg⁻¹ NaOH electrolyte within the potential window of -1.1 V ~ 0.3 V vs Ag|AgCl_(sat) is shown in Figure 5.1-9. An anodic peak at very negative potentials in the positive scans was observed, corresponding to the oxidation of nickel to nickel hydroxide [239]. This anodic peak decreased along the scans and finally disappeared due to the depletion of metallic nickel on the surface of nickel disk electrode. Apart from that, the current observed in the CV measurements of the nickel disk electrode in the 1 mol kg⁻¹ NaOH electrolyte was negligible (< ±0.1 mA cm⁻² at -1.1 or 0.3 V vs Ag|AgCl_(sat)) compared to that in aqueous polysulphide electrolytes. As a result, it can be concluded that all the anodic and cathodic peaks in Figure 5.1-6 - 5.1-8

were related to sulphide and polysulphide species. And the effect of OH^- on the cyclic voltammograms of nickel in aqueous polysulphide electrolytes can be neglected.

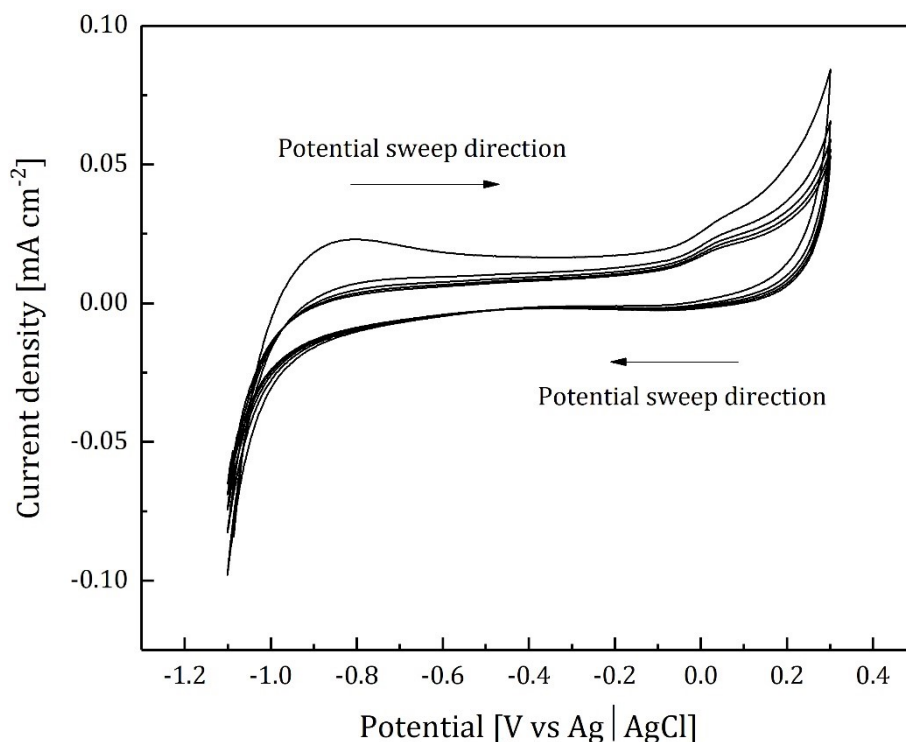


Figure 5.1-9 Cyclic voltammograms (5 cycles) nickel disk electrode in the 1 mol kg⁻¹ NaOH electrolyte at the scan rate of 20 mV s⁻¹ and within the potential window of -1.1 V ~ 0.3 V vs Ag/AgCl_(sat)

5.2 Polarization Tests

5.2.1 Potentiodynamic Polarization Tests

Potentiodynamic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte were conducted by LSV with a slow scan rate of 1 mV s⁻¹, as demonstrated in Figure 5.2-1.

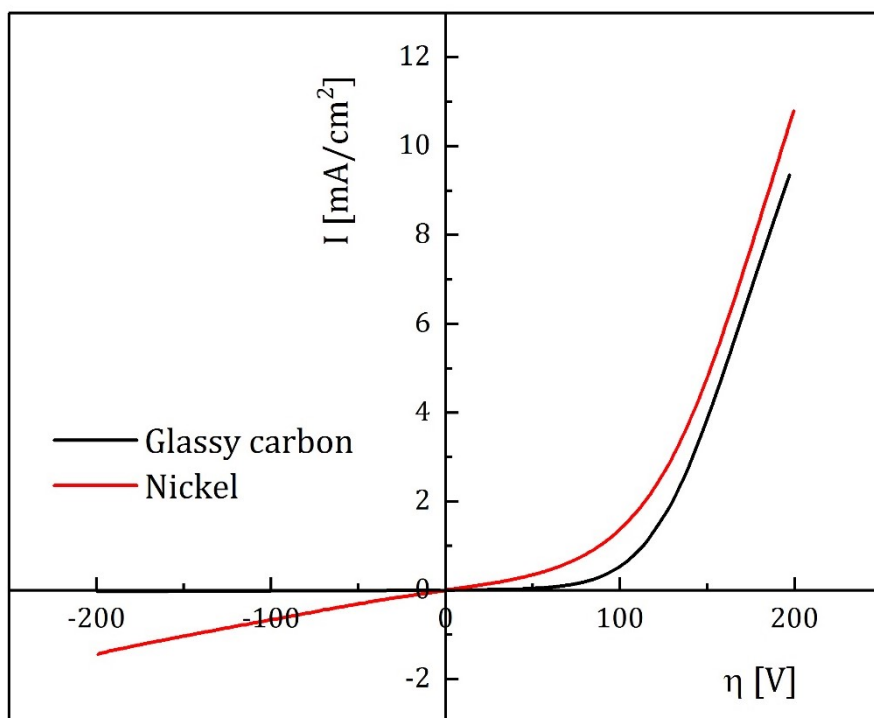


Figure 5.2-1 Potentiodynamic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

It was clear from Figure 5.2-1 that nickel exhibited better catalytic activities than glassy carbon in aqueous polysulphide electrolytes, especially for the cathodic polarization process. In addition, both glassy carbon and nickel had displayed better catalytic activities for the anodic polarization process than for the cathodic polarization process of aqueous polysulphide electrolytes.

5.2.2 Potentiostatic Polarization Tests

Potentiodynamic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte were performed by chronoamperometry. The overpotentials and their corresponding current for the potentiostatic polarization of glassy carbon and nickel disk electrodes are summarized in Table 5.2-1.

Table 5.2-1 Potentiostatic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Electrode	Anodic polarization		Cathodic polarization	
	Overpotential / mV	Current density / mA cm ⁻²	Overpotential / mV	Current density / mA cm ⁻²
Glassy carbon	20	1.12×10 ⁻³	-20	6.12×10 ⁻⁴
	40	3.52×10 ⁻³	-40	1.02×10 ⁻³
	60	9.44×10 ⁻³	-60	1.53×10 ⁻³
	80	2.58×10 ⁻²	-80	2.04×10 ⁻³
	100	7.52×10 ⁻²	-100	2.45×10 ⁻³
	120	2.18×10 ⁻¹	-120	2.96×10 ⁻³
	140	6.07×10 ⁻¹	-140	3.57×10 ⁻³
	160	1.14	-160	4.39×10 ⁻³
	180	4.30	-180	4.80×10 ⁻³
	200	5.99	-200	6.22×10 ⁻³
nickel	20	7.55×10 ⁻²	-20	-6.79×10 ⁻²
	40	1.91×10 ⁻¹	-40	-1.42×10 ⁻¹
	60	3.87×10 ⁻¹	-60	-2.40×10 ⁻¹
	80	7.50×10 ⁻¹	-80	-3.70×10 ⁻¹
	100	1.36	-100	-5.51×10 ⁻¹
	120	2.35	-120	-7.96×10 ⁻¹
	140	3.82	-140	-1.13
	160	5.77	-160	-1.54
	180	7.91	-180	-2.18
	200	1.01×10 ¹	-200	-2.72

5.2.3 Exchange Current Densities

In order to have a quantitative comparison of the catalytic activities between glassy carbon and nickel disk electrodes, results of both potentiodynamic and potentiostatic polarization tests are displayed in Tafel plots, as shown in Figure 5.2-2 and 5.2-3 .

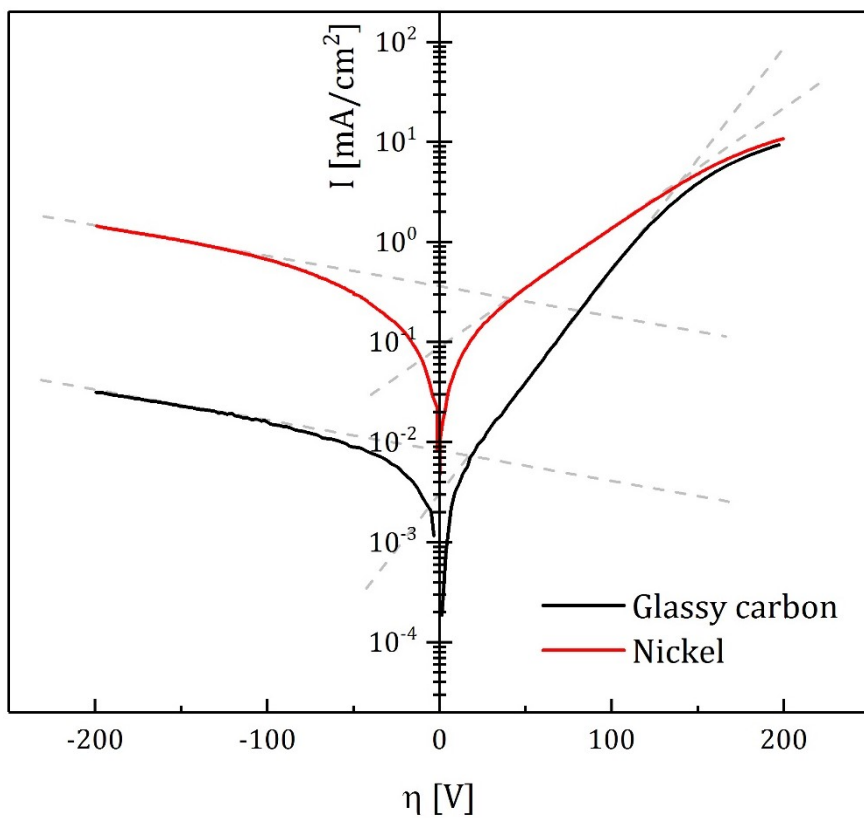


Figure 5.2-2 Tafel plots of the potentiodynamic polarization of glassy carbon and nickel disk electrodes in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte

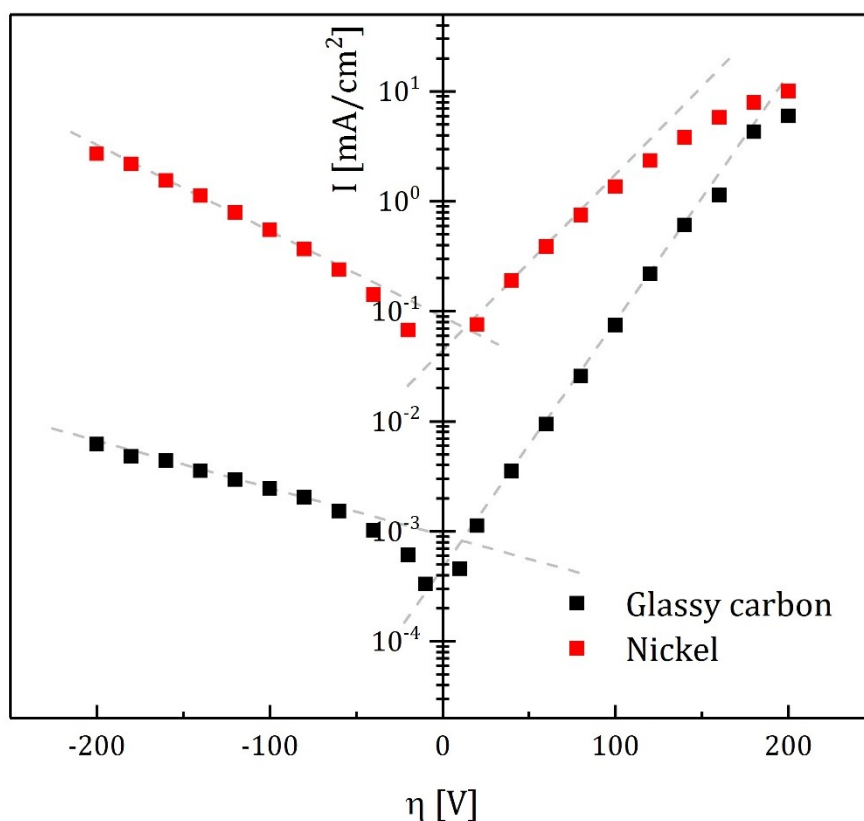


Figure 5.2-3 Tafel plots of the potentiostatic polarization of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

It can be seen from Figure 5.2-2 and 5.2-3, that neither glassy carbon nor nickel disk electrode showed classic Tafel relationships in the aqueous polysulphide electrolyte, which was identical to the findings of Remick and Camara [136]. However, it was shown from Figure 5.2-2 and 5.2-3 that the potentiostatic polarization of both glassy carbon and nickel disk electrodes had shown better Tafel relationships than their corresponding potentiodynamic polarization. As a result, the exchange current densities (i_0) of all electrodes characterized in the next chapter (Chapter 6) were derived based on potentiostatic polarization measurements.

Due to the asymmetry of the anodic and cathodic polarization of both glassy carbon and nickel disk electrodes, the exchange current densities of the anodic and cathodic polarization processes were individually extrapolated for the two electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte. The averaged values of the anodic and cathodic exchange current densities were then used to represent the exchange current densities

of the corresponding electrode, as adopted by Mahmoudzadeh et al [46]. The derived exchange current densities from both potentiodynamic and potentiostatic polarization tests of the glassy carbon and nickel disk electrodes are summarized in Table 5.2-2 .

Table 5.2-2 Exchange current densities of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Electrode	Method	<i>i</i>₀ / mA cm⁻²
Glassy carbon	LSV	5.40×10 ⁻³
	Chronoamperometry	6.97×10 ⁻⁴
Nickel	LSV	2.25×10 ⁻¹
	Chronoamperometry	6.75×10 ⁻²

It shows that the exchange current density of nickel disk electrode was nearly 2 orders of magnitude higher than that of the glassy carbon disk electrode, showing nickel to be a better catalyst for aqueous S_x²⁻/HS⁻ redox reactions than glassy carbon.

5.3 Conclusions

Multiple peaks were observed in the cyclic voltammograms of glassy carbon and nickel disk electrodes in aqueous polysulphide electrolytes, indicating that the electrochemical processes associated with the polarization of aqueous polysulphide electrolytes with glassy carbon or nickel disk electrode were highly complex and involved multiple reactions.

Three anodic peaks and two cathodic peaks were observed in the cyclic voltammograms of glassy carbon and nickel disk electrode in the 0.02 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte within the potential window of -1.1 ~ 0.3 V vs Ag|AgCl_(sat). The first anodic peak likely corresponded to the deposition of a thin layer of elemental sulphur on the surface of the glassy carbon disk electrode or the formation of a NiS 3D layer on the surface of the nickel disk electrode [152, 153]. The second and third anodic peaks were likely related to the electrochemical formation of polysulphide and sulphur species

respectively on the initially formed thin sulphur layer or NiS 3D layer [152-155]. The cathodic peaks corresponded to the reduction of polysulphides and sulphur species on the electrode surface[152]. However, there has not been any direct experimental proof confirming the existence of the initially formed sulphur/NiS 3D layers or the absorbed polysulphide/sulphur species on the surface of the electrode during the polarization of the aqueous polysulphide electrolytes.

At high anodic potentials (≥ 0.1 V vs vs Ag|AgCl_(sat)), both glassy carbon and nickel disk electrodes had suffered from passivation problems according to this study. Notably, passivation of the nickel disk electrode was more prominent than the glassy carbon disk electrode under the same anodic polarization conditions. Cathodic polarization at considerably negative potentials was found useful to reactive the passivated nickel disk electrode.

Polarization tests of glassy carbon and nickel disk electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte suggested that both glassy carbon and nickel exhibited better catalytic activities towards the oxidation than the reduction of aqueous polysulphide electrolytes. The exchange current density of the nickel disk electrode derived from both potentiodynamic and potentiostatic polarization tests were nearly 2 magnitude higher than that of the glassy carbon disk electrode, suggesting nickel as a better catalyst for aqueous S_x²⁻/HS⁻ redox reactions compared to glassy carbon.

Chapter 6 Electrodes for aqueous polysulphide electrolyte

This chapter discusses the electrocatalytic performances of carbon paper, Ni foam and nickel sulphide/carbon paper electrodes for aqueous S_x^{2-}/HS^- redox reactions, using potentiodynamic polarization measurements. Exchange current densities of each electrode were derived from the polarization measurements based on the geometric area of the electrodes. A 0.9 mm thick sulphidised Ni foam was demonstrated as the anode for a 5 cm² single-cell polysulphide-air RFB.

6.1 Carbon Paper

SGL 10AA GDL carbon paper was heat-treated under a variety conditions, as summarized in Table 3.4-1 (Chapter 3), to increase its hydrophilicity. After the thermal treatment, drop tests using deionized water were conducted for the untreated and heat-treated SGL 10AA carbon papers, as shown in Figure 6.1-1.

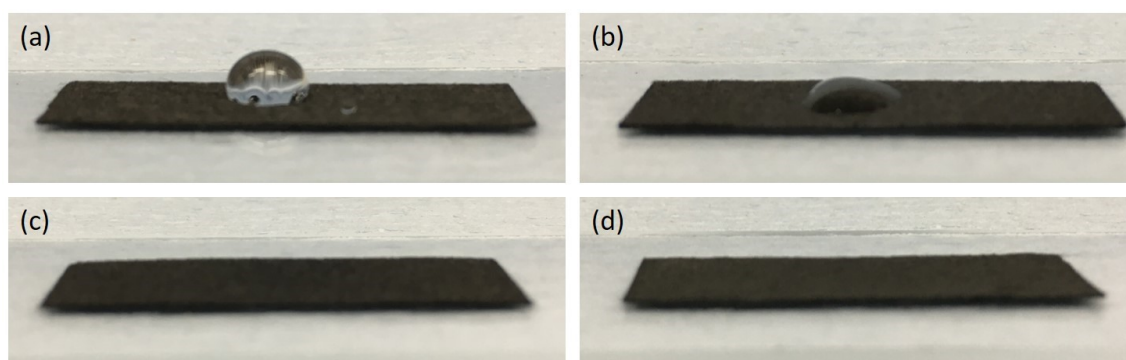


Figure 6.1-1 Drop test with deionized water of SGL 10AA carbon papers heat-treated under various conditions: (a) untreated, (b) 400°C - 30 hr treated, (c) 450°C - 6 hr treated, and (d) 500°C - 6 hr treated.

It is clear from Figure 6.1-1 that the hydrophilicity of SGL 10AA carbon paper increased with the temperature of the thermal treatment. The contact angle between the deionized water droplet and the 400°C-6hr treated carbon paper was much smaller than that of the untreated carbon paper. The 450°C-6 hr and 500°C-6 hr treated carbon papers showed complete wetting by deionized water.

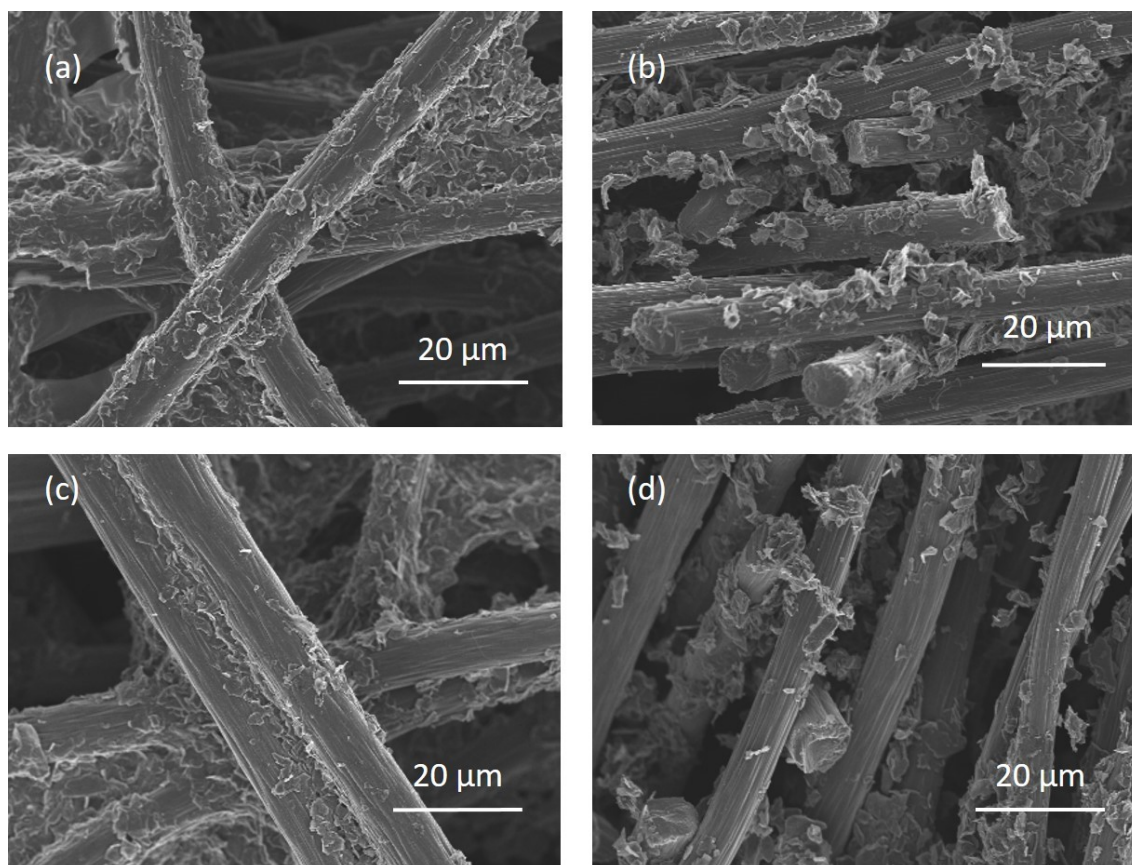


Figure 6.1-2 Cross-section SEM images of the untreated and 450°C-6hr treated SGL 10AA carbon papers: (a) surface of the untreated carbon paper, (b) cross-section of the untreated carbon paper, (c) surface of the 450°C-6hr treated carbon paper, and (d) cross-section of the 450°C-6hr treated carbon paper

However, the rigidity of the SGL 10AA carbon paper decreased with increasing temperature and duration of the thermal treatment, probably due to the increasing loss of binder within the carbon paper as shown in Figure 6.1-2. In addition, a weight loss of

~1.25% was observed for the 450°C-6hr treated carbon paper, which further proved the loss of binders during the thermal treatment.

As a result, 450°C for 6 hr was chosen in this study to pre-treat the SGL 10AA carbon paper before further processing or characterization, which gave the carbon paper sufficient hydrophilicity while maintaining most of its mechanical strength.

Potentiodynamic polarization of the untreated and 450°C-6hr treated carbon paper in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte are demonstrated in Figure 6.1-3. Similar to the glassy carbon disk electrode, the carbon paper electrodes exhibited much better anodic catalytic activities than cathodic catalytic activities towards aqueous S_x²⁻/HS⁻ redox reactions, as shown in Figure 6.1-3 (a). In addition, the 450°C-6hr treated carbon paper exhibited better catalytic activities than the untreated carbon paper for both anodic and cathodic polarization of the aqueous polysulphide electrolyte, due to the better wetting of the heat-treated carbon paper.

The exchange current densities (averaged value of anodic and cathodic exchange current densities) of the untreated and 450°C-6hr treated carbon paper electrodes, derived from Figure 6.1-3 (b), together with the current densities achieved at ±200 mV of each electrode are summarized in Table 6.1-1. Note that the exchange current densities were calculated based on the geometric area rather than the true surface area of the electrodes.

Table 6.1-1 Exchange current densities and current densities at ±200 mV of the untreated and 450°C-6hr treated carbon paper electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Carbon paper electrode	Exchange current density / mA cm⁻²	Current density at 200 mV / mA cm⁻²	Current density at -200 mV / mA cm⁻²
Untreated	0.29	13.3	-0.51
450°C-6hr treated	0.839	17.2	-1.14

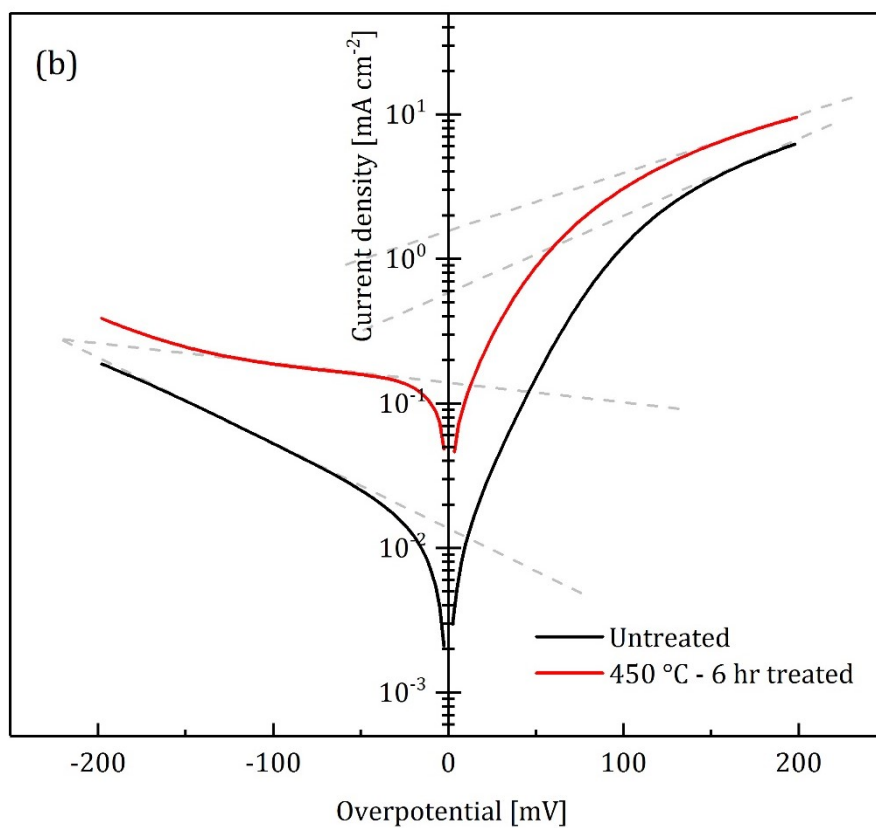
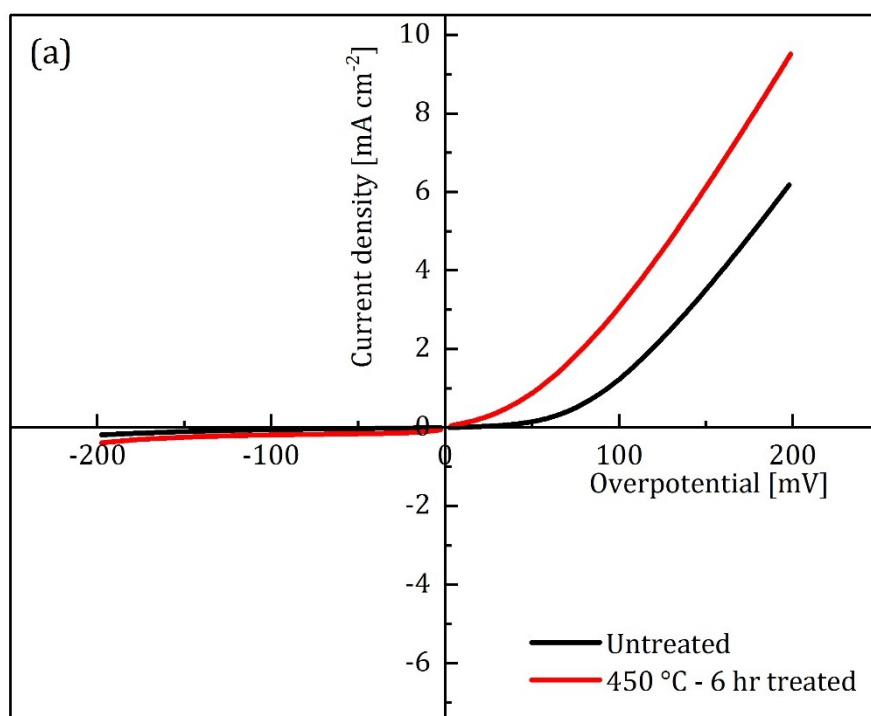


Figure 6.1-3 Potentiodynamic polarization of the untreated and 450°C-6hr treated carbon papers in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte: (a) linear plot, (b) Tafel plot.

6.2 Ni Foam

Three Ni foam electrodes (0.9 mm thick, 99.5%, GoodFellow) were characterized in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte in this study, including an acid-treated Ni foam and two sulphidised acid-treated Ni foams. Acid treatment and sulphidisation treatment of nickel foams are discussed in detail in Section 3.4.

SEM images of these three Ni foam electrodes are shown in Figure 6.2-1. It can be seen from Figure 6.2-1 (b) that the surface of the acid-treated Ni foam was much coarser than the untreated Ni foam, suggesting that acid-treatment not only removed the surface oxide scale but also increased the surface roughness and hence surface area of the Ni foam. After sulphidisation, the surface of the Ni foams were covered with a layer of nickel sulphides [45], as shown in Figure 6.2-1 (c, d).

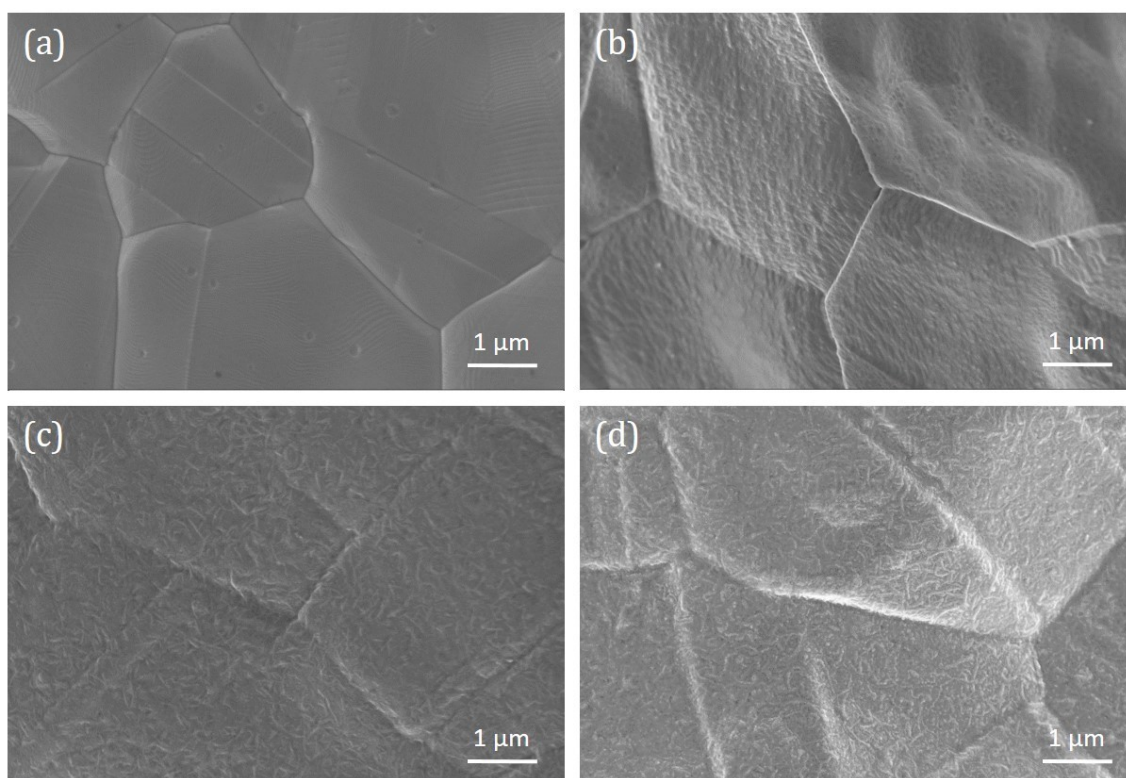


Fig. 6.2-1 SEM images of Ni foams: (a) untreated, (b) acid-treated, (c) acid-treated and impregnated at room temperature for 72 hr, (d) acid-treated and boiled for 30 min

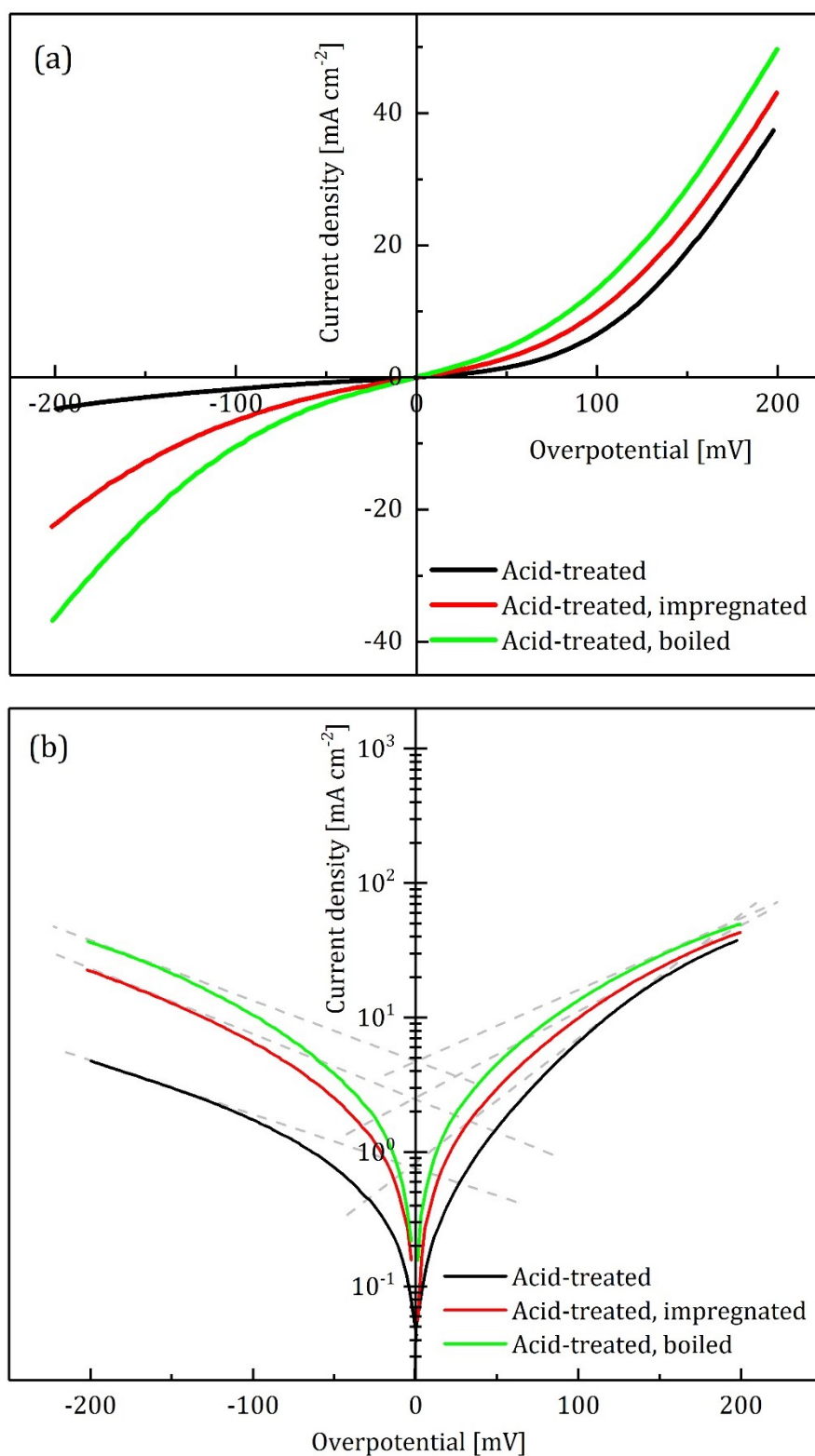


Figure 6.2-2 Potentiodynamic polarization of the three Ni foam electrodes in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte: (a) linear plot and (b) Tafel plot.

Potentiodynamic polarization of the three Ni foam electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte are presented in Figure 6.2-2. It is obvious from Figure 6.1-3 (a) and 6.2-2 (a) that the catalytic activities of the Ni foam electrodes increased considerably compared to the carbon paper electrodes, for both anodic and cathodic polarizations, and especially the cathodic polarization of the aqueous polysulphide electrolyte. However, for all three Ni foam electrodes, the anodic catalytic activities were higher than their cathodic catalytic activities, with the sulphidised Ni foam showing the most symmetrical performance towards the anodic and cathodic polarization of aqueous polysulphide electrolytes.

The exchange current densities of the three Ni foam electrodes, derived from Figure 6.2-2 (b), together with the current densities achieved at ± 200 mV of each Ni foam electrode are summarized in Table 6.2-1. As previously, the exchange current densities were calculated based on the geometric area of the electrodes.

Table 6.2-1 Exchange current densities and current densities at ± 200 mV of the three Ni foam electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Ni foam electrode	Exchange current density / mA cm⁻²	Current density at 200 mV / mA cm⁻²	Current density at -200 mV / mA cm⁻²
Acid-treated	0.76	37.38	-4.76
Acid-treated & impregnated	2.44	43.03	-22.53
Acid-treated & boiled	4.88	49.66	-36.78

From Table 6.2-1, it can be concluded that boiling in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte for 30 min was a more effective method to sulphidise the Ni foam than the impregnating method, requiring less time for the sulphidisation process and leading to higher catalytic activity of the nickel foam electrode. As a result, the boiling method was used to sulphidise all NiS_x/carbon paper composite electrodes discussed later in this chapter.

As a comparison, Zhao et al presented a 2.5 mm thick Ni foam, sulphidised by boiling in a 1.3 mol l⁻¹ Na₂S₄ solution for 15 min, which exhibited much lower overpotentials as compared to this study under the same current densities within a 1.3 mol l⁻¹ Na₂S₄/1 mol l⁻¹ NaOH electrolyte and at 299K [34]. The significantly lower overpotentials under a certain current density in Zhao's experiment was mainly attributed to the higher concentrations of polysulphide and supersulphide ions in the electrolyte, the larger thickness of the Ni foam and the higher temperature under which the experiments were conducted.

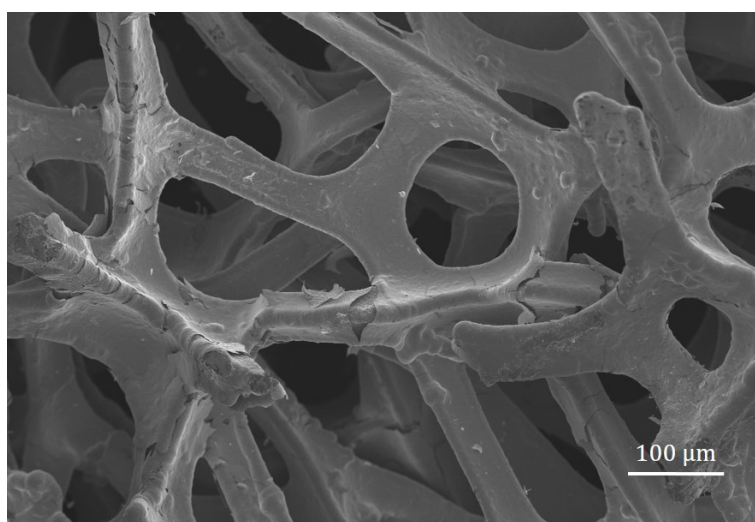


Figure 6.2-3 SEM image of the acid-treated Ni foam boiled in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte for 30 min

In addition, the NiS_x layer formed did not seem to be tightly adhered to the surface of the Ni foam, as shown in Figure 6.2-3. In addition, the aqueous polysulphide solution used for the sulphidisation process became dark after the sulphidisation of nickel foams, indicating that a certain amount of NiS_x fell off the nickel foam surface during the sulphidisation process. However, due to the fact that the NiS_x could be replenished through the reaction of fresh nickel surface and aqueous polysulphide electrolyte, the catalytic activity of Ni foam electrodes in aqueous polysulphide electrolytes should be maintained although at the cost of losing electrode materials. In fact, the sulphidised nickel foam appeared stable over all the measurements of the single-cell polysulphide-

air RFB in this study since no precipitates of NiS_x was found in the anolyte reservoir throughout the experiments. In addition, Zhao et al also indicated that when a sulphidised Ni foam was used as the negative electrode the performance of a single-cell PSB did not exhibit any significant change over 50 cycles [34].

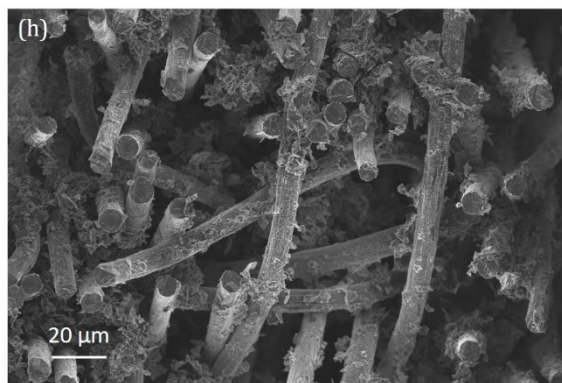
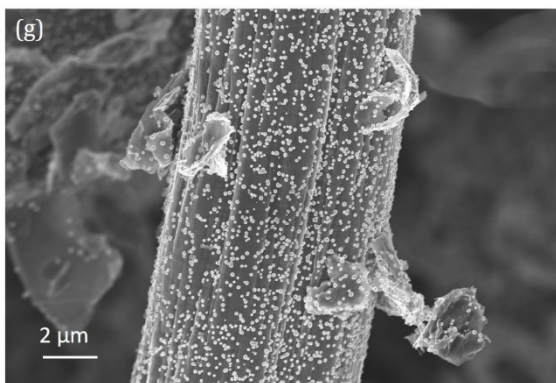
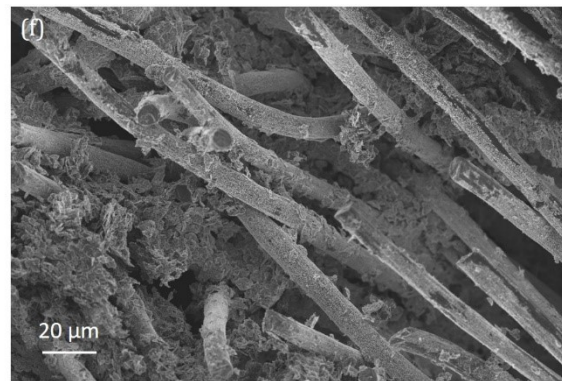
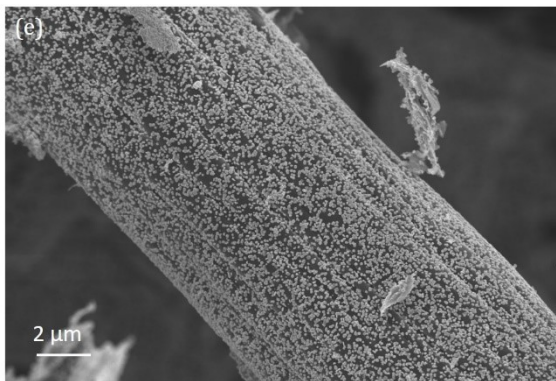
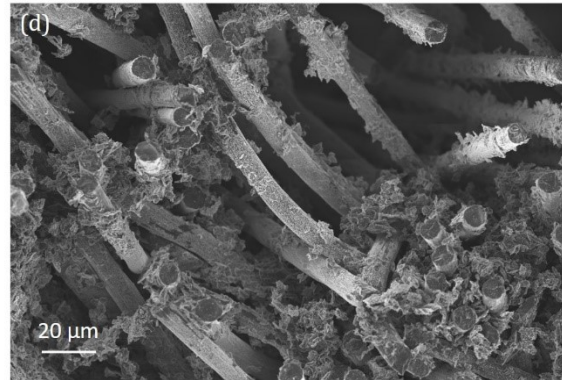
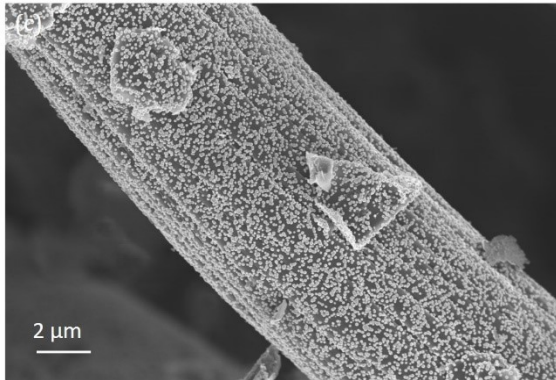
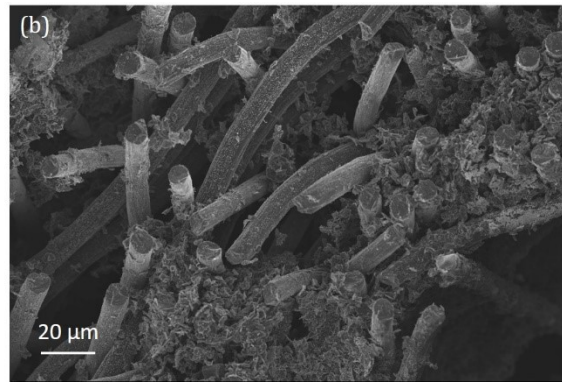
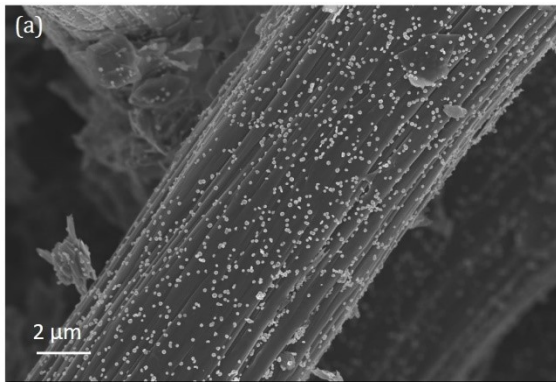
6.3 NiS_x /carbon paper Electrodes

The NiS_x /carbon paper electrodes were prepared by first depositing nickel onto the 450°C-6hr treated SGL 10AA carbon paper followed by a subsequent sulphidisation of the as-prepared Ni/carbon paper electrode. Nickel was deposited on the carbon paper using three methods, namely electrodeposition, impregnation and electroless deposition, as discussed in Section 3.2.4.3.

6.3.1 Electrodeposition Method

The first method directly electrodeposited nickel onto the heat-treated carbon paper using a nickel sulfamate/boric acid plating bath. The deposition was carried out in galvanostatic mode (constant current). Six samples were prepared varying the current density, current profile (continuous/pulse) and duration of the deposition processes, as shown in Table 3.4-3.

The resultant Ni/carbon paper electrodes were characterized by SEM imaging, as shown in Figure 6.3-1. From Figure 6.3-1 (a, c, e, g, i, k), it can be seen that the deposited nickel on the carbon fibres and binders appeared as nanoparticles with a diameter of ~ 100 nm. Increasing nickel loading lead to the merger of nickel particles. Cross-section SEM images, as shown in Figure 6.3-1 (b, d, f, h, j, l), confirmed that nickel nanoparticles had been successfully deposited inside the carbon paper for all six samples.



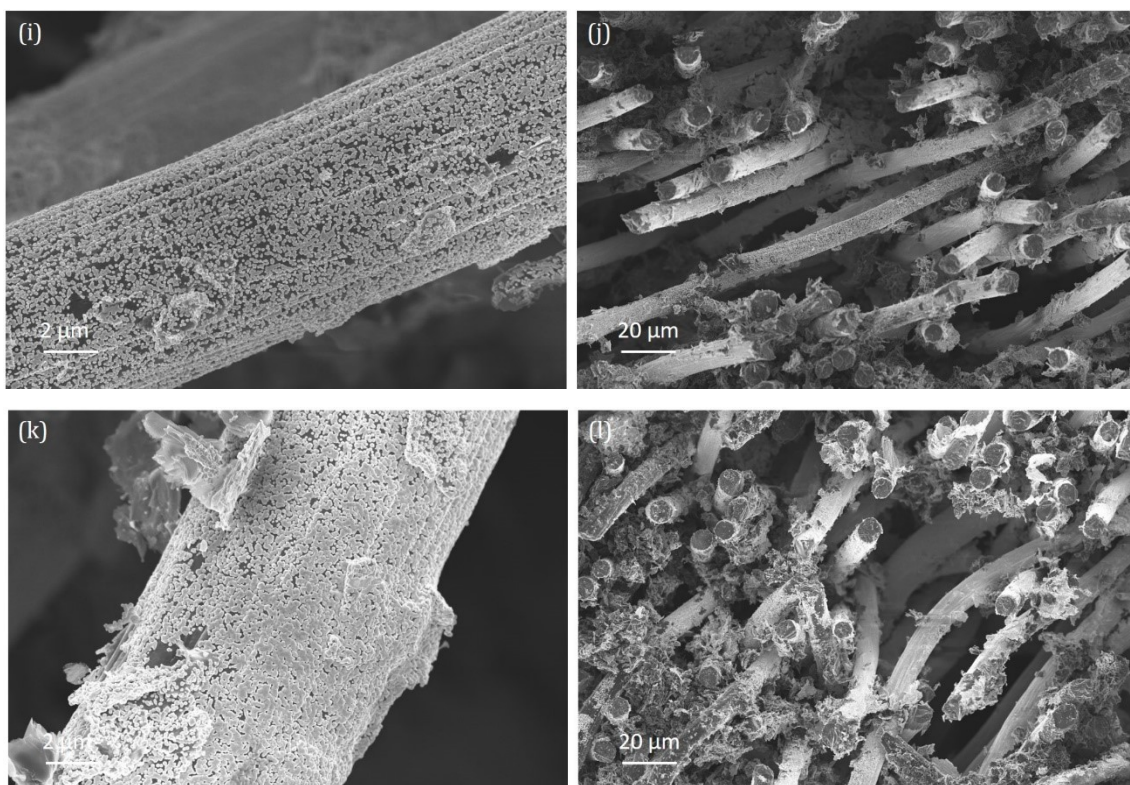


Figure 6.3-1 Cross-section SEM images of the Ni/carbon paper electrodes prepared by electrodeposition method with various nickel loading: (a, b) 7.82 wt%, (c, d) 9.90 wt%, (e, f) 16.32 wt%, (g, h) 10.55 wt%, (i, j) 20.85 wt%, and (k, l) 26.22 wt%.

For all six samples, the carbon paper was weighed before and after the nickel deposition in order to calculate the nickel loading and the coulombic efficiency of the corresponding deposition, as summarized in Table 6.3-1.

Table 6.3-1 Ni/carbon paper electrodes prepared by electrodeposition method

Electrode #	Weight of carbon paper / g	Deposition method	Current density/ mA cm^{-2}	Duration / s	wt% of nickel	Coulombic efficiency / %
1	0.0957	Continuous	10	262	7.82	78.2
2	0.0960	Continuous	10	526.00	9.90	50.0
3	0.0969	Continuous	100	53	16.32	81.5
4	0.0987	Pulse (5s on/off)	10	541	10.55	52.8
5	0.1004	Continuous	10	825	20.85	69.5
6	0.0958	Continuous	10	1050	26.22	65.5

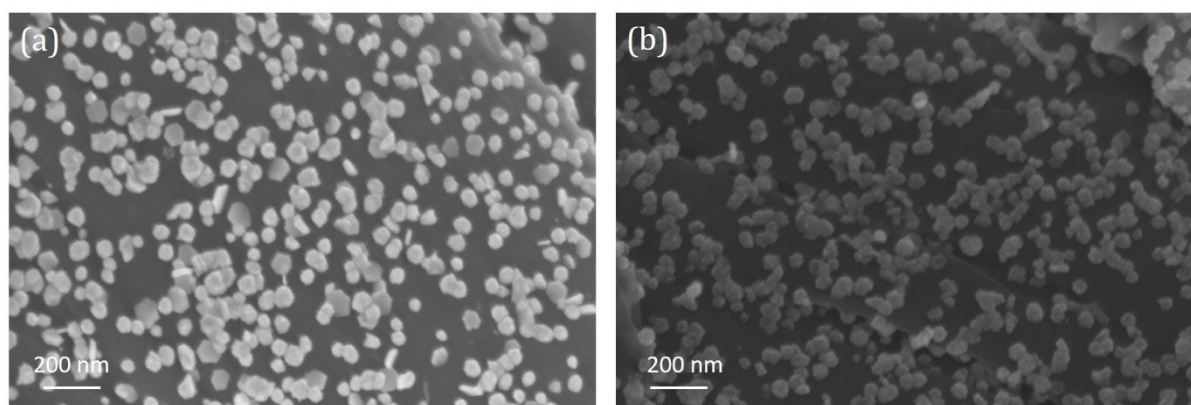


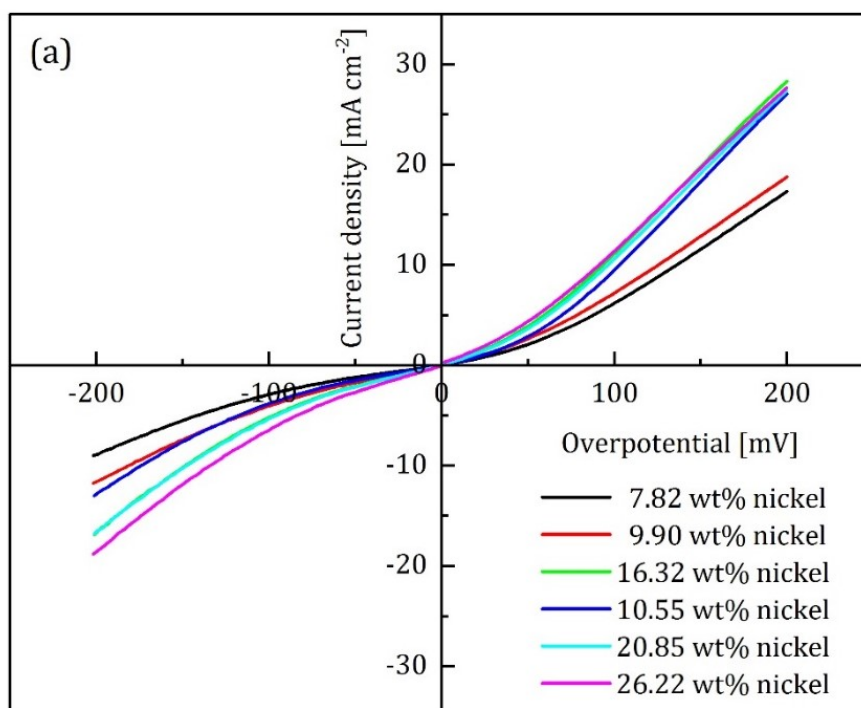
Figure 6.3-2 Cross-section SEM images of the 7.82 wt% Ni/carbon paper electrode (a) before and (b) after sulphidisation treatment.

The as-prepared Ni/carbon paper electrodes were subsequently sulphidised in the aqueous polysulphide solution using the boiling method, as discussed previously. After sulphidisation, Ni nanoparticles had been converted to NiS_x with coarser surface, as demonstrated in Figure 6.3-2.

It is worth noting here that, similar to the sulphidisation of nickel foams, the aqueous polysulphide solution used became dark after the sulphidisation of the Ni/carbon paper electrodes, suggesting some loss of nickel during the boiling sulphidisation treatment. As a result, the metallic nickel loading before sulphidisation did not represent the final Ni

content in the NiS_x/carbon paper electrodes. Nevertheless, it is reasonable to assume that higher initial nickel loadings would result in higher content of NiS_x catalysts on the NiS_x/carbon paper composite electrodes.

Potentiodynamic polarization of the prior six NiS_x/carbon paper electrodes prepared by the electrodeposition method were conducted in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte, whose results are demonstrated in Figure 6.3-3.



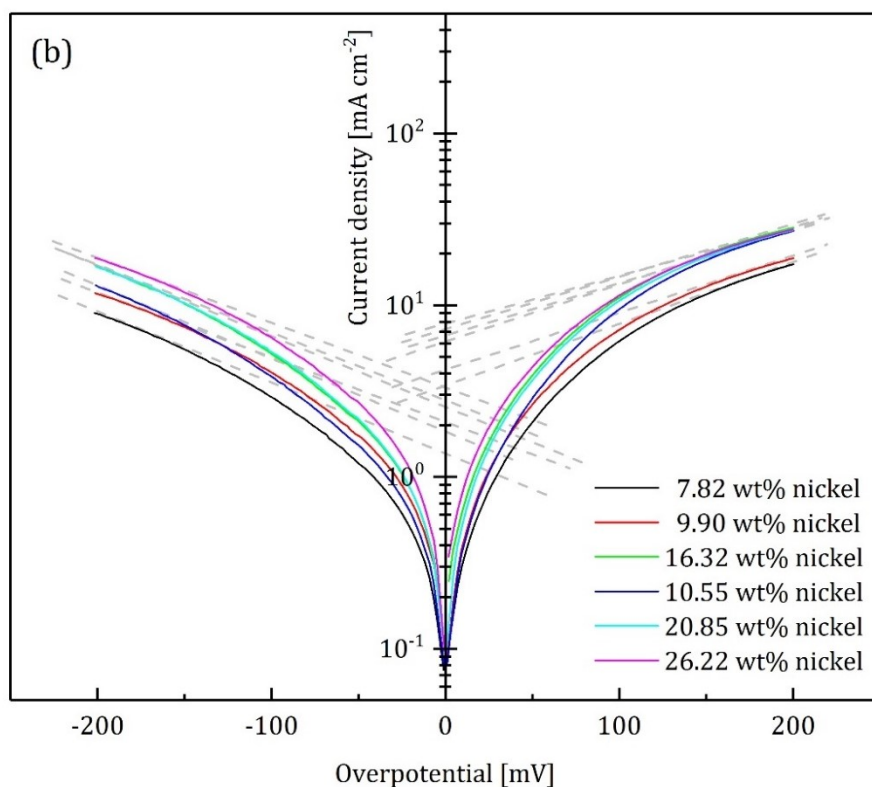


Figure 6.3-3 Potentiodynamic polarization of the NiS_x /carbon paper electrodes, prepared by electrodeposition method, in the $1 \text{ mol kg}^{-1} \text{Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{NaOH}$ electrolyte: (a) linear plot and (b) Tafel plot.

Considerable increases of both anodic and cathodic catalytic activities were observed for the NiS_x /carbon paper electrodes compared to bare heat-treated carbon paper electrode. Still, the anodic catalytic activities of all six NiS_x /carbon paper electrodes were better than their cathodic catalytic activities. In general, the catalytic activity of the NiS_x /carbon paper electrodes increased with the increase of Ni loading, for both anodic and cathodic polarization of the aqueous polysulphide electrolyte.

Exchange current densities of the six NiS_x /carbon paper electrodes, prepared by the electrodeposition method, were derived from Figure 6.3-3 (b) and are summarized in Table 6.3-2. Also presented in the Table 6.3-2 are the current densities achieved with each NiS_x /carbon paper electrodes at $\pm 200 \text{ mV}$.

Table 6.3-2 Exchange current densities and current densities at ± 200 mV of the NiS_x /carbon paper electrodes prepared by electrodeposition method in the $1 \text{ mol kg}^{-1} \text{Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{NaOH}$ electrolyte

Electrode	Wt% of nickel before sulphidisation	Exchange current density / mA cm^{-2}	Current density at 200 mV / mA cm^{-2}	Current density at -200 mV / mA cm^{-2}
#1	7.82	2.41	17.3	-9.01
#2	9.90	3.13	18.7	-11.8
#3	16.32	4.99	28.3	-16.9
#4	10.55	4.21	27.0	-13.0
#5	20.85	4.41	27.3	-16.8
#6	26.22	5.58	27.6	-18.8

Plotting the exchange current densities against the nickel loading before sulphidisation, as shown in Figure 6.3-4, shows that an increase of nickel loading lead to an approximately linear increase in the electrocatalytic activities of NiS_x /carbon paper electrodes, which confirms the appropriateness of the previous assumption that higher initial nickel loadings after deposition would result in higher NiS_x catalyst loadings on the composite electrodes.

Increase of deposition current density and pulse deposition both not only increased the coulombic efficiency of the deposition, hence higher nickel loadings, but also enhanced the catalytic activity per unit mass of nickel. This was likely due to the smaller sizes of nickel nanoparticles deposited at higher current density and with the pulse deposition method.

No limit was observed in the performance increase of the NiS_x /carbon paper electrodes along with the increase of nickel loading up to 26.22 w%, indicating that further increase in the nickel loading might lead to better performance of the electrode.

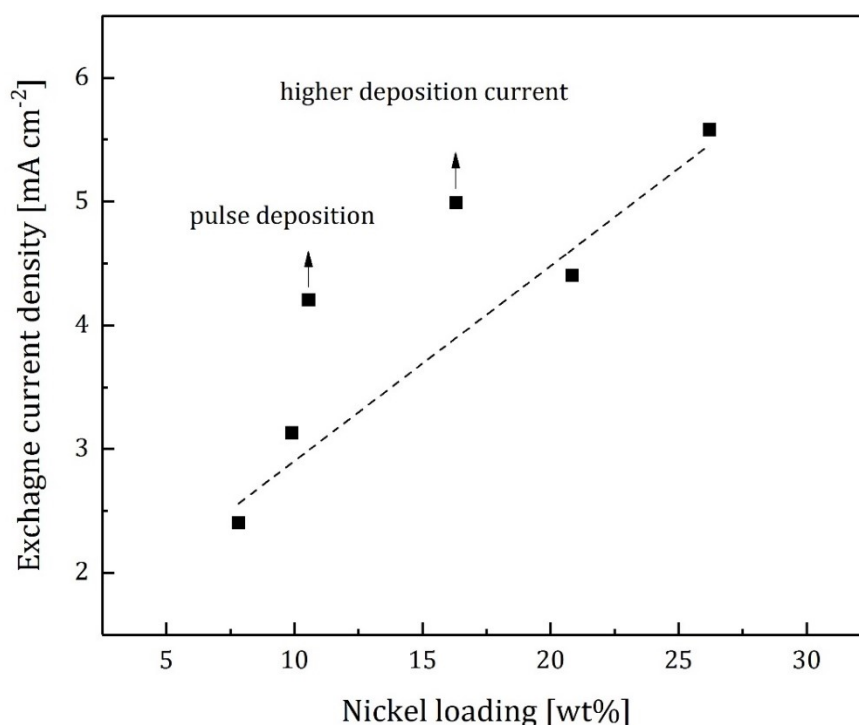


Figure 6.3-4 Exchange current densities against nickel loading before sulphidisation of the NiS_x /carbon paper electrodes prepared by the electrodeposition method

Comparing Figure 6.2-2 and 6.3-3, it shows that even the best-performance NiS_x /carbon paper electrodes prepared by the electrodeposition method exhibited lower catalytic activity towards the polarization of aqueous polysulphide electrolytes compared to the sulphidised nickel foam. However, it must be noted that the thickness of the NiS_x /carbon paper electrodes were only 400 μm whereas the thickness of the nickel foam was 900 μm . As a result, it can be speculated that by stacking layers, the NiS_x /carbon paper electrodes may perform equally or even better than the sulphidised nickel foam.

6.3.2 Impregnation Method

The second method of preparing Ni/carbon paper electrodes was to first impregnate the heat-treated carbon paper with nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) using an ethanol or isopropanol solvent followed by a subsequent reduction in $\text{H}_{2(g)}$, as discussed in Section 3.4.2.

Six samples were prepared using either a $\text{Ni}(\text{NO}_3)_2$ /ethanol or a $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution. Nickel loadings of the derived Ni/carbon paper electrodes are summarized in Table 6.3-3.

Table 6.3-3 NiS_x /carbon paper electrodes prepared by the impregnation method

Sample #	Solution	Weight of carbon paper / g	Weight of nickel / g	wt% of nickel
1	$\text{Ni}(\text{NO}_3)_2$ /ethanol	0.0271	0.0007	2.6
2	$\text{Ni}(\text{NO}_3)_2$ /ethanol	0.0257	0.0035	13.6
3	$\text{Ni}(\text{NO}_3)_2$ /ethanol	0.0263	0.0061	23.2
4	$\text{Ni}(\text{NO}_3)_2$ /isopropanol	0.0266	0.0020	7.5
5	$\text{Ni}(\text{NO}_3)_2$ /isopropanol	0.0257	0.0032	12.5
6	$\text{Ni}(\text{NO}_3)_2$ /isopropanol	0.0256	0.0066	25.8

SEM images of the Ni/carbon paper electrodes, prepared by the impregnation method, are shown in Figure 6.3-5 and 6.3-6. It was obvious from Figure 6.3-1, 6.3-5 and 6.3-6 that the nickel deposited by the impregnation method was in irregular shapes with a broad size range, whereas the electrodeposited nickel appeared as regular spheres of almost constant size. The different hydrophilicity of ethanol and isopropanol, which were used to dissolve nickel nitrate for the impregnation, lead to nickel being deposited at different locations of the carbon paper. It can be seen from Figure 6.3-5 and 6.3-6 that when ethanol is used as the solvent, nickel was mostly deposited in the surface crevices of the carbon fibres, whereas when isopropanol was used as the solvent, more nickel was deposited onto the surface of the carbon fibres. In addition, large numbers of small nickel nanoparticles (~ 10 nm) were formed on the surface of the carbon fibres when using isopropanol as the solvent for the impregnation, as can be seen from Figure 6.3-6.

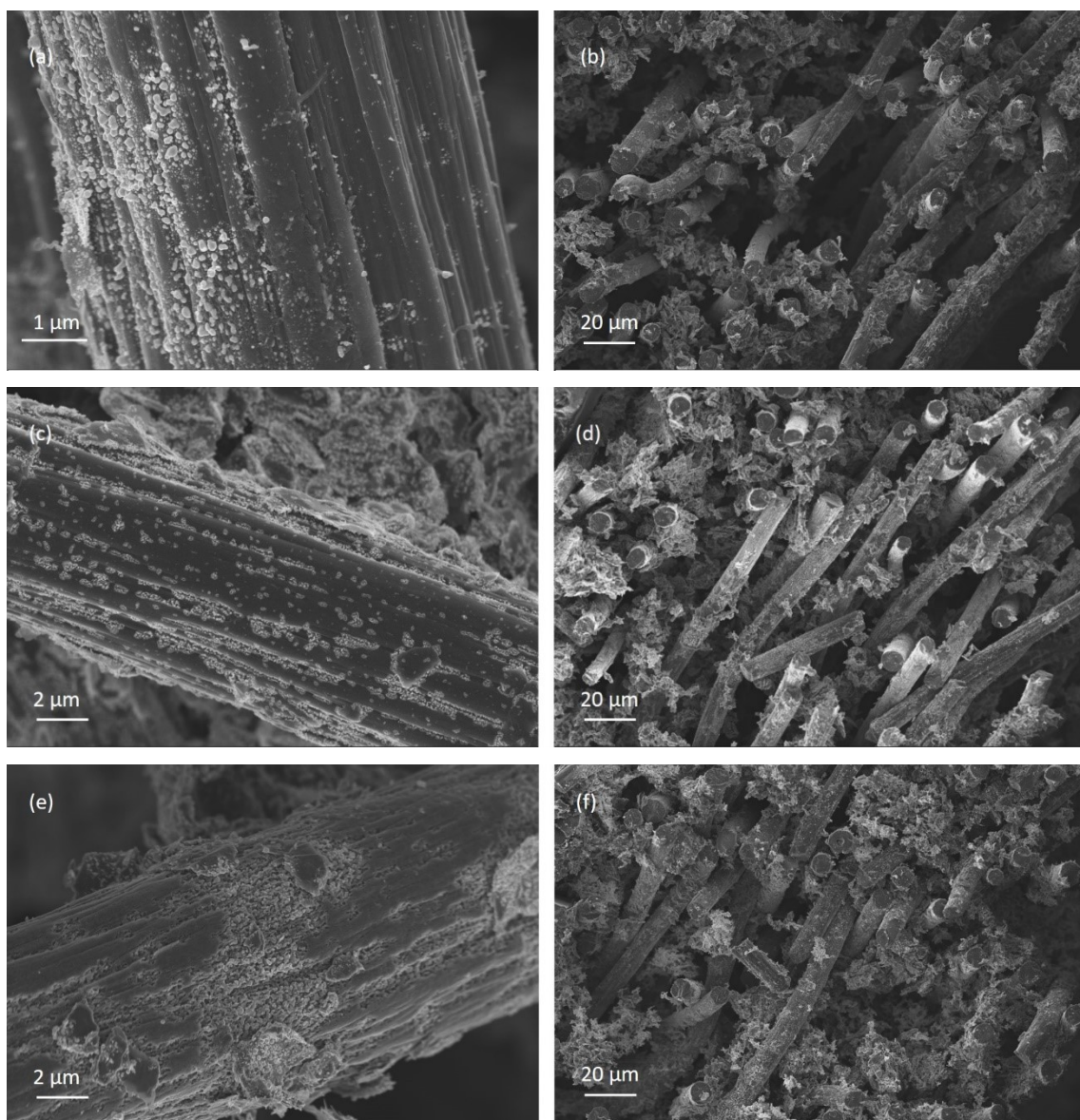


Figure 6.3-5 Cross-section SEM images of the Ni/carbon paper electrodes prepared by impregnation method using a $\text{Ni}(\text{NO}_3)_2$ /ethanol solution with various nickel loading: (a, b) 2.6 wt%, (c, d) 13.6 wt%, (e, f) 23.2 wt%

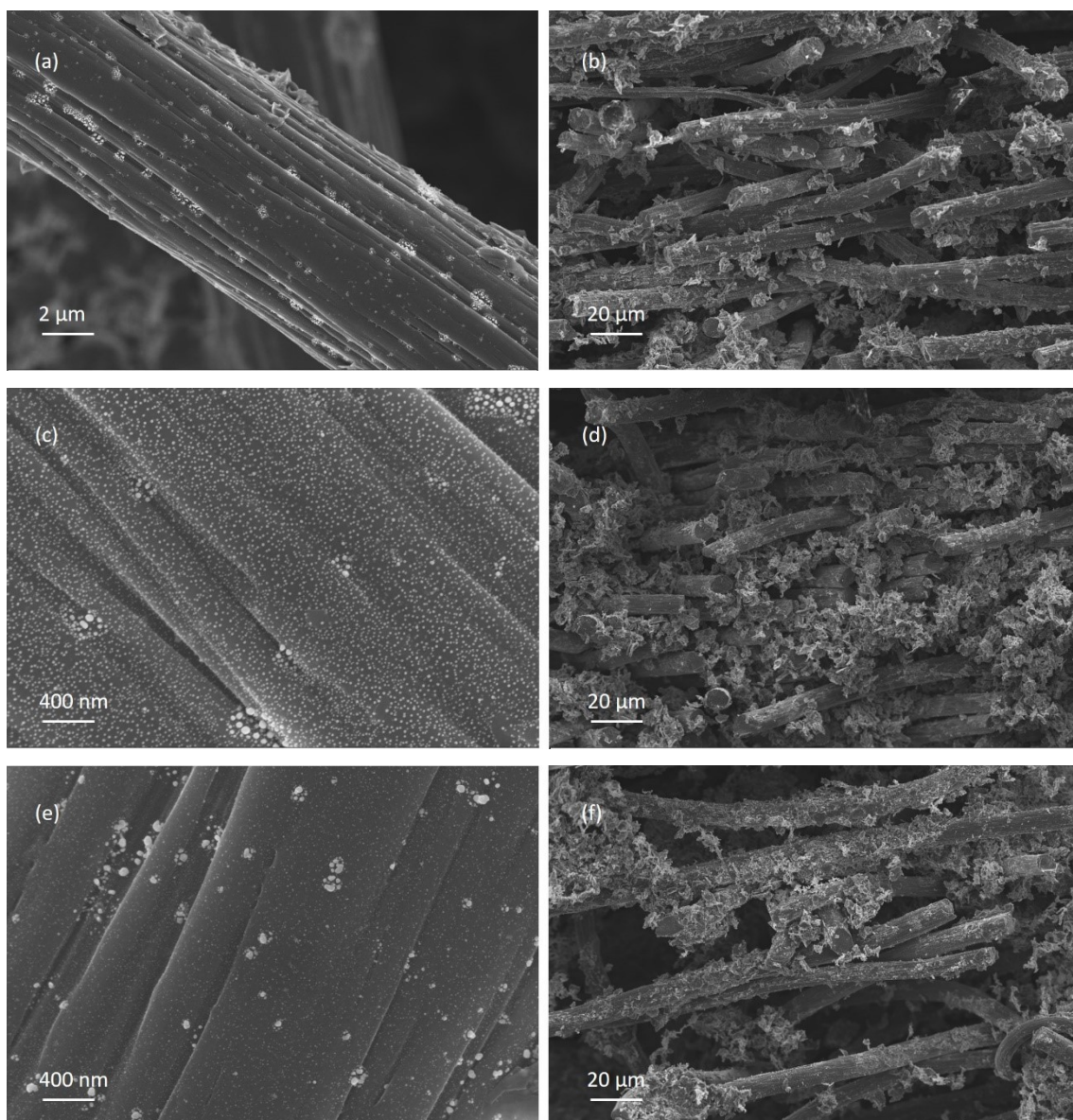


Figure 6.3-6 Cross-section SEM images of the Ni/carbon paper electrodes prepared by impregnation method using a $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution with various nickel loading: (a, b) 7.5 wt%, (c, d) 12.5 wt%, (e, f) 25.8 wt%

Figure 6.3-7 shows the SEM images before and after sulphidisation of the 23.2 wt% Ni/carbon paper electrode prepared using $\text{Ni}(\text{NO}_3)_2$ /ethanol solution and the 25.8 wt% Ni/carbon paper electrode prepared using $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution. It is obvious from Figure 6.3-7 that Ni nanoparticles were converted to NiS_x with a coarser surface, as identical to Figure 6.3-2.

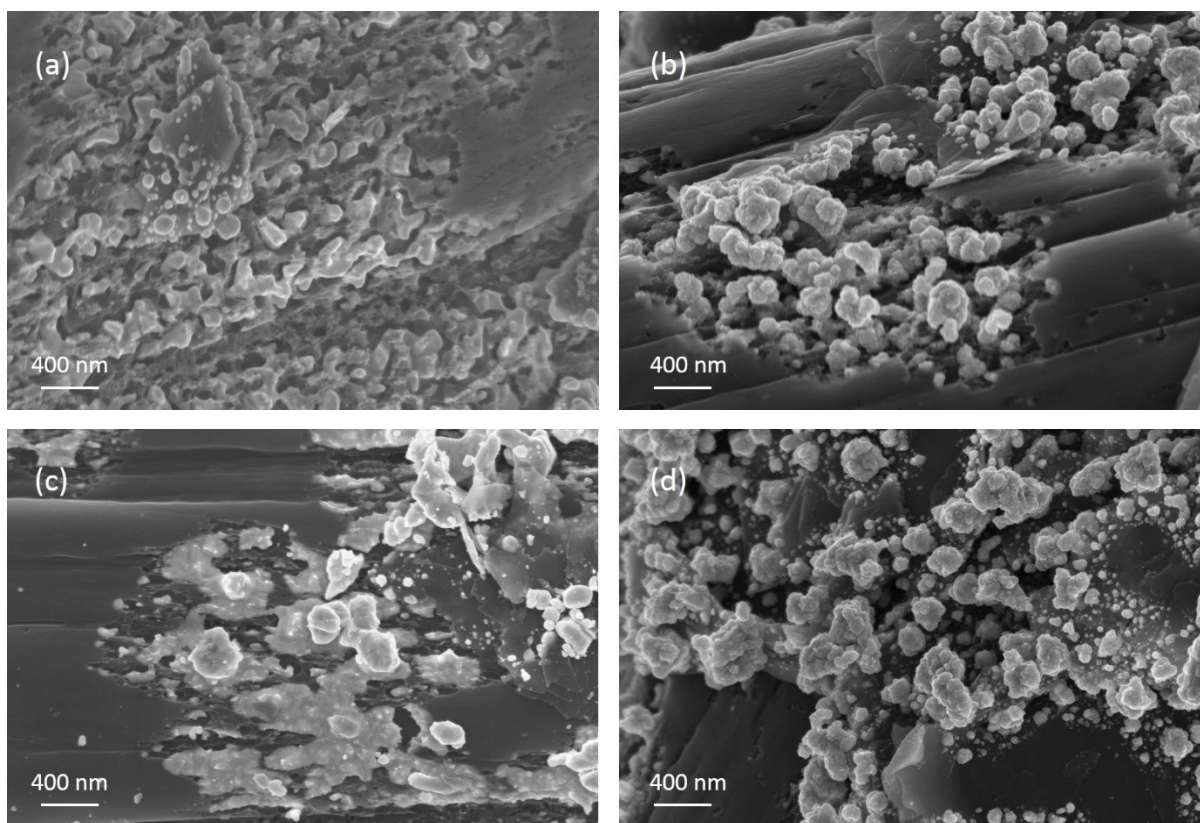


Figure 6.3-7 Cross-section SEM images of the 23.2 wt% Ni/carbon paper electrode prepared using $\text{Ni}(\text{NO}_3)_2$ /ethanol solution (a) before and (b) after sulphidisation treatment and the 25.8 wt% Ni/carbon paper electrode prepared using $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution (a) before and (b) after sulphidisation treatment.

Potentiodynamic polarization of the prior six NiS_x /carbon paper electrodes, prepared with the impregnation method, in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte are demonstrated in Figure 6.3-8.

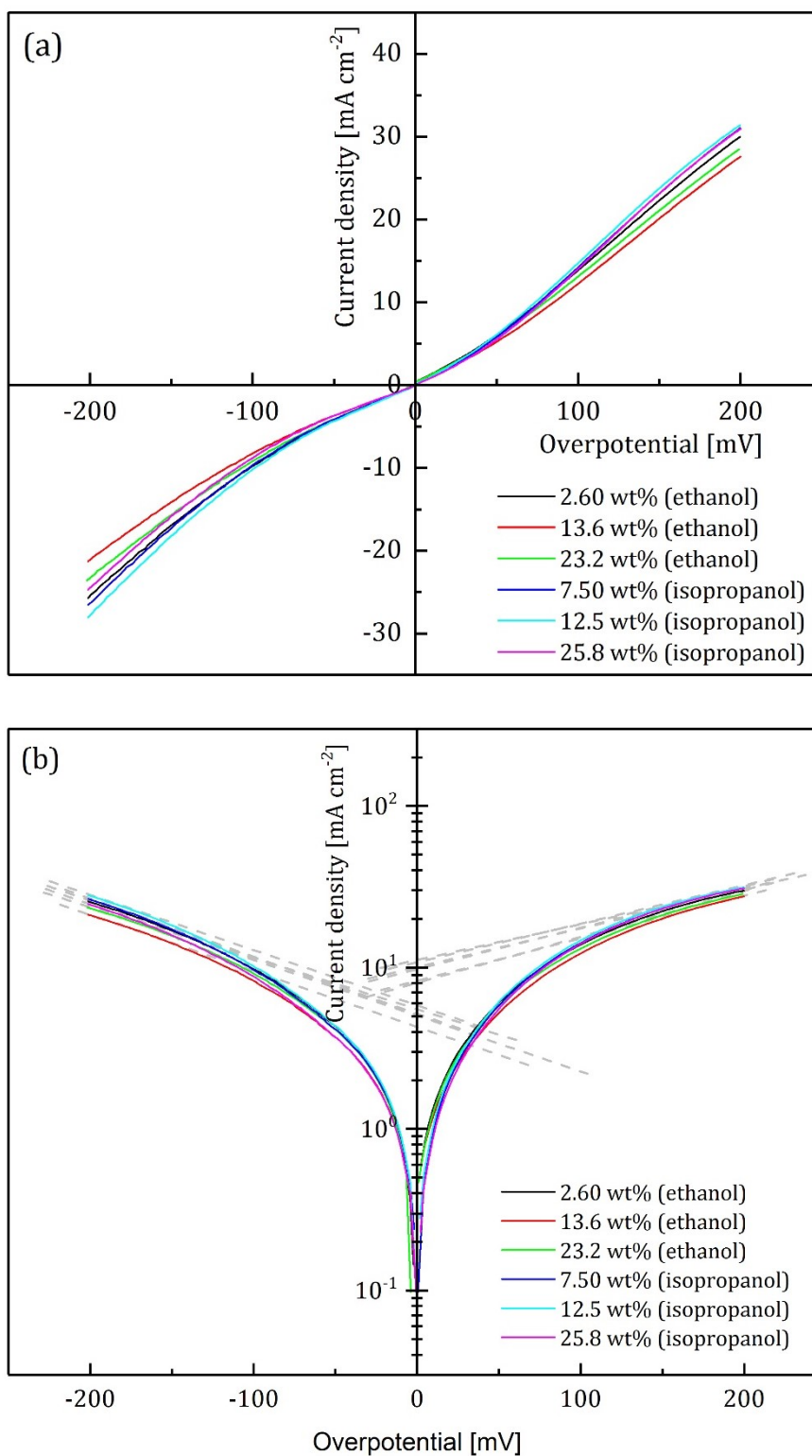


Figure 6.3-8 Potentiodynamic polarization of the $\text{NiS}_x/\text{carbon paper}$ electrodes, prepared by impregnation method, in the $1 \text{ mol kg}^{-1} \text{Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{NaOH}$ electrolyte: (a) linear plot and (b) Tafel plot.

In general, the NiS_x/carbon paper electrodes prepared with impregnation method exhibited higher catalytic activities compared to the ones prepared with electrodeposition method, especially for the cathodic polarization of aqueous polysulphide electrolyte. This was mainly attributed to the increased surface areas of nickel for the NiS_x/carbon paper electrodes prepared with impregnation method, as can be seen in Figure 6.3-1, 6.3-5 and 6.3-6.

Exchange current densities of the six NiS_x/carbon paper electrodes, prepared by impregnation method, were derived from Figure 6.3-8 (b) and summarized in Table 6.3-4. Also presented in the Table 6.3-4 are the current densities achieved with each NiS_x/carbon paper electrodes at ± 200 mV.

Table 6.3-4 Exchange current densities and current densities at ± 200 mV of the NiS_x/carbon paper electrodes prepared by impregnation method in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Electrode	Solvent	Wt% of nickel before sulphidisation	Exchange current density / mA cm⁻²	Current density at 200 mV / mA cm⁻²	Current density at -200 mV / mA cm⁻²
#1	ethanol	2.6	7.54	30.00	-25.69
#2	ethanol	13.6	6.27	23.89	-18.06
#3	ethanol	23.2	7.38	28.47	-23.59
#4	isopropanol	7.5	7.44	31.00	-26.53
#5	isopropanol	12.5	8.28	31.39	-28.00
#6	isopropanol	25.8	8.28	30.92	-24.70

The exchange current densities of the NiS_x/carbon paper electrodes prepared by the impregnation method were plotted against their corresponding nickel loading, as shown in Figure 6.3-9. In general, the catalytic activities of the NiS_x/carbon paper electrode prepared using Ni(NO₃)₂/isopropanol solution were higher than the ones prepared using Ni(NO₃)₂/isopropanol solution. This is due to the increased nickel surface area

introduced by the large number of small nickel nanoparticles (~ 10 nm), as can be seen in Figure 6.3-6.

Except for electrode #1 with the nickel loading of 2.6%, other NiS_x /carbon paper electrodes prepared with the impregnation method followed the trend that with the increase of nickel loading, the catalytic activity of the NiS_x /carbon paper electrode increased. The exception of electrode #1 could be attributed to the sulphidisation process, during which the amount of Ni being lost was unknown.

It is worth noting that the differences among the various NiS_x /carbon paper electrodes prepared by the impregnation method were fairly small, making it greatly challenging to analyse the effects of experimental conditions, such as nickel loadings and solvent used, on the catalytic performances of the NiS_x /carbon paper composite electrodes.

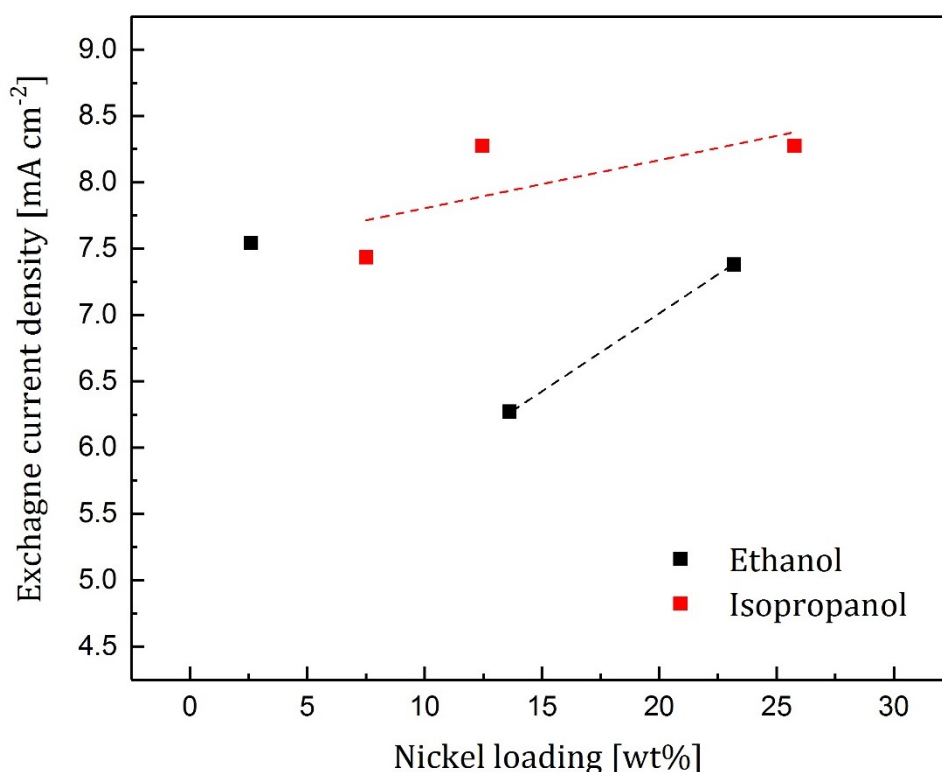


Figure 6.3-9 Exchange current densities against nickel loading before sulphidisation of the NiS_x /carbon paper electrodes prepared by impregnation method

6.3.3 Electroless Deposition Method

The third method was to deposit nickel onto the heat-treated carbon paper via the intermediate of NiOOH which was reduced to metallic nickel by $H_{2(g)}$. The as-prepared Ni/carbon paper electrode had a nickel loading of 14.55% before sulphidisation.

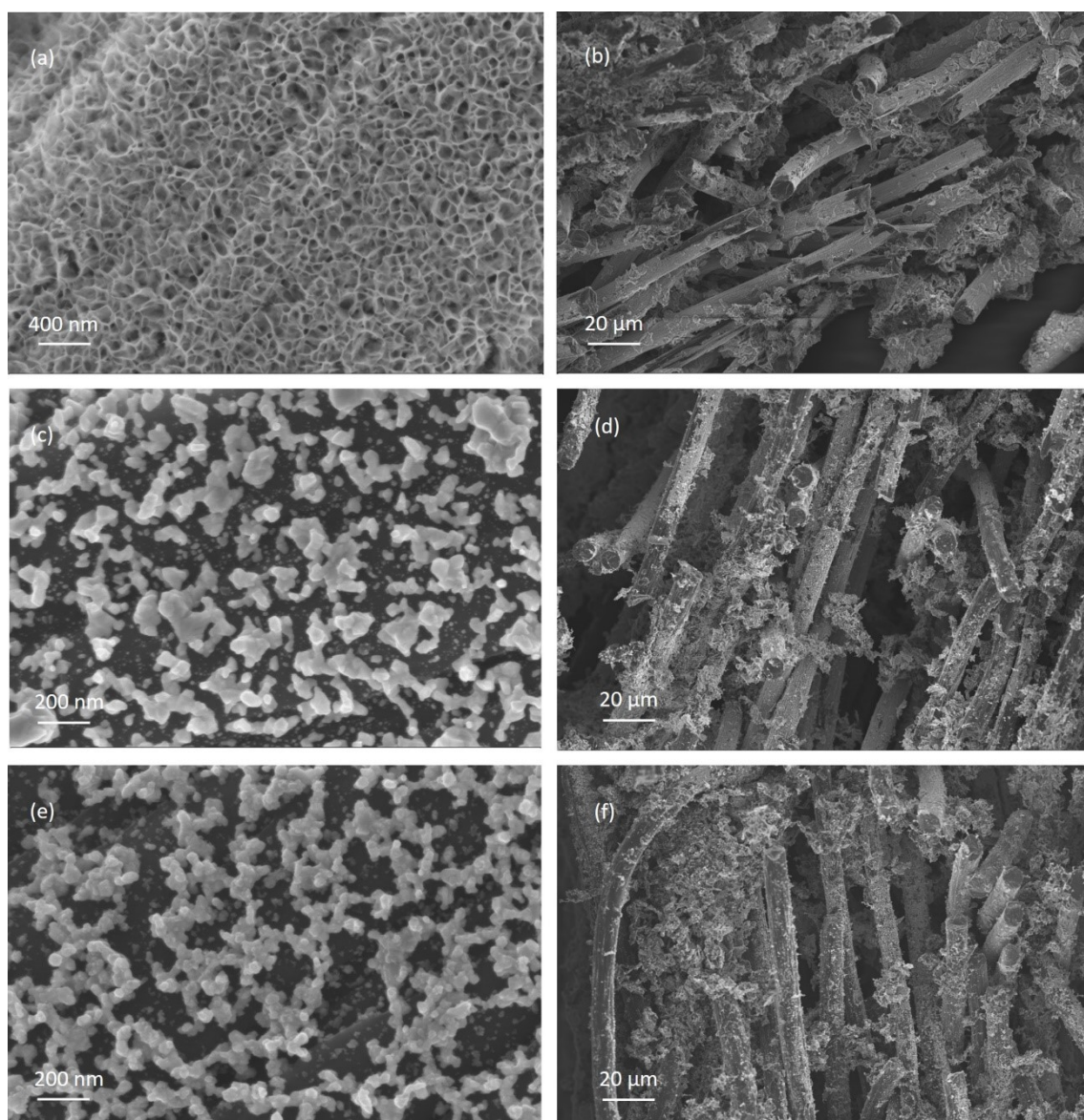


Figure 6.3-10 SEM images of: (a, b) as-deposited NiOOH/carbon paper, (c, d) reduced NiOOH/carbon paper, and (e, f) sulphidised Ni/carbon paper. Note: (a), (c) and (e) are surface SEM images; (b), (d) and (f) are cross-section SEM images

Figure 6.3-10 shows the SEM images of the as-deposited NiOOH/carbon paper electrode, the $\text{H}_{2(\text{g})}$ reduced NiOOH/carbon paper electrode and the sulphidised Ni/carbon paper electrode.

As shown in Figure 6.3-10 (a), NiOOH was successfully deposited onto the carbon fibres of the carbon paper, with a highly porous 3D structure. After reduction in hydrogen at elevated temperature, the as-reduced Ni however did not preserve the 3D structure of the NiOOH, as shown in Figure 6.3-10 (c). Nevertheless, nickel was distributed evenly over the carbon fibres. After sulphidisation treatment, nickel again transformed into NiS_x , as shown in Figure 6.3-10 (e).

Potentiodynamic polarization of the NiS_x /carbon paper electrode prepared by the electroless deposition method in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte is presented in Figure 6.3-11.

Comparing Figure 6.3-3, 6.3-8 and 6.3-11, it can be derived that the NiS_x /carbon paper electrode prepared by the electroless deposition method was one of the least catalytically active among all NiS_x /carbon paper electrodes. The exchange current density of this NiS_x /carbon paper electrode was 4.34 mA cm^{-2} , as derived from Figure 6.3-11 (b). The current density achieved at $\pm 200 \text{ mV}$ with this electrode were -18.34 and 19.6 mA cm^{-2} respectively, indicating that the NiS_x /carbon paper electrode prepared by the electroless deposition method exhibited a more symmetrical performance towards the anodic and cathodic polarization of aqueous polysulphide electrolyte.

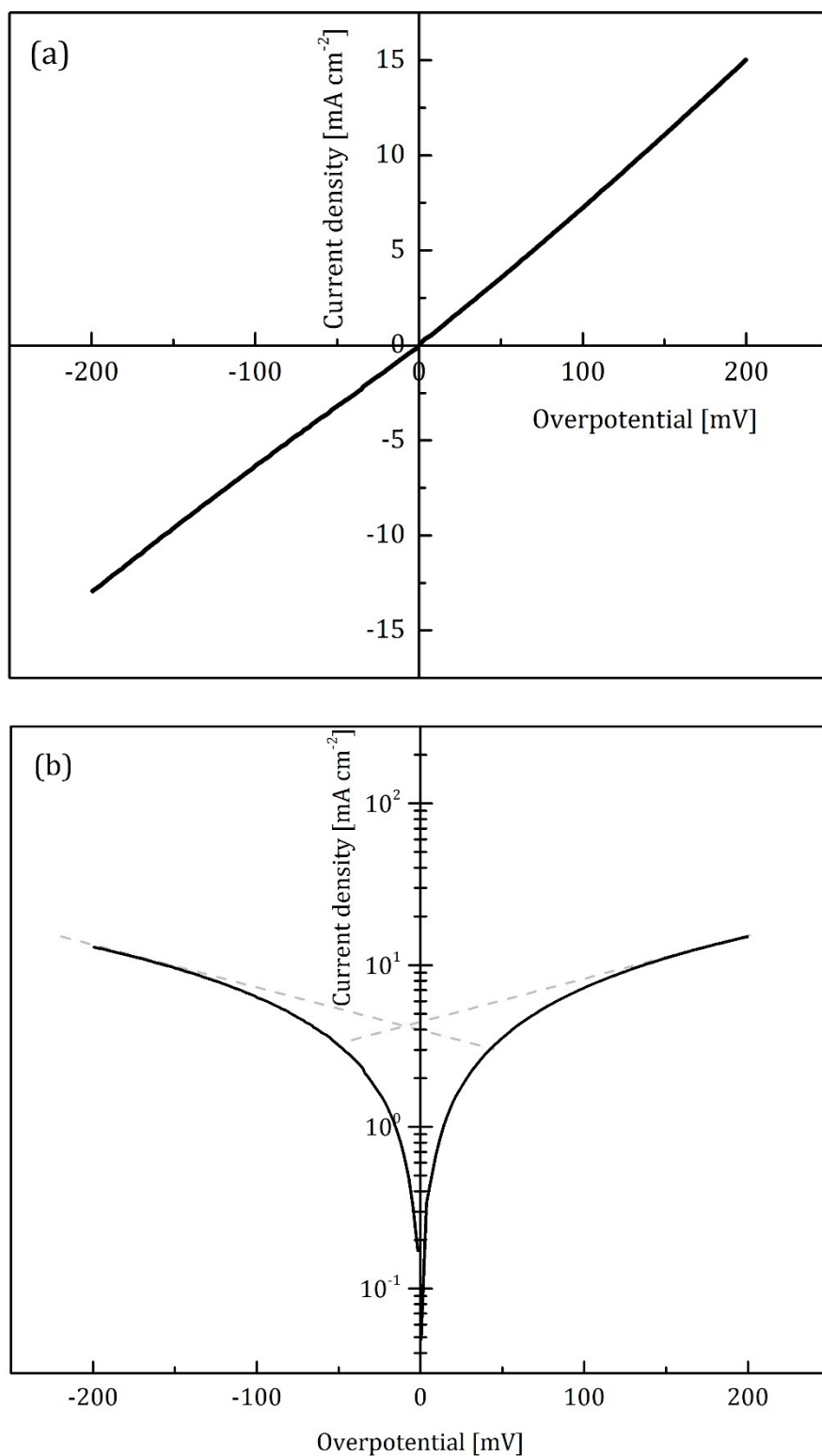


Figure 6.3-11 Potentiodynamic polarization of the $\text{NiS}_x/\text{carbon paper}$ electrodes, prepared by electroless deposition method, in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte: (a) linear plot and (b) Tafel plot.

6.4 Demonstration of Polysulphide-Air Redox RFB

The 0.9 mm thick acid-treated and sulphidised Ni foam was chosen as the negative electrode to demonstrate the 5 cm² single-cell polysulphide-air RFB since it exhibited the highest performance among all porous electrodes prepared in this study, as can be seen in Table 6.5-1. It also provided with the benefit of sustainable catalytic activities in aqueous polysulphide electrolytes since the NiS_x catalyst layer could be replenished by the reaction of metallic nickel and the aqueous polysulphide electrolyte once the NiS_x catalyst layer was damaged during the operation of the RFB.

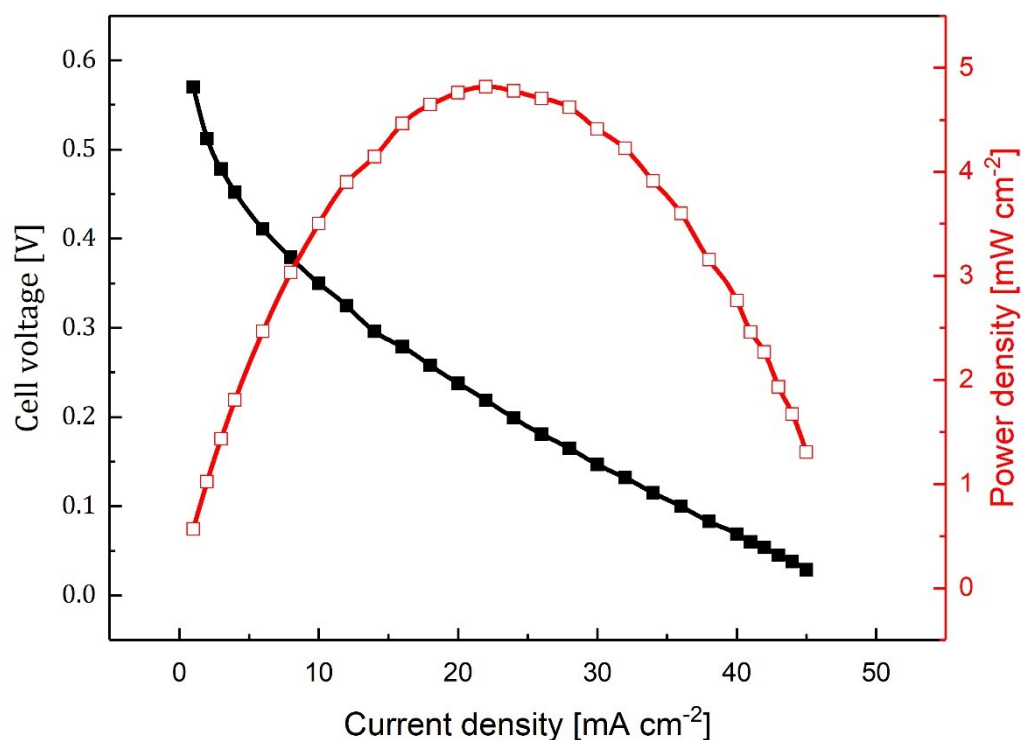


Figure 6.4-1 Polarization curve and power density curve of the 5 cm² single-cell polysulphide-air RFB at 20±3 °C

The construction of the 5 cm² single-cell polysulphide-air RFB and the characterization procedures are presented in detail in Section 3.1.2 and 3.5.2. The 5 cm² single-cell

polysulphide-air RFB exhibited a stable OCV of ~ 0.68 V with fresh electrolytes, which was identical to the previous demonstration [21].

Figure 6.4-1 shows the polarization curve and the power density curve of this single-cell polysulphide-air RFB. As can be seen from Figure 6.4-1, a maximum power density of ~ 4.8 mW cm^{-2} was achieved at the current density of 22 mA cm^{-2} , which was more than twice of the maximum power density achieved in the previous demonstration (2.1 mW cm^{-2}) with an untreated SGL 10AA carbon paper anode [21].

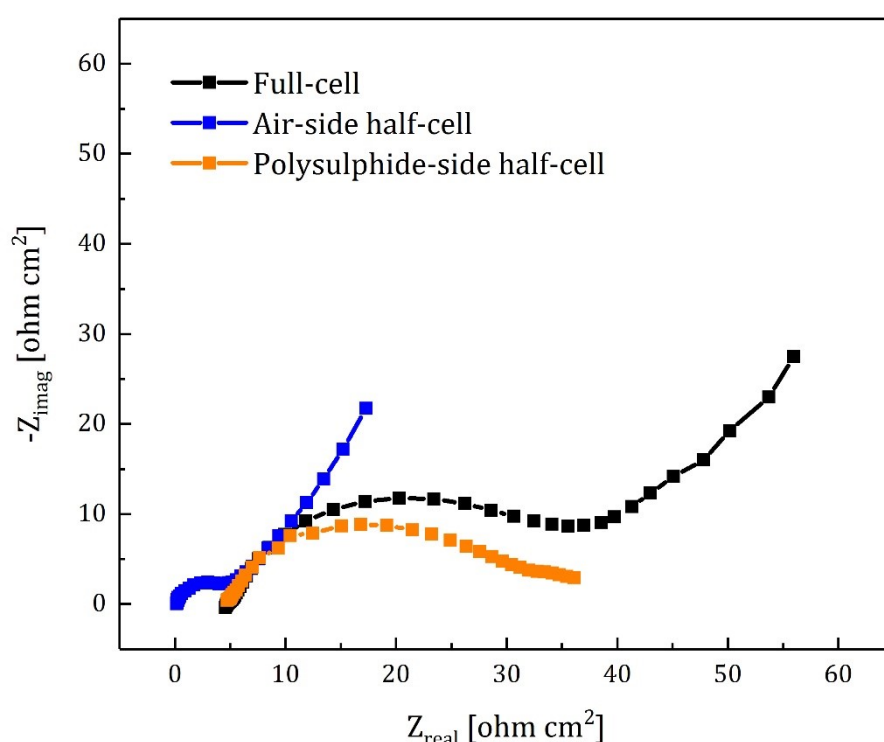


Figure 6.4-2 EIS measurements at OCV of the 5 cm^2 single-cell polysulphide-air RFB at 20 ± 3 °C

EIS measurements at OCV of the full-cell and both negative and positive half-cells of the 5 cm^2 single-cell polysulphide-air RFB are shown in Figure 6.4-2. Comparing to the EIS measurements from the previous demonstration [21], it can be concluded that the performance improvement of the single-cell polysulphide/air RFB in this work was mainly attributed to the improved catalytic activity of the anode. The impedance of the

polysulphide side half-cell under the equilibrium potential of the polysulphide electrolyte had reduced more than 20 times, compared to the previous results. Nevertheless, measurement of the overpotentials at certain current densities during the charge and discharge of the polysulphide-air RFB would have provided a more straightforward conclusion on the performance limiting side of the polysulphide-air RFB, which should be conducted in the future work.

It also shows in Figure 6.4-2 that the ohmic resistance of the single-cell polysulphide/air RFB mainly came from the polysulphide-side half-cell, likely indicating a poor Na⁺ conductivity and hence high resistance of the Nafion® 117 membrane. Hence, better pre-treatment method of the Nafion® 117 membrane and/or better Na⁺-conductive CEM is needed to further improve the performance of the polysulphide-air RFB.

Unfortunately, due to the significant electrolyte imbalance, likely caused by the damage of the Nafion® 117 membrane, the single-cell polysulphide-air RFB had not been characterized with charge and discharge cycles. In addition to the charge/discharge cycling, EIS measurements under load and overpotentials of each half-cell at certain current densities should also be measured in the future work.

6.5 Conclusions

This chapter discusses the thermal treatment of SGL 10AA carbon paper, the sulphidisation method for nickel, the catalytic performances of a variety of porous electrodes including carbon papers, nickel foams and a number of NiS_x/carbon paper electrodes, as summarized in Table 6.5-1, and lastly presents the demonstration result of a 5 cm² single-cell polysulphide-air RFB with a 0.9 mm thick sulphidised Ni foam as the anode.

Thermal treatment at 450°C for 6 hr was proved to be an efficient way of increasing the hydrophilicity of SGL 10AA carbon paper, enabling a complete wetting against water while maintaining a good mechanical strength.

Two sulphidisation methods were investigated by means of the aqueous polysulphide solution, including impregnating at room temperature for 72 hr and boiling for 30 min. The latter proved to be a more efficient way to sulphidise Ni foam, and was adopted in

this study to sulphidise the Ni/carbon paper electrodes. However, loss of NiS_x from the electrode surface was observed during the sulphidisation process, introducing some uncertainty into the analysis of experimental results.

Electrodeposition proved to be an effective method of preparing NiS_x /carbon paper electrodes. Increase of deposition current density and pulse deposition both not only increased the coulombic efficiency of the deposition which led to higher nickel loadings but also enhanced the catalytic activity per unit nickel mass, probably due to the increase of nickel surface area via the formation of smaller nickel nanoparticles. No limit of performance increase along the increase of nickel loading had been observed for the NiS_x /carbon paper electrode prepared by continuous deposition at 10 mA cm^{-2} up to the highest nickel loading of 26.22 w%, indicating that further increase in the nickel loading might lead to better performance of the electrode.

The impregnation method produced the most catalytically active NiS_x /carbon paper electrodes among the three preparation methods. Impregnation using a $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution seemed to produce better electrodes than using a $\text{Ni}(\text{NO}_3)_2$ /ethanol solution. The differences among the various NiS_x /carbon paper electrodes prepared by the impregnation method were small making it challenging to analyse the effects of experimental conditions on the catalytic performances of the NiS_x /carbon paper composite electrodes.

NiOOH with excellent 3D nanostructures had been successively deposited onto the heat-treated. However, the 3D nano-networks was not preserved after the reduction of NiOOH in $\text{H}_{2(\text{g})}$. The performance of the NiS_x /carbon paper electrode derived from the electroless deposition method showed the worst yet most symmetrical performances of the anodic and cathodic polarization of aqueous polysulphide electrolytes.

The NiS_x /carbon paper electrodes exhibited much higher catalytic activities towards the polarization of aqueous polysulphide electrolytes compared to the heat-treated carbon paper without NiS_x catalyst. Although the exchange current densities of a few NiS_x /carbon paper electrodes were larger than that of the sulphidised and acid-treated Ni foam, none of the NiS_x /carbon paper electrodes had shown higher current densities at $\pm 200 \text{ mV}$ overpotentials than the sulphidised and acid-treated Ni foam, likely due to the poorer mass transport inside the NiS_x /carbon paper electrodes than inside the Ni foam.

Stephens et al pointed out that an exchange current density of $\sim 200 \text{ mA cm}^{-2}$ geometric surface area would be needed to achieve an economically viable Regenesys PSB system [188]. Although a different target value of the exchange current density for the anode of the polysulphide-air RFB would be expected compared to the PSB system, even the best performed porous electrodes prepared in this study fall far below the exchange current density of 200 mA cm^{-2} by a factor of ~ 25 , as can be seen from Table 6.5-1.

Nevertheless, the 0.9 mm thick sulphidised nickel foam was chosen from the various porous electrodes to demonstrate the 5 cm^2 single-cell polysulphide-air RFB, considering its high catalytic activity and the sustainability of its catalytic activity in aqueous polysulphide electrolyte.

The 5 cm^2 single-cell polysulphide-air RFB exhibited a stable OCV of $\sim 0.68 \text{ V}$ with fresh electrolytes. A maximum power density of $\sim 4.8 \text{ mW cm}^{-2}$ was achieved at the current density of 22 mA cm^{-2} , which increases more than twice compared to a previous demonstration. EIS measurement at OCV of the full-cell and both negative and positive half-cells suggested that the improvement of performance for the single-cell polysulphide-air RFB mainly came from the improved catalytic activity of the anode. It also suggested by the EIS measurements that polysulphide-side half-cell was still the performance limiting side and better negative electrode and better Na^+ -conductive membrane is needed for the further improvement of the polysulphide-air RFB. However, measurement of the overpotentials of each half-cell during the charge and discharge of the polysulphide-air RFB could have provided a more straightforward answer to the question that which half-cell is limiting the performance of the polysulphide-air RFB, which should be performed in the future work.

However, due to the significant electrolyte imbalance, likely caused by the damage of the Nafion® 117 membrane, the single-cell polysulphide-air RFB had not been characterized with EIS measurements under load and charge/discharge cycling which shall be performed in the future work.

Table 6.5-1 Catalytic performances of various porous electrodes in the 1 mol kg⁻¹ Na₂S₂/1 mol kg⁻¹ NaOH electrolyte

Electrode	Preparation method	Exchange current density / mA cm ⁻²	Current density at 200 mV / mA cm ⁻²	Current density at -200 mV / mA cm ⁻²
Untreated carbon paper	-	0.29	13.3	-0.51
450°C-6hr treated carbon paper	-	0.839	17.2	-1.14
Acid-treated nickel foam	-	0.76	37.38	-4.76
Acid-treated & impregnated nickel foam	-	2.44	43.03	-22.53
Acid-treated & boiled nickel foam	-	4.88	49.66	-36.78
7.82 wt% NiS _x /carbon paper	Electrodeposition, 10 mA cm ⁻²	2.41	17.3	-9.01
9.90 wt% NiS _x /carbon paper	Electrodeposition, 10 mA cm ⁻²	3.13	18.7	-11.8
16.32 wt% NiS _x /carbon paper	Electrodeposition, 100 mA cm ⁻²	4.99	28.3	-16.9
10.55 wt% NiS _x /carbon paper	Pulse electrodeposition, 10 mA cm ⁻²	4.21	27.0	-13.0
20.85 wt% NiS _x /carbon paper	Electrodeposition, 10 mA cm ⁻²	4.41	27.3	-16.8
26.22 wt% NiS _x /carbon paper	Electrodeposition, 10 mA cm ⁻²	5.58	27.6	-18.8
2.6 wt% NiS _x /carbon paper	Impregnation (ethanol)	7.54	30.00	-25.69
13.6 wt% NiS _x /carbon paper	Impregnation (ethanol)	6.27	23.89	-18.06
23.2 wt% NiS _x /carbon paper	Impregnation (ethanol)	7.38	28.47	-23.59
7.5 wt% NiS _x /carbon paper	Impregnation (isopropanol)	7.44	31.00	-26.53
12.5 wt% NiS _x /carbon paper	Impregnation (isopropanol)	8.28	31.39	-28.00
25.8 wt% NiS _x /carbon paper	Impregnation (isopropanol)	8.28	30.92	-24.70
14.55 wt% NiS _x /carbon paper	Electroless deposition	4.34	19.6	-18.34

Chapter 7 Conclusion

This thesis investigated into chemistry and electrochemistry of aqueous polysulphide solutions and developed a number of porous electrodes for application in the polysulphide-air RFB.

Firstly, a numerical model expanded from previous work was used to calculate the equilibrium concentrations of sulphide and polysulphide species within aqueous polysulphide solutions. S_4^{2-} and S_3^{2-} were suggested as the dominant polysulphide species within the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ and the $0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolytes. The equilibrium constants among polysulphides utilised in the numerical model were shown to have a great impact on the calculated polysulphide concentrations. Activity coefficients of the sulphide and polysulphide species are required for further improvement of the numerical model. Aqueous S_x^{2-}/HS^- redox reactions reported previously were summarized in this study, whose potentials were calculated based on the equilibrium concentrations of the ionic species within aqueous polysulphide solutions. A metastable Eh-pH diagram of the S-H₂O system at 25°C with a total dissolved sulphur concentration of 2 mol kg^{-1} was built based on the thermodynamic data.

Secondly, glassy carbon and nickel, as disk-shaped electrodes, were investigated in aqueous polysulphide electrolytes in a three-electrode cell setup. CV measurements at 20 mV s^{-1} with both glassy carbon and nickel showed multiple peaks in the anodic and cathodic polarizations of aqueous polysulphide electrolytes. The first anodic peak corresponded to the deposition of a thin layer of elemental sulphur on the surface of the glassy carbon disk electrode, or the formation of a NiS_x 3D layer on the surface of the nickel disk electrode. The second and third anodic peaks corresponded to the electrochemical formation of polysulphide and sulphur species on the surface of the electrodes. The cathodic peak(s) corresponded to the reduction of polysulphides and sulphur species on the electrode surface. Both glassy carbon and nickel electrode suffered from passivation issues at high anodic potentials, especially for the nickel electrode, which however could be partially compensated by more negative and longer cathodic polarizations.

Polarization tests suggested that nickel had a better catalytic activity towards aqueous S_x^{2-}/HS^- redox reactions than glassy carbon. The derived exchange current density of nickel disk electrode was nearly two magnitude higher than that of glassy carbon disk electrode in the $1 \text{ mol kg}^{-1} \text{ Na}_2\text{S}_2/1 \text{ mol kg}^{-1} \text{ NaOH}$ electrolyte. In fact, previous studies suggested that the actual catalysts for the aqueous S_x^{2-}/HS^- redox reactions of nickel-based electrodes are nickel sulphides [45, 166, 213]. As a result, nickel sulphides were chosen as the catalysts for the preparation of high-surface-area electrodes with carbon paper substrate.

Thirdly, a number of NiS_x /carbon paper composite electrodes were prepared and characterized, together with catalyst-free carbon papers and nickel foams. Thermal treatment at 450°C for 6 hr was shown to be an effective way to increase the hydrophilicity of the SGL 10AA carbon paper. Sulphidisation of the acid-treated nickel foam via boiling in a concentrated aqueous polysulphide solution for 30 min was proven to be better than impregnating in the same solution for 72 hr, which was hence adopted to sulphidise the Ni/carbon paper electrodes. The Ni/carbon paper electrodes were prepared by three methods, including electrodeposition, impregnation and electroless deposition. NiS_x /carbon paper electrodes prepared by all three methods showed comparable catalytic activities of the sulphidised acid-treated nickel foam, whose exchange current densities were in the same magnitude. However, the NiS_x /carbon paper electrodes prepared by impregnation method using a $\text{Ni}(\text{NO}_3)_2$ /isopropanol solution exhibited the best catalytic performance whereas the NiS_x /carbon paper electrodes prepared by electroless deposition method showed the lowest yet most reversible (towards anodic and cathodic polarizations) catalytic activities.

Lastly, a 0.9 mm thick sulphidised acid-treated nickel foam was demonstrated as the negative electrode for a 5 cm^2 single-cell polysulphide-air RFB. A maximum power density of $\sim 4.8 \text{ mW cm}^{-2}$ was achieved at a current density of 22 mA cm^{-2} , which improved more than twice compared to the previous demonstration result with an untreated SGL 10AA carbon paper as the negative electrode. EIS measurements at OCV indicated that the impedance of the polysulphide side half-cell, mainly comprised of the charge transfer resistance, decreased more than 20 times compared to the previous demonstration yet still much higher than that of the air side half-cell. Hence, better

polysulphide electrodes are needed to further improve the performance of the Polysulphide-air RFB.

7.1 Future Work

The NiS_x modified carbon paper electrodes prepared in this study using a variety of methods had shown catalytic activities of the same magnitude as the sulphidised Ni foam towards aqueous S_x²⁻/HS⁻ redox reactions and much higher compared to the catalyst-free carbon paper electrodes. Yet, the performance of NiS_x/carbon paper electrodes can be further improved by increasing the nickel loading on the carbon paper substrate. This can be achieved by simply increasing the duration of electroplating or electroless deposition or the amount of impregnation solution used. Optimisation of the electroplating conditions, such as current density, temperature and agitation of electrolyte, and the H_{2(g)} reduction conditions, such as temperature and duration, would further improve the performance of the NiS_x/carbon paper electrodes by increasing their true surface area per unit mass of the catalyst (nickel).

In addition, conditions of the sulphidisation treatment for the Ni/carbon paper electrodes need to be further optimised in the future work, in order to reduce the losses of active materials (Ni/NiS_x) during the sulphidisation process. Impregnation at temperatures below the boiling point in the aqueous polysulphide electrolyte for longer periods of time would be a possible solution.

Other transition metal chalcogenides, such as CoS, CoS₂ and MoS₂, had also been reported as possessing high catalytic activities towards aqueous S_x²⁻/HS⁻ redox reactions. CoS which has been widely adopted as the catalyst for aqueous polysulphide electrolytes in recent studies shall also be adopted to prepare highly active polysulphide electrodes in the future work, apart from NiS_x.

Carbon paper although exhibiting better mechanical stability however provides much lower surface areas as compared to carbon/graphite felt or cloth or activated carbon. Such carbon materials with much higher surface areas might be adopted as the substrate to prepare highly active polysulphide electrodes in the future work. Same methods of preparing NiS_x/carbon paper electrodes would be transferable to the preparation of

carbon/graphite felt or cloth -based electrodes. When activated carbon is used as the substrate, binders such as PTFE or PVDF might be used to combine the catalysts and the activated carbon to prepare mechanically stable electrodes.

Besides the optimisation of aqueous polysulphide electrodes, the polysulphide-air RFB needs to be more systematically characterized in the future work. The following measurements shall be conducted:

1. polarization curve measurement;
2. measurement of overpotentials of each half-cell at certain current densities (for both charging and discharging processes);
3. EIS measurements of the full cell and both half-cells with/without load;
4. charge/discharge cycling under various current densities (measurement of cell voltage against capacity/SoC).

References

1. IEA, *World Energy Outlook 2017*. 2017.
2. BP, *BP Statistical Review of World Energy*. 2018.
3. Buckle, S. and F. Whitmarsh, *Climate change, greenhouse gases and radiative forcing*. 2013.
4. UNFCCC, *The Paris Agreement*. 2015.
5. IEA, *World Energy Balance 2018*. 2018.
6. IEA, *Electricity Information 2018*. 2018.
7. IEA, *Renewables Information 2018*. 2018.
8. IEA, *Renewables 2017: Analysis and Forecasts to 2022*. 2017.
9. Strbac, G., et al., *Strategic assessment of the role and value of energy storage systems in the UK low carbon energy future*. Report for Carbon Trust, 2012.
10. Strbac, G., et al., *Understanding the balancing challenge*. DECC, London, 2012.
11. IEA, *Energy Technology Perspectives 2014*. 2014.
12. IEA, *Technology Roadmap: Energy Storage*. 2014.
13. Brandon, N. and J.S. Edge, *Foresight review of energy storage: The key to safe, secure and sustainable energy systems*. 2017, Lloyd's Register Foundation.
14. Chakrabarti, M.H., et al., *Redox Flow Battery for Energy Storage*. Arabian Journal for Science and Engineering, 2013. **38**(4): p. 723-739.
15. Brandon, N.P., et al., *UK Research Needs in Grid Scale Energy Storage Technologies*. 2016.
16. Ponce de León, C., et al., *Redox flow cells for energy conversion*. Journal of Power Sources, 2006. **160**(1): p. 716-732.
17. Chalamala, B.R., et al., *Redox Flow Batteries: An Engineering Perspective*. Proceedings of the IEEE, 2014. **102**(6): p. 976-999.
18. Zhang, H., X. Li, and J. Zhang, *Redox Flow Batteries: Fundamentals and Applications*. 2017: CRC Press.
19. Su, L., et al., *Toward an Inexpensive Aqueous Polysulfide-Polyiodide Redox Flow Battery*. Industrial & Engineering Chemistry Research, 2017. **56**(35): p. 9783-9792.
20. Brandon, N., A. Kucernak, and V. Yufit, *Regenerative fuel cells*. 2012, Google Patents.
21. Xia, Y., *Polysulphide-air Redox Flow Battery - A Novel Solution for Grid Scale Energy Storage*. 2014, Imperial College London.
22. Leung, P., et al., *Progress in redox flow batteries, remaining challenges and their applications in energy storage*. RSC Advances, 2012. **2**(27): p. 10125-10156.
23. Wang, W., et al., *Recent Progress in Redox Flow Battery Research and Development*. Advanced Functional Materials, 2013. **23**(8): p. 970-986.
24. Sun, B. and M. Skyllas-Kazacos, *Modification of graphite electrode materials for vanadium redox flow battery application—I. Thermal treatment*. Electrochimica Acta, 1992. **37**(7): p. 1253-1260.
25. Pierozynski, B., *The effect of thermal treatments on the mechanical and electrical properties of nickel-coated carbon fibre composites*, in *Polish Journal of Chemical Technology*. 2011. p. 16.
26. Pezeshki, A.M., et al., *High performance electrodes in vanadium redox flow batteries through oxygen-enriched thermal activation*. Journal of Power Sources, 2015. **294**: p. 333-338.

27. Il-Han, Y. and S. Hyungtak, *Electrode Properties for Water Electrolysis of Hydrophilic Carbon Paper with Thermal Anneal*. Korean Journal of Materials Research, 2016. **26**(5): p. 241-245.
28. Sun, B. and M. Skyllas-Kazacos, *Chemical modification of graphite electrode materials for vanadium redox flow battery application—part II. Acid treatments*. Electrochimica Acta, 1992. **37**(13): p. 2459-2465.
29. Cheng, Z., et al., *Surface activation of carbon paper with potassium dichromate lotion and application as a supercapacitor*. Applied Surface Science, 2015. **349**: p. 833-838.
30. Pittman, C.U., et al., *Surface properties of electrochemically oxidized carbon fibers*. Carbon, 1999. **37**(11): p. 1797-1807.
31. Sun, B. and M. Skyllas-Kazacos, *Chemical modification and electrochemical behaviour of graphite fibre in acidic vanadium solution*. Electrochimica Acta, 1991. **36**(3): p. 513-517.
32. Ahn, S.H., et al., *Electrochemical preparation of Pt-based catalysts on carbon paper treated with Sn sensitization and Pd activation*. International Journal of Hydrogen Energy, 2012. **37**(1): p. 41-50.
33. Zhou, H., et al., *Novel cobalt coated carbon felt as high performance negative electrode in sodium polysulfide/bromine redox flow battery*. Electrochemistry, 2006. **74**(4): p. 296-298.
34. Zhao, P., et al., *Nickel foam and carbon felt applications for sodium polysulfide/bromine redox flow battery electrodes*. Electrochimica Acta, 2005. **51**(6): p. 1091-1098.
35. Prifti, H., et al., *Membranes for redox flow battery applications*. Membranes, 2012. **2**(2): p. 275-306.
36. Gandomi, Y.A., et al., *Critical Review-Experimental Diagnostics and Material Characterization Techniques Used on Redox Flow Batteries*. Journal of the Electrochemical Society, 2018. **165**(5): p. A970-A1010.
37. Chen, H., G. Cong, and Y.-C. Lu, *Recent progress in organic redox flow batteries: Active materials, electrolytes and membranes*. Journal of Energy Chemistry, 2018. **27**(5): p. 1304-1325.
38. Ding, Y., et al., *Molecular engineering of organic electroactive materials for redox flow batteries*. Chemical Society Reviews, 2018. **47**(1): p. 69-103.
39. Winsberg, J., et al., *Redox-Flow Batteries: From Metals to Organic Redox-Active Materials*. Angewandte Chemie International Edition, 2017. **56**(3): p. 686-711.
40. Wei, X.L., et al., *Materials and Systems for Organic Redox Flow Batteries: Status and Challenges*. Acs Energy Letters, 2017. **2**(9): p. 2187-2204.
41. Leung, P., et al., *Recent developments in organic redox flow batteries: A critical review*. Journal of Power Sources, 2017. **360**: p. 243-283.
42. Kowalski, J.A., et al., *Recent advances in molecular engineering of redox active organic molecules for nonaqueous flow batteries*. Current Opinion in Chemical Engineering, 2016. **13**: p. 45-52.
43. Remick, R.J. and P.G.P. Ang, *Electrically rechargeable anionically active reduction-oxidation electrical storage-supply system*. 1984, Google Patents.
44. Zhou, H.T., et al., *A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery*. Electrochimica Acta, 2006. **51**(28): p. 6304-6312.

45. Ge, S.H., B.L. Yi, and H.M. Zhang, *Study of a high power density sodium polysulfide/bromine energy storage cell*. Journal of Applied Electrochemistry, 2004. **34**(2): p. 181-185.
46. Mahmoudzadeh, M.A., et al., *A high energy density solar rechargeable redox battery*. Journal of Materials Chemistry A, 2016. **4**(9): p. 3446-3452.
47. Li, Z., et al., *A high-energy and low-cost polysulfide/iodide redox flow battery*. Nano Energy, 2016. **30**: p. 283-292.
48. Wei, X., et al., *An Aqueous Redox Flow Battery Based on Neutral Alkali Metal Ferri/ferrocyanide and Polysulfide Electrolytes*. Journal of The Electrochemical Society, 2016. **163**(1): p. A5150-A5153.
49. Li, Z., et al., *Air-Breathing Aqueous Sulfur Flow Battery for Ultralow-Cost Long-Duration Electrical Storage*. Joule, 2017. **1**(2): p. 306-327.
50. Xia, Y., V. Yufit, and N.P. Brandon, *Polysulphide Air Redox Flow Battery - a Novel Solution for Grid Scale Energy Storage*. Meeting Abstracts, 2015. **MA2015-03**(3): p. 654.
51. *RWE abandons Regenesys project*, in *Tce*. 2004. p. 9-9.
52. Weber, A.Z., et al., *Redox flow batteries: a review*. Journal of Applied Electrochemistry, 2011. **41**(10): p. 1137-1164.
53. Zheng, Q., et al., *Investigation on the performance evaluation method of flow batteries*. Journal of Power Sources, 2014. **266**: p. 145-149.
54. Aaron, D., et al., *Polarization curve analysis of all-vanadium redox flow batteries*. Journal of Applied Electrochemistry, 2011. **41**(10): p. 1175-1182.
55. Bard, A., J and L. Faulkner, R, *Electrochemical methods: fundamentals and applications*. Department of Chemistry and Biochemistry University of Texas at Austin, John Wiley & Sons, Inc, 2001: p. 156-176.
56. Lvovich, V.F., *Impedance spectroscopy: applications to electrochemical and dielectric phenomena*. 2012: John Wiley & Sons.
57. Bard, A., J and L. Faulkner, R, *Electrochemical methods: fundamentals and applications*. 2001: John Wiley & Sons, Inc.
58. Dewage, H.H., *Investigation of hydrogen based redox flow batteries*, in *Earth Science and Engineering*. 2016, Imperial College London.
59. Mellor, J.W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry: Volume X*. 1930: Longmans, Green and Company.
60. Rickard, D., *Chapter 2 Sulfur Chemistry in Aqueous Solutions*, in *Sulfidic sediments and sedimentary rocks*, D. Rickard, Editor. 2012, Newnes.
61. Kamysny, A., et al., *Equilibrium distribution of polysulfide ions in aqueous solutions at different temperatures by rapid single phase derivatization*. Environmental science & technology, 2007. **41**(7): p. 2395-2400.
62. Kamysny, A., *Solubility of cyclooctasulfur in pure water and sea water at different temperatures*. Geochimica et Cosmochimica Acta, 2009. **73**(20): p. 6022-6028.
63. Behm, M. and D. Simonsson, *Electrochemical production of polysulfides and sodium hydroxide from white liquor: Part I: Experiments with rotating disc and ring-disc electrodes*. Journal of Applied Electrochemistry, 1997. **27**(5): p. 507-518.
64. Hodes, G., J. Manassen, and D. Cahen, *Electrocatalytic Electrodes for the Polysulfide Redox System*. Journal of the Electrochemical Society, 1980. **127**(3): p. 544-549.

65. Dong, Y.F., W.J. Li, and S. Jin, *Highly active metal pyrites catalysts for a low-cost, high-performance polysulfide/ferrocyanide redox flow battery*. Abstracts of Papers of the American Chemical Society, 2017. **254**.
66. Wei, X.L., et al., *An Aqueous Redox Flow Battery Based on Neutral Alkali Metal Ferri/ferrocyanide and Polysulfide Electrolytes*. Journal of the Electrochemical Society, 2016. **163**(1): p. A5150-A5153.
67. Kamyshny, A., et al., *Equilibrium distribution of polysulfide ions in aqueous solutions at 25 degrees C: A new approach for the study of polysulfides equilibria*. Environmental science & technology, 2004. **38**(24): p. 6633-6644.
68. Lessner, P., et al., *Kinetics of Aqueous Polysulfide Solutions: II. Electrochemical Measurement of the Rates of Coupled Electrochemical and Chemical Reactions by the Potential Step Method*. Journal of The Electrochemical Society, 1986. **133**(12): p. 2517-2522.
69. Giggenbach, W., *On the nature of the blue solutions of sulfur*. Journal of Inorganic and Nuclear Chemistry, 1968. **30**(12): p. 3189-3201.
70. Giggenbach, W., *Blue solutions of sulfur in water at elevated temperatures*. Inorganic chemistry, 1971. **10**(6): p. 1306-1308.
71. Giggenbach, W., *The blue supersulphide ion, S²⁻*. Journal of the Chemical Society, Dalton Transactions, 1973(7): p. 729-731.
72. Giggenbach, W., *Equilibria Involving Polysulfide Ions in Aqueous Sulfide Solutions Up to 240°*. Inorganic chemistry, 1974. **13**(7): p. 1724-1730.
73. Arntson, R.H., F.W. Dickson, and G. Tunell, *Saturation Curves of Orthorhombic Sulfur in the System S-Na₂S-H₂O at 25° and 50°C*. Science, 1958. **128**(3326): p. 716-718.
74. Teder, A., *The Equilibrium between Elementary Sulfur and Aqueous Polysulfide Solutions*. Acta chemica Scandinavica, 1971. **25**(5): p. 1722-&.
75. Giggenbach, W., *Optical Spectra and Equilibrium Distribution of Polysulfide Ions in Aqueous-Solution at 20°*. Inorganic chemistry, 1972. **11**(6): p. 1201-&.
76. Licht, S. and J. Davis, *Disproportionation of aqueous sulfur and sulfide: Kinetics of polysulfide decomposition*. Journal of Physical Chemistry B, 1997. **101**(14): p. 2540-2545.
77. Licht, S., G. Hodes, and J. Manassen, *Numerical analysis of aqueous polysulfide solutions and its application to cadmium chalcogenide/polysulfide photoelectrochemical solar cells*. Inorganic chemistry, 1986. **25**(15): p. 2486-2489.
78. Vorobets, V., S. Kovach, and G.Y. Kolbasov, *Distribution of ion species and formation of ion pairs in concentrated polysulfide solutions in photoelectrochemical transducers*. Russian journal of applied chemistry, 2002. **75**(2): p. 229-234.
79. Clever, H.L., *The ion product constant of water: Thermodynamics of water ionization*. Journal of Chemical Education, 1968. **45**(4): p. 231.
80. Fisher, J.R. and H.L. Barnes, *Ion-product constant of water to 350.deg*. The Journal of Physical Chemistry, 1972. **76**(1): p. 90-99.
81. Covington, A.K., M.I.A. Ferra, and R.A. Robinson, *Ionic product and enthalpy of ionization of water from electromotive force measurements*. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1977. **73**(0): p. 1721-1730.
82. Brandariz, I., S. Fiol, and M.S. De Vicente, *Study of the Influence of Ionic Strength on the Ionic Product of Water in Saline Media at 25°C Using the Pitzer Equations*.

- Berichte der Bunsengesellschaft für physikalische Chemie, 1995. **99**(5): p. 749-752.
83. Kron, I., et al., *The ionic product of water in highly concentrated aqueous electrolyte solutions*. Monatshefte für Chemie / Chemical Monthly, 1995. **126**(8-9): p. 819-837.
 84. Tawa, G.J. and L.R. Pratt, *Theoretical Calculation of the Water Ion Product K_w* . Journal of the American Chemical Society, 1995. **117**(5): p. 1625-1628.
 85. Sun, W., et al., *Equilibrium Expressions Related to the Solubility of the Sour Corrosion Product Mackinawite*. Industrial & Engineering Chemistry Research, 2008. **47**(5): p. 1738-1742.
 86. Ellis, A.J. and W. Giggenbach, *Hydrogen sulphide ionization and sulphur hydrolysis in high temperature solution*. Geochimica et Cosmochimica Acta, 1971. **35**(3): p. 247-260.
 87. Meyer, B., et al., *Second dissociation constant of hydrogen sulfide*. 1983. **22**(Generic): p. 2345-2346.
 88. Myers, R.J., *The new low value for the second dissociation constant for H_2S : Its history, its best value, and its impact on the teaching of sulfide equilibria*. Journal of Chemical Education, 1986. **63**(8): p. 687.
 89. Licht, S. and J. Manassen, *The second dissociation constant of H_2S* . Journal of The Electrochemical Society, 1987. **134**(4): p. 918-921.
 90. Schoonen, M. and H.L. Barnes, *An approximation of the second dissociation constant for H_2S* . Geochimica et Cosmochimica Acta, 1988. **52**(3): p. 649-654.
 91. Licht, S., F. Forouzan, and K. Longo, *Differential densometric analysis of equilibria in highly concentrated media: determination of the aqueous second acid dissociation constant of H_2S* . Analytical Chemistry, 1990. **62**(13): p. 1356-1360.
 92. Licht, S., et al., *Conductometric analysis of the second acid dissociation constant of H_2S in highly concentrated aqueous media*. Journal of electroanalytical chemistry and interfacial electrochemistry, 1991. **318**(1): p. 111-129.
 93. Kelsall, G.H. and I. Thompson, *Redox chemistry of H_2S oxidation in the British Gas Stretford Process Part I: Thermodynamics of sulphur-water systems at 298 K*. Journal of Applied Electrochemistry, 1993. **23**(4): p. 279-286.
 94. Phillips, D.J. and S.L. Phillips, *High Temperature Dissociation Constants of HS^- and the Standard Thermodynamic Values for S_2* . Journal of Chemical & Engineering Data, 2000. **45**(6): p. 981-987.
 95. Migdisov, A.A., et al., *Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur*. Geochimica et Cosmochimica Acta, 2002. **66**(10): p. 1713-1725.
 96. Giggenbach, W., *Optical spectra of highly alkaline sulfide solutions and the second dissociation constant of hydrogen sulfide*. Inorganic Chemistry, 1971. **10**(7): p. 1333-1338.
 97. Stephens, H.P. and J.W. Cobble, *Thermodynamic properties of the aqueous sulfide and bisulfide ions and the second ionization constant of hydrogen sulfide over extended temperatures*. Inorganic Chemistry, 1971. **10**(3): p. 619-625.
 98. Rao, C.N.R. and K.P.R. Pisharody, *Transition metal sulfides*. Progress in Solid State Chemistry, 1976. **10**: p. 207-270.
 99. Khan, S.A., *UV-ATR Spectroscopy Study of the Speciation in Aqueous Polysulfide Electrolyte Solutions*. International Journal of Electrochemical Science, 2012. **7**(1): p. 561-568.

100. Danielsson, L.-G., et al., *UV characterization of sulphide-polysulphide solutions and its application for process monitoring in the electrochemical production of polysulphides*. Journal of pulp and paper science, 1996. **22**(6): p. J187-J191.
101. Chen, K.Y. and S.K. Gupta, *Formation of Polysulfides in Aqueous Solution*. Environmental Letters, 1973. **4**(3): p. 187-200.
102. Giggenbach, W., *The blue supersulphide ion, S₂*. Journal of the Chemical Society, Dalton Transactions, 1973(7): p. 729-731.
103. Janz, G.J., et al., *Raman Studies of Sulfur-Containing Anions in Inorganic Polysulfides - Sodium Polysulfides*. Inorganic chemistry, 1976. **15**(8): p. 1759-1763.
104. Ward, A.T., *Raman spectrum and force constants of S₄²⁻*. Materials Research Bulletin, 1969. **4**(8): p. 581-590.
105. Meyer, B., M. Ospina, and L. Peter, *Raman spectrometric determination of oxysulfur anions in aqueous systems*. Analytica Chimica Acta, 1980. **117**: p. 301-311.
106. Khan, S.A., R.W. Hughes, and P.A. Reynolds, *Raman spectroscopic determination of oxoanions in aqueous polysulfide electrolyte solutions*. Vibrational Spectroscopy, 2011. **56**(2): p. 241-244.
107. Filpponen, I., et al., *Spectral Monitoring of the Formation and Degradation of Polysulfide Ions in Alkaline Conditions*. Industrial & Engineering Chemistry Research, 2006. **45**(22): p. 7388-7392.
108. Argyropoulos, D.S., et al., *Quantitative ¹H NMR analysis of alkaline polysulfide solutions*. Holzforschung, 2005. **59**(2): p. 124-131.
109. Gun, J., et al., *Electrospray ionization mass spectrometric analysis of aqueous polysulfide solutions*. Microchimica Acta, 2004. **146**(3-4): p. 229-237.
110. Douek, M., J. Sullivan, and J. Ing, *Effect of Sample-Related Sources of Error on the Analysis of Pulp and Paper Mill Process Liquids by Ion Chromatography: Part I—Determination of Sulphur Species*. Journal of Wood Chemistry and Technology, 1993. **13**(3): p. 439-462.
111. Ciglenečki, I., et al., *Electroanalytical methods in characterization of sulfur species in aqueous environment*. Journal of Electrochemical Science and Engineering, 2014. **4**(4): p. 155-163.
112. Vorobets, V., S. Kovach, and G.Y. Kolbasov, *Potentiometric and spectrophotometric determination of the ionic composition of concentrated sodium polysulfides*. Russian journal of applied chemistry, 2003. **76**(3): p. 391-395.
113. Licht, S., J. Manassen, and G. Hodes, *The High Aqueous Solubility of K₂S and Its Effect on Bulk and Photoelectrochemical Characteristics of Cd (SeTe) / S_x = Cells: I. Polysulfide Variation at Constant Sulfur/Sulfide Ratio*. Journal of The Electrochemical Society, 1986. **133**(2): p. 272-277.
114. Licht, S., *An energetic medium for electrochemical storage utilizing the high aqueous solubility of potassium polysulfide*. Journal of the Electrochemical Society, 1987. **134**(9): p. 2137-2141.
115. Mellor, J.W., *A Comprehensive Treatise On Inorganic And Theoretical Chemistry: Volume II*. 1922: Long Mans, Green And Co.; London.
116. Licht, S., *Aqueous Solubilities, Solubility Products and Standard Oxidation-Reduction Potentials of the Metal Sulfides*. Journal of The Electrochemical Society, 1988. **135**(12): p. 2971-2975.

117. Rosen, E. and R. Tegman, *A Preparative and X-Ray Powder Diffraction Study of Polysulfides Na₂S₂, Na₂S₄ and Na₂S₅*. Acta chemica Scandinavica, 1971. **25**(9): p. 3329-&.
118. Oei, D.-G., *Sodium-sulfur system. II. Polysulfides of sodium*. Inorganic Chemistry, 1973. **12**(2): p. 438-441.
119. Brown, A.P. and J.E. Battles, *The Direct Synthesis of Sodium Polysulfides from Sodium and Sulfur*. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 1984. **14**(7): p. 945-951.
120. Rule, A. and J.S. Thomas, *CCLXIV.-The polysulphides of the alkali metals. Part II. The polysulphides of potassium*. Journal of the Chemical Society, Transactions, 1914. **105**(0): p. 2819-2829.
121. Rule, A. and J.S. Thomas, *XXIII.-The polysulphides of the alkali metals. Part I. The polysulphides of sodium*. Journal of the Chemical Society, Transactions, 1914. **105**(0): p. 177-189.
122. Pearson, T.G. and P.L. Robinson, *CLXXXIX.-The polysulphides of the alkali metals. Part I. Sodium (i)*. Journal of the Chemical Society (Resumed), 1930(0): p. 1473-1497.
123. Pearson, T.G. and P.L. Robinson, *CLXXXIII.-The polysulphides of the alkali metals. Part III. Potassium*. Journal of the Chemical Society (Resumed), 1931(0): p. 1304-1314.
124. Licht, S. and J. Manassen, *The Effect of Hydroxide Ion on Cd-Chalcogenide/Aqueous Polysulfide Photoelectrochemical Cells*. Journal of The Electrochemical Society, 1985. **132**(5): p. 1076-1081.
125. Chen, K.Y. and J.C. Morris, *Kinetics of oxidation of aqueous sulfide by oxygen*. Environmental Science & Technology, 1972. **6**(6): p. 529-537.
126. Kuhn, A.T., M.S. Chana, and G.H. Kelsall, *A review of the air oxidation of aqueous sulphide solutions*. Journal of Chemical Technology and Biotechnology. Chemical Technology, 1983. **33**(8): p. 406-414.
127. Steudel, R., G. Holdt, and R. Nagorka, *On the Autoxidation of Aqueous Sodium Polysulfide*. Zeitschrift für Naturforschung B, 1986. **41**(12): p. 1519-1522.
128. Fischer, H., G. Schulz-Ekloff, and D. Wöhrle, *Oxidation of aqueous sulfide solutions by dioxygen Part I: Autoxidation reaction*. Chemical Engineering & Technology, 1997. **20**(7): p. 462-468.
129. Kleinjan, W.E., A.d. Keizer, and A.J.H. Janssen, *Kinetics of the chemical oxidation of polysulfide anions in aqueous solution*. Water Research, 2005. **39**(17): p. 4093-4100.
130. Arntson, R.H., F.W. Dickson, and G. Tunell, *Systems S-Na₂O-H₂O and S-H₂O: Application to the mode of origin of natural alkaline polysulfide and thiosulfate solutions*. American Journal of Science, 1960. **258**(8): p. 574-582.
131. Giggenbach, W., *Kinetics of the polysulfide-thiosulfate disproportionation up to 240°*. Inorganic Chemistry, 1974. **13**(7): p. 1730-1733.
132. Allen, P.L. and A. Hickling, *Electrochemistry of sulphur. Part 1.-Overpotential in the discharge of the sulphide ion*. Transactions of the Faraday Society, 1957. **53**(0): p. 1626-1635.
133. Milazzo, G., S. Caroli, and V.K. Sharma, *Tables of standard electrode potentials*. 1978: Wiley.
134. Haynes, W.M., *CRC handbook of chemistry and physics (96th Edition)*. 2016.
135. Bard, A.J., R. Parsons, and J. Jordan, *Standard potentials in aqueous solution*. 1985: CRC press.

136. Remick, R. and E. Camara, *Electrochemistry of the Sulfide/Polysulfide Couple*, in *Institute of Gas Technology, Lawrence Berkeley Laboratory Report No. LBL-16850 (July 1983). Seal Glassy carbon counter electrode Molybdenum cap Graded glass-^{\Lambda} Tungsten feedthrough*. 1983.
137. Lessner, P.M., et al., *The Dependence of Aqueous Sulfur-Polysulfide Redox Potential on Electrolyte Composition and Temperature*. Journal of The Electrochemical Society, 1993. **140**(7): p. 1847-1849.
138. Bratsch, S.G., *Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K*. Journal of Physical and Chemical Reference Data, 1989. **18**(1): p. 1-21.
139. Peramunage, D. and S. Licht, *A Solid Sulfur Cathode for Aqueous Batteries*. Science, 1993. **261**(5124): p. 1029-1032.
140. Latimer, W.M., *The oxidation states of the elements and their potentials in aqueous solutions*. Second Edition ed. 1952, New York: Prentice-Hall.
141. Pourbaix, M., *Atlas of electrochemical equilibria in aqueous solutions*. 1966.
142. Wierse, D.G., M.M. Lohrengel, and J.W. Schultze, *Electrochemical properties of sulfur adsorbed on gold electrodes*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1978. **92**(2): p. 121-131.
143. Hamilton, I.C. and R. Woods, *An investigation of the deposition and reactions of sulphur on gold electrodes*. Journal of Applied Electrochemistry, 1983. **13**(6): p. 783-794.
144. Kapusta, S., et al., *The anodic oxidation of sulfide on platinum electrodes*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1983. **153**(1): p. 157-174.
145. Gennero De Chialvo, M.R. and A.J. Arvia, *The electrochemical behaviour of copper in alkaline solutions containing sodium sulphide*. Journal of Applied Electrochemistry, 1985. **15**(5): p. 685-696.
146. Buckley, A.N., I.C. Hamilton, and R. Woods, *An investigation of the sulphur(-II)/sulphur(0) system on gold electrodes*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1987. **216**(1): p. 213-227.
147. Briceno, A. and S. Chander, *Oxidation of hydrosulphide ions on gold Part II: Characterization of gold/aqueous hydrosulphide solution interface*. Journal of Applied Electrochemistry, 1990. **20**(3): p. 512-517.
148. Briceno, A. and S. Chander, *Oxidation of hydrosulphide ions on gold Part I: A cyclic voltammetry study*. Journal of Applied Electrochemistry, 1990. **20**(3): p. 506-511.
149. Anani, A.A., et al., *Electrochemical Production of Hydrogen and Sulfur by Low-Temperature Decomposition of Hydrogen Sulfide in an Aqueous Alkaline Solution*. Journal of The Electrochemical Society, 1990. **137**(9): p. 2703-2709.
150. Lezna, R.O., N.R. de Tacconi, and A.J. Arvia, *Modulated reflectance spectroscopy and voltammetry of the sulphide/gold system*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1990. **283**(1): p. 319-336.
151. Buckley, A.N. and R. Woods, *Electrochemical and XPS studies of the surface oxidation of synthetic heazlewoodite (Ni₃S₂)*. Journal of Applied Electrochemistry, 1991. **21**(7): p. 575-582.
152. Kelsall, G.H. and I. Thompson, *Redox chemistry of H₂S oxidation by the British Gas Stretford Process Part. II: Electrochemical behaviour of aqueous hydrosulphide (HS⁻) solutions*. Journal of Applied Electrochemistry, 1993. **23**(4): p. 287-295.

153. Bohé, A.E., J.R. Vilche, and A.J. Arvia, *The voltammetric behaviour of nickel in sodium hydroxide-sodium sulphide solutions*. Corrosion Science, 1993. **34**(1): p. 151-162.
154. Szynekarczuk, J., P.G. Komorowski, and J.C. Donini, *Redox reactions of hydrosulphide ions on the platinum electrode—I. The presence of intermediate polysulphide ions and sulphur layers*. Electrochimica Acta, 1994. **39**(15): p. 2285-2289.
155. Szynekarczuk, J., P.G. Komorowski, and J.C. Donini, *Redox reactions of hydrosulphide ions on the platinum electrode—II. An impedance spectroscopy study and identification of the polysulphide intermediates*. Electrochimica Acta, 1995. **40**(4): p. 487-494.
156. Behm, M. and D. Simonsson, *Nickel as anode material for the electrochemical production of polysulfides in white liquor*. Journal of New Materials for Electrochemical Systems, 1999. **2**(1): p. 11-18.
157. Yi, Q.F., *Investigation of Anodic Oxidation Mechanism of Na₂S Solution on Graphite Electrode*. Acta Physico-Chimica Sinica, 2000. **16**(3): p. 263-268.
158. Radford, G.J.W., et al., *Electrochemical characterisation of activated carbon particles used in redox flow battery electrodes*. Journal of Power Sources, 2008. **185**(2): p. 1499-1504.
159. Xiao, L., et al., *Copper/cuprous sulfide electrode: preparation and performance*. Science China Chemistry, 2015. **58**(6): p. 1039-1043.
160. Stephens, I.E.L., *Polysulfide Electrocatalysis at Transition Metal Sulfides*. 2010, University of Cambridge.
161. Lessner, P., et al., *Kinetics of Aqueous Polysulfide Solutions: Part III. Investigation of Homogeneous and Electrode Kinetics by the Rotating Disk Method*. Journal of The Electrochemical Society, 1987. **134**(11): p. 2669-2677.
162. Licht, S., *Comment on "Kinetics of Aqueous Polysulfide Solutions" [J. Electrochem. Soc., 133, 2510]: I. Theory of Coupled Electrochemical and Chemical Reactions, Response to a Potential Step*. Journal of The Electrochemical Society, 1988. **135**(1): p. 258-259.
163. Licht, S., *Comment on "Kinetics of Aqueous Polysulfide Solutions" [J. Electrochem. Soc., 133, 2517]: II. Electrochemical Measurement of the Rates of Coupled Electrochemical and Chemical Reactions by the Potential Step Method*. Journal of The Electrochemical Society, 1988. **135**(1): p. 258-259.
164. Licht, S., *A description of energy conversion in photoelectrochemical solar cells*. Nature, 1987. **330**(6144): p. 148-151.
165. Winnick, J., et al., *Solution processes in photoelectrochemical cells*. Applied physics letters, 1988. **53**(20): p. 1985-1987.
166. Hodes, G., J. Manassen, and D. Cahen, *Photo-electrochemical energy conversion: electrocatalytic sulphur electrodes*. Journal of Applied Electrochemistry, 1977. **7**(2): p. 181-182.
167. Esposito, D.V., et al., *Comparative study of tungsten monocarbide and platinum as counter electrodes in polysulfide-based photoelectrochemical solar cells*. Journal of The Electrochemical Society, 2009. **156**(8): p. B962-B969.
168. Behm, M. and D. Simonsson, *Graphite as anode material for the electrochemical production of polysulfide ions in white liquor*. Journal of applied electrochemistry, 1999. **29**(4): p. 521-524.
169. Calver, T.J., et al., *Carbon based electrodes*. 1999, Google Patents.

170. Smart, R.S., et al., *Sims studies of oxidation mechanisms and polysulfide formation in reacted sulfide surfaces*. Minerals Engineering, 2000. **13**(8-9): p. 857-870.
171. Li, Y., V.P. Kotzeva, and D.J. Fray, *Electrochemical performance of CdS nanomaterials synthesized by microemulsion techniques*. Materials Letters, 2006. **60**(21): p. 2743-2746.
172. Shu, T. and Z.-L. Ku, *TiO₂-poly(3,4-ethylenedioxythiophene) composite counter electrode to improve the performance of CdS quantum-dot-sensitized solar cell with polysulfide electrolyte*. Journal of Alloys and Compounds, 2014. **586**: p. 257-260.
173. Faber, M.S., et al., *Earth-Abundant Cobalt Pyrite (CoS₂) Thin Film on Glass as a Robust, High-Performance Counter Electrode for Quantum Dot-Sensitized Solar Cells*. The Journal of Physical Chemistry Letters, 2013. **4**(11): p. 1843-1849.
174. Faber, M.S., et al., *Earth-Abundant Metal Pyrites (FeS₂, CoS₂, NiS₂, and Their Alloys) for Highly Efficient Hydrogen Evolution and Polysulfide Reduction Electrocatalysis*. The Journal of Physical Chemistry C, 2014. **118**(37): p. 21347-21356.
175. Faber, M.S. and S. Jin, *Earth-abundant inorganic electrocatalysts and their nanostructures for energy conversion applications*. Energy & Environmental Science, 2014. **7**(11): p. 3519-3542.
176. Faber, M.S., et al., *High-performance electrocatalysis using metallic cobalt pyrite (CoS₂) micro-and nanostructures*. Journal of the American Chemical Society, 2014. **136**(28): p. 10053-10061.
177. Giovanelli, D., et al., *Electrochemical determination of sulphide at nickel electrodes in alkaline media: a new electrochemical sensor*. Sensors and Actuators B: Chemical, 2003. **88**(3): p. 320-328.
178. Giovanelli, D., et al., *Anodic stripping voltammetry of sulphide at a nickel film: towards the development of a reagentless sensor*. Talanta, 2003. **61**(2): p. 211-220.
179. Balis, N., et al., *Quantum dot sensitized solar cells based on an optimized combination of ZnS, CdS and CdSe with CoS and CuS counter electrodes*. Electrochimica Acta, 2013. **91**: p. 246-252.
180. Hsu, S.-H., et al., *Platinum-Free Counter Electrode Comprised of Metal-Organic-Framework (MOF)-Derived Cobalt Sulfide Nanoparticles for Efficient Dye-Sensitized Solar Cells (DSSCs)*. Sci. Rep., 2014. **4**.
181. Lessner, P., et al., *Aqueous polysulphide flow-through electrodes: Effects of electrocatalyst and electrolyte composition on performance*. Journal of applied electrochemistry, 1992. **22**(10): p. 927-934.
182. Ke, W., et al., *In Situ Synthesis of NiS Nanowall Networks on Ni Foam as a TCO-Free Counter Electrode for Dye-Sensitized Solar Cells*. ACS Applied Materials & Interfaces, 2014. **6**(8): p. 5525-5530.
183. Sun, H., et al., *Dye-sensitized solar cells with NiS counter electrodes electrodeposited by a potential reversal technique*. Energy & Environmental Science, 2011. **4**(8): p. 2630-2637.
184. Kim, H.-J., et al., *Highly efficient solution processed nanorice structured NiS counter electrode for quantum dot sensitized solar cells*. Electrochimica Acta, 2014. **127**: p. 427-432.
185. Gopi, C.V.V.M., et al., *Highly effective nickel sulfide counter electrode catalyst prepared by optimal hydrothermal treatment for quantum dot-sensitized solar cells*. Journal of Power Sources, 2015. **275**(0): p. 547-556.

186. Macijauskienė, B. and E. Griškonis, *Graphite felt modified with electroless Co–Ni–P alloy as an electrode material for electrochemical oxidation and reduction of polysulfide species*, in *Chemical Papers*. 2016. p. 1611.
187. Remick, R. and E. Camara, *Electrochemistry of the Sulfide/Polysulfide Couple*. Institute of Gas Technology, Lawrence Berkeley Laboratory Report No. LBL-16850 (July 1983). Seal Glassy carbon counter electrode Molybdenum cap Graded glass-[^] Tungsten feedthrough, 1983.
188. Stephens, I.E.L., C. Ducati, and D.J. Fray, *Correlating Microstructure and Activity for Polysulfide Reduction and Oxidation at WS₂ Electrocatalysts*. Journal of the Electrochemical Society, 2013. **160**(6): p. A757-A768.
189. Licht, S., et al., *A light-variation insensitive high efficiency solar cell*. Nature, 1987. **326**(6116): p. 863-864.
190. Licht, S. and J. Manassen, *Thin Film Cadmium Chalcogenide/Aqueous Polysulfide Photoelectrochemical Solar Cells with In-Situ Tin Storage*. Journal of The Electrochemical Society, 1987. **134**(5): p. 1064-1070.
191. Shen, Q., et al., *CdSe quantum dot-sensitized solar cell employing TiO₂ nanotube working-electrode and Cu₂S counter-electrode*. Applied Physics Letters, 2010. **97**(12): p. 123107.
192. Radich, J.G., R. Dwyer, and P.V. Kamat, *Cu₂S Reduced Graphene Oxide Composite for High-Efficiency Quantum Dot Solar Cells. Overcoming the Redox Limitations of S₂–/Sn₂– at the Counter Electrode*. The Journal of Physical Chemistry Letters, 2011. **2**(19): p. 2453-2460.
193. Xu, J., et al., *Large-scale synthesis of Cu₂SnS₃ and Cu_{1.8}S hierarchical microspheres as efficient counter electrode materials for quantum dot sensitized solar cells*. Nanoscale, 2012. **4**(20): p. 6537-6542.
194. Cao, Y., et al., *Highly Electrocatalytic Cu₂ZnSn(S₁–xSex)₄ Counter Electrodes for Quantum-Dot-Sensitized Solar Cells*. ACS Applied Materials & Interfaces, 2013. **5**(3): p. 479-484.
195. Kozytiskiy, A., et al., *Structured Films of Cu x S–Counter Electrodes for Solar Cells Based on FTO/ZnO/CdS Heterostructures and Sulfide/Polysulfide Redox Couple*. Theoretical and Experimental Chemistry, 2013. **49**(4): p. 213-218.
196. Wang, Y.-q., et al., *A Facile in Situ Synthesis Route for CuInS₂ Quantum-Dots/In₂S₃ Co-Sensitized Photoanodes with High Photoelectric Performance*. ACS Applied Materials & Interfaces, 2013. **5**(22): p. 11858-11864.
197. Yu, X., et al., *Metal chalcogenide complex-mediated fabrication of Cu₂S film as counter electrode in quantum dot sensitized solar cells*. Science China Chemistry, 2013. **56**(7): p. 977-981.
198. Zhao, K., et al., *Electroplating Cuprous Sulfide Counter Electrode for High-Efficiency Long-Term Stability Quantum Dot Sensitized Solar Cells*. The Journal of Physical Chemistry C, 2014. **118**(11): p. 5683-5690.
199. Lin, J.-Y., J.-H. Liao, and S.-W. Chou, *Cathodic electrodeposition of highly porous cobalt sulfide counter electrodes for dye-sensitized solar cells*. Electrochimica Acta, 2011. **56**(24): p. 8818-8826.
200. Kim, B.-M., et al., *Improved performance of CdS/CdSe quantum dot-sensitized solar cells using Mn-doped PbS quantum dots as a catalyst in the counter electrode*. Electrochimica Acta, 2014. **117**: p. 92-98.
201. Zito, R., *Electrochemical apparatus for energy storage and/or power delivery comprising multi-compartment cells*. 1994, Google Patents.

202. Zito, R., *Electrochemical apparatus for power delivery utilizing an air electrode*. 1994, Google Patents.
203. Zito, R., *Electrochemical energy storage and power delivery process utilizing iron-sulfur couple*. 1994, Google Patents.
204. Zito, R., *Process for energy storage and/or power delivery with means for restoring electrolyte balance*. 1997, Google Patents.
205. Calver, T.J., et al., *Carbon based electrodes*. 1999, Google Patents.
206. Clark, D.G., et al., *Vitrified carbon compositions*. 2000, Google Patents.
207. Cooley, G.E., et al., *Method of carrying out electrochemical reactions with an electrocatalyst*. 2000, Google Patents.
208. Cranstone, W.R.I., et al., *Process for the preparation of reticulated copper or nickel sulfide*. 2000, Google Patents.
209. Morrissey, P.J., *Method of operating a fuel cell*. 2001, Google Patents.
210. Fletcher, S. and D.N.J. Van, *An electrode for the reduction of polysulfide species*. 2003, Google Patents.
211. Ponce-de-León, C., et al., *Characterization of the reaction environment in a filter-press redox flow reactor*. *Electrochimica acta*, 2007. **52**(19): p. 5815-5823.
212. Ge, S.H., et al., *Study on a novel sodium polysulfide/bromine regenerative fuel cell*. *Chinese Journal of Power Sources*, 2002. **26**(5): p. 355-358.
213. Ge, S.H., B. Yi, and H. Zhang, *High performance electrode for a novel sodium polysulfide-bromine energy storage cell*. *Chinese Journal of Power Sources*, 2003. **27**(5): p. 446-450.
214. Ge, S.H., et al., *Study on high efficiency sodium polysulfide/bromine energy storage cell*. *BATTERY BIMONTHLY*, 2003. **33**(1): p. 12-14.
215. Ge, S.H., et al., *Sodium polysulfide-bromine energystorage cell stack*. *chinese Journal of Power Sources*, 2004. **28**(6): p. 373-375.
216. Zhao, P., et al., *Primary study on sodium polysulfide/bromine redox flow cell*. *Battery Bimonthly*, 2004. **34**(5): p. 321-322.
217. Zhao, P., et al., *Study on Negative Electrode Materials for Sodium Polysulfide/Brome Redox Flow Energy Storage Battery*. *Chemical Research*, 2005. **16**(1): p. 49-51.
218. Zhao, P., et al., *Study on sodium polysulfide/bromide redox flow battery*. *Chinese Journal of Power Sources*, 2005. **29**(5): p. 322-324.
219. Zhou, H.T., et al., *Porous carbon electrodes for sodium polysulfide-bromine redox flow energy storage cell*. *Chinese Journal of Power Sources*, 2005. **29**(3): p. 170-174.
220. Licht, S., et al., *A Pronounced Cation Effect on Performance and Stability of Cd-Chalcogenide/Polysulfide Photoelectrochemical Cells*. *Journal of The Electrochemical Society*, 1984. **131**(4): p. 950-951.
221. Licht, S., et al., *Cation effects on the electrochemistry of anions in polysulfide photoelectrochemical cells*. *Journal of The Electrochemical Society*, 1986. **133**(1): p. 52-59.
222. Scamman, D.P., G.W. Reade, and E.P.L. Roberts, *Numerical modelling of a bromide-polysulphide redox flow battery Part 1: Modelling approach and validation for a pilot-scale system*. *Journal of Power Sources*, 2009. **189**(2): p. 1220-1230.
223. Wang, J., *Analytical electrochemistry*. 2006: John Wiley & Sons.
224. Yuan, C., et al., *Ultrathin Mesoporous NiCo₂O₄ Nanosheets Supported on Ni Foam as Advanced Electrodes for Supercapacitors*. *Advanced Functional Materials*, 2012. **22**(21): p. 4592-4597.

225. Fazli, Y., et al., *Electrochemical synthesis and structure characterization of nickel sulfide nanoparticles*. Materials Science in Semiconductor Processing, 2014. **27**: p. 362-367.
226. Fazli, Y., et al., *Synthesis, characterization and photocatalytic property of nickel sulfide nanoparticles*. Journal of Materials Science: Materials in Electronics, 2016. **27**(7): p. 7192-7199.
227. Gutierrez, A., et al., *Solvothermal Synthesis of NiO, Ni and NiS Nanoparticles*. Journal of Nanoscience and Nanotechnology, 2013. **13**(1): p. 461-466.
228. Meng, Z., et al., *Solvothermal synthesis and phase control of nickel sulfides with different morphologies*. Materials Chemistry and Physics, 2002. **74**(2): p. 230-233.
229. Olivas, A., et al., *Synthesis and characterization of nickel sulfide catalysts*. Journal of Vacuum Science & Technology A, 1998. **16**(6): p. 3515-3520.
230. Jeong, Y.U. and A. Manthiram, *Synthesis of Nickel Sulfides in Aqueous Solutions Using Sodium Dithionite*. Inorganic Chemistry, 2001. **40**(1): p. 73-77.
231. Jiang, X., et al., *Synthesis of Novel Nickel Sulfide Layer-Rolled Structures*. Advanced Materials, 2001. **13**(16): p. 1278-1281.
232. Mondal, D., et al., *Synthesis, characterization and evaluation of unsupported porous NiS₂ sub-micrometer spheres as a potential hydrodesulfurization catalyst*. Applied Catalysis A: General, 2013. **450**: p. 230-236.
233. Zhang, L., et al., *A General Solution-Phase Approach to Oriented Nanostructured Films of Metal Chalcogenides on Metal Foils: The Case of Nickel Sulfide*. Journal of the American Chemical Society, 2004. **126**(26): p. 8116-8117.
234. Mordechay, S. and P. Milan, *Modern Electroplating, Fifth Edition*. 2011.
235. Tsuru, Y., M. Nomura, and F. Foulkes, *Effects of boric acid on hydrogen evolution and internal stress in films deposited from a nickel sulfamate bath*. Journal of Applied Electrochemistry, 2002. **32**(6): p. 629-634.
236. Galetti, A.E., et al., *Synthesis of Nickel Nanoparticles Supported on Carbon Using a Filter Paper as Biomimetic Pattern for Application in Catalysis*. Materials Research, 2015. **18**: p. 1278-1283.
237. Ruiz-Trejo, E., et al., *New Method for the Deposition of Nickel Oxide in Porous Scaffolds for Electrodes in Solid Oxide Fuel Cells and Electrolyzers*. ChemSusChem, 2017. **10**(1): p. 258-265.
238. Åkerlöf, G. and G. Kegeles, *Thermodynamics of concentrated aqueous solutions of sodium hydroxide*. Journal of the American Chemical Society, 1940. **62**(3): p. 620-640.
239. Seghioer, A., et al., *Electrochemical oxidation of nickel in alkaline solutions: a voltammetric study and modelling*. Journal of Electroanalytical Chemistry, 1998. **442**(1-2): p. 113-123.

Appendices

A Properties of Nafion® 117 CEM

Thickness and Basis Weight Properties ¹		
Membrane Type	Typical Thickness (μm)	Basis Weight (g/m ²)
Nafion® N115	127	250
Nafion® N117	183	360
Nafion® N1110	254	500
Physical and Other Properties ²		
	Typical Value	Test Method
Physical Properties		
Tensile Modulus, MPa (kpsi)		
50% RH, 23 °C (73 °F)	249 (36)	ASTM D882
water soaked, 23 °C (73 °F)	114 (16)	ASTM D882
water soaked, 100 °C (212 °F)	64 (9.4)	ASTM D882
Tensile Strength, Max., MPa (kpsi)		
50% RH, 23 °C (73 °F)	43 (6.2) in MD, 32 (4.6) in TD	ASTM D882
water soaked, 23 °C (73 °F)	34 (4.9) in MD, 26 (3.8) in TD	ASTM D882
water soaked, 100 °C (212 °F)	25 (3.6) in MD, 24 (3.5) in TD	ASTM D882
Elongation at Break, %		
50% RH, 23 °C (73 °F)	225 in MD, 310 in TD	ASTM D882
water soaked, 23 °C (73 °F)	200 in MD, 275 in TD	ASTM D882
water soaked, 100 °C (212 °F)	180 in MD, 240 in TD	ASTM D882
Tear Resistance—Initial, g/mm		
50% RH, 23 °C (73 °F)	6000 in MD, TD	ASTM D1004
water soaked, 23 °C (73 °F)	3500 in MD, TD	ASTM D1004
water soaked, 100 °C (212 °F)	3000 in MD, TD	ASTM D1004
Tear Resistance ³ —Propagating, g/mm		
50% RH, 23 °C (73 °F)	>100 in MD, >150 in TD	ASTM D1922
water soaked, 23 °C (73 °F)	92 in MD, 104 in TD	ASTM D1922
water soaked, 100 °C (212 °F)	74 in MD, 85 in TD	ASTM D1922
Specific Gravity	1.98	—
Other Properties		
Conductivity, S/cm	0.10 min.	See footnote ⁴
Available Acid Capacity, meq/g	0.90 min.	See footnote ⁵
Total Acid Capacity, meq/g	0.95–1.01	See footnote ⁵
Hydrolytic Properties ²		
Water Content, % water ⁶	5	ASTM D570
Water Uptake, % water ⁷	38	ASTM D570
Thickness Change, % increase		
from 50% RH, 23 °C (73 °F) to water soaked, 23 °C (73 °F)	10	ASTM D756
from 50% RH, 23 °C (73 °F) to water soaked, 100 °C (212 °F)	14	ASTM D756
Linear Expansion, % increase ⁸		
from 50% RH, 23 °C (73 °F) to water soaked, 23 °C (73 °F)	10	ASTM D756
from 50% RH, 23 °C (73 °F) to water soaked, 100 °C (212 °F)	15	ASTM D756

¹Measurements taken with membrane conditioned to 23 °C (73 °F), 50% RH.

²Physical properties measured for Nafion® N115. Where specified, MD—machine direction, TD—transverse direction. Conditioning state of membrane given. Measurements taken at 23 °C (73 °F), 50% RH.

³Tear resistance (g/mm) of dry membrane increases with thickness. Values given measured using 50 μm membrane.

⁴Conductivity measurement as described by Zawodzinski et al., J. Phys. Chem., 95 (15), 6040 (1991). Membrane conditioned in 100 °C (212 °F) water for 1 hr. Measurement cell submerged in 25 °C (77 °F) DI water during experiment. Membrane impedance (real) taken at zero imaginary impedance.

⁵A base titration procedure measures the equivalents of sulfonic acid in the polymer and uses the measurement to calculate the acid capacity or equivalent weight of the membrane.

⁶Water content of membrane conditioned to 23 °C (73 °F), 50% relative humidity (RH), compared to dry weight basis.

⁷Water uptake from dry membrane to water soaked at 100 °C (212 °F) for 1 hr (dry weight basis).

⁸Typical MD and TD values. MD expansion is slightly less than TD.

B Properties of Fumapem® FAA-3-PK-75 AEM

fumasep®		FAA-3-PK-75
membrane type		anion exchange membrane
appearance		Trans-illuminant, but not fully transparent / dark yellow to brown
backing foil		none
reinforcement		PK
counter ion		bromide (Br ⁻)
delivery form		dry
thickness (dry)	µm	60 - 80
weight per unit area	mg cm ⁻²	10 – 15
ion exchange capacity (as chloride form)	meq g ⁻¹	1.39
area resistance in Cl ⁻ form ^{a)}	Ω cm ²	< 2,0
specific conductivity in Cl ⁻ form ^{a)}	mS cm ⁻¹	> 2,5
proton transfer rate ^{c)}	µmol min ⁻¹ cm ⁻²	< 2500
selectivity 0.1 / 0.5 mol/kg KCl at T = 25 °C ^{d)}	%	> 90
uptake in H ₂ O at T = 25 °C ^{e)}	wt %	13
dimensional swelling in H ₂ O at T = 25 °C ^{f)}	%	0
Young's modulus at 23 °C / 50 % r.h. ^{g)}	MPa	> 1500
tensile strength at 23 °C / 50 % r.h. ^{g)}	MPa	20 – 45
elongation at break at 23 °C / 50 % r.h. ^{g)}	%	30 – 50
bubble point test in water at T = 25 °C	bar	> 3

a) in Cl⁻ form in 0.5 M NaCl @ T = 25 °C, measured in standard measuring cell (through-plane).

b) in SO₄²⁻ form (0.5 M H₂SO₄) @ T = 25 °C, measured in standard measuring cell (through-plane).

c) determined from pH potential measurement in a concentration cell 0.1 M HCl / 0.1 M KCl @ T = 25 °C.

d) determined from membrane potential measurement in a concentration cell 0.1 M KCl / 0.5 M KCl @ T = 25 °C.

e) in Br⁻ form, membrane as received stored in water for 24 hrs, reference membrane dried over P₂O₅ *in vacuo*.

f) in Br⁻ form, membrane as received stored in water for 24 hrs, reference membrane as received.

g) determined by stress-strain measurement at T = 25°C and 50 % r.h., according to DIN EN 527-1.