

EXPERIMENTAL CHARACTERISATION AND  
MODELING OF A VANADIUM REDOX FLOW  
BATTERY

MOHD RUSLLIM BIN MOHAMED

DOCTOR OF PHILOSOPHY  
UNIVERSITI MALAYSIA PAHANG

## UNIVERSITI MALAYSIA PAHANG

### DECLARATION OF THESIS AND COPYRIGHT

Author's full name : **MOHD RUSLLIM BIN MOHAMED**

Date of birth : **26<sup>TH</sup> OCTOBER 1977**

Title : **EXPERIMENTAL CHARACTERISATION AND MODELING OF A VANADIUM REDOX FLOW BATTERY**

Academic Session : **2012 / 2013**

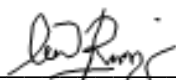
I declare that this thesis is classified as:

- CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)\*
- RESTRICTED** (Contains restricted information as specified by the organization where research was done)\*
- OPEN ACCESS** I agree that my thesis to be published as online open access (Full text)

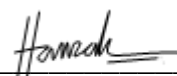
I acknowledge that Universiti Malaysia Pahang reserve the right as follows:

1. The Thesis is the Property of Universiti Malaysia Pahang.
2. The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only.
3. The Library has the right to make the copies of the thesis for academic exchange.

Certified By:



\_\_\_\_\_  
(Signature of Student)



\_\_\_\_\_  
(Signature of Supervisor)

\_\_\_\_\_  
771026-03-6323

\_\_\_\_\_  
DR. HAMZAH BIN AHMAD

New IC / Passport Number  
Date : 08<sup>TH</sup> APRIL 2013

Name of Supervisor  
Date: 08<sup>TH</sup> APRIL 2013

**NOTES** : \*If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reason for confidentiality or restriction.

EXPERIMENTAL CHARACTERISATION AND MODELING OF A VANADIUM  
REDOX FLOW BATTERY

MOHD RUSLLIM BIN MOHAMED


Thesis submitted in fulfilment of the requirements  
for the award of the degree of  
Doctor of Philosophy in Electrical Engineering


Faculty of Electrical & Electronics Engineering  
UNIVERSITI MALAYSIA PAHANG

APRIL 2013

## SUPERVISOR'S DECLARATION


We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy in Electrical Engineering.

Signature :   
Name of Supervisor : DR. HAMZAH BIN AHMAD  
Position : SENIOR LECTURER  
FACULTY OF ELECTRICAL &  
ELECTRONICS ENGINEERING  
UNIVERSITI MALAYSIA PAHANG  
Date : 08<sup>TH</sup> APRIL 2013

Signature :   
Name of co-supervisor : DR. MAZRUL NIZAM BIN ABU SEMAN  
Position : SENIOR LECTURER  
FACULTY OF CHEMICAL ENGINEERING &  
NATURAL RESOURCES  
UNIVERSITI MALAYSIA PAHANG  
Date : 08<sup>TH</sup> APRIL 2013

## STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotation and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :   
Name of Student : MOHD RUSLLIM BIN MOHAMED  
ID Number : PEE11003  
Date : 08<sup>TH</sup> APRIL 2013

## TABLE OF CONTENTS

<b>TITLE PAGE</b>	<b>III</b>
<b>SUPERVISOR’S DECLARATION</b>	<b>IV</b>
<b>STUDENT’S DECLARATION</b>	<b>V</b>
<b>DEDICATION</b>	<b>VI</b>
<b>ACKNOWLEDGEMENTS</b>	<b>VIII</b>
<b>ABSTRACT</b>	<b>IX</b>
<b>ABSTRAK</b>	<b>X</b>
<b>TABLE OF CONTENTS</b>	<b>XI</b>
<b>LIST OF TABLES</b>	<b>XVI</b>
<b>LIST OF FIGURES</b>	<b>XVII</b>
<b>LIST OF SYMBOLS</b>	<b>XXVI</b>
<b>LIST OF ABBREVIATIONS</b>	<b>XXIX</b>
<b>CHAPTER 1</b>	<b>1</b>
<b>INTRODUCTION</b>	<b>1</b>
<b>1.1 CHAPTER OVERVIEW</b>	<b>1</b>
<b>1.2 BACKGROUND AND MOTIVATIONS</b>	<b>1</b>
<b>1.3 RESEARCH GOALS AND APPROACHES</b>	<b>5</b>
<b>1.4 SCOPE AND LIMITATIONS</b>	<b>7</b>
<b>1.5 STATEMENT OF CONTRIBUTIONS</b>	<b>8</b>
<b>1.6 THESIS OUTLINE</b>	<b>10</b>
<b>CHAPTER 2</b>	<b>12</b>
<b>LITERATURE REVIEW</b>	<b>12</b>
<b>2.1 CHAPTER OVERVIEW</b>	<b>12</b>

<b>2.2</b>	<b>INTRODUCTION</b>	<b>12</b>
<b>2.3</b>	<b>DIFFERENT TECHNOLOGIES FOR ENERGY STORAGE</b>	<b>14</b>
	2.3.1 Mechanical Storage Systems	15
	2.3.2 Electrical Storage Systems	15
	2.3.3 Electrochemical Storage Systems	16
<b>2.4</b>	<b>OVERVIEW OF REDOX FLOW BATTERIES (RFBs)</b>	<b>18</b>
<b>2.5</b>	<b>COMPONENT OF REDOX FLOW BATTERIES AND DESIGN CONSIDERATIONS</b>	<b>22</b>
	2.5.1 Cell Stack (or Unit Cell Stack)	22
	2.5.2 Electrode Material	23
	2.5.3 Membrane	24
	2.5.4 Redox Couples	25
<b>2.6</b>	<b>TYPES OF REDOX FLOW BATTERIES</b>	<b>26</b>
	2.6.1 Bromide – polysulfide RFB	26
	2.6.2 Iron – chromium RFB	27
	2.6.3 Zinc – based RFB	29
	2.6.4 Single – flow RFB	31
	2.6.5 Vanadium – based RFB	34
<b>2.7</b>	<b>ELECTROCHEMISTRY OF V-RFB</b>	<b>37</b>
	2.7.1 V-RFB Kinetic Reaction	37
	2.7.2 Formation Charge	38
	2.7.3 Overcharged and Over-discharged	38
	2.7.4 Water Transport	39
<b>2.8</b>	<b>RESEARCH PROSPECTS FOR V-RFB</b>	<b>39</b>
	2.8.1 V-RFB Cell Design and System	40
	2.8.2 Open-circuit Voltage and State-of-charge Estimation	40
	2.8.3 V-RFB Characterisations	41
	2.8.4 Electric Circuit Modeling	41
	2.8.5 RFB for HEVs Applications	43
	2.8.6 Energy Management of RFB for HEVs Application	45
<b>2.9</b>	<b>CHAPTER CONCLUSION</b>	<b>46</b>

<b>CHAPTER 3</b>	<b>48</b>
<b>METHODOLOGY</b>	<b>48</b>
<b>3.1 CHAPTER OVERVIEW</b>	<b>48</b>
<b>3.2 THEORETICAL STUDY FOR ESTIMATING V-RFB'S SOC</b>	<b>48</b>
3.1.1 Derivation of Nernst Equation	49
<b>3.3 ELECTROLYTE &amp; SUPPORTING ELECTROLYTE PREPARATION</b>	<b>51</b>
<b>3.4 CHAPTER CONCLUSION</b>	<b>53</b>
<b>CHAPTER 4</b>	<b>54</b>
<b>DESIGN AND DEVELOPMENT OF UNIT CELL AND SYSTEM FOR VANADIUM REDOX FLOW BATTERY</b>	<b>54</b>
<b>4.1 CHAPTER OVERVIEW</b>	<b>54</b>
<b>4.2 INTRODUCTION</b>	<b>55</b>
<b>4.3 EXPERIMENTAL SETUP</b>	<b>57</b>
4.3.1 Cell Test and Preparation	61
4.3.2 Electrolyte and Supporting Electrolyte–Acid Preparation	62
<b>4.4 RESULTS AND DISCUSSIONS</b>	<b>63</b>
4.4.1 Charge-discharge Characteristic of V-RFB	63
4.4.2 V-RFB Operating Under a Failure Mode	64
4.4.3 Technical Issues on Design of 100 cm <sup>2</sup> V-RFB	66
4.4.4 Alternative Cell Design	71
4.4.5 Implementation	72
4.4.6 Experimental Results	76
<b>4.5 CHAPTER CONCLUSION</b>	<b>79</b>
<b>CHAPTER 5</b>	<b>80</b>
<b>ESTIMATING STATE-OF-CHARGE OF VANADIUM REDOX FLOW BATTERY USING A DIVIDED, OPEN-CIRCUIT POTENTIOMETRIC CELL</b>	<b>80</b>
<b>5.1 CHAPTER OVERVIEW</b>	<b>80</b>
<b>5.2 INTRODUCTION</b>	<b>81</b>



<b>5.3</b>	<b>METHODOLOGY ESTABLISHMENT</b>	<b>82</b>
<b>5.4</b>	<b>THEORETICAL EXPRESSION</b>	<b>84</b>
<b>5.5</b>	<b>EXPERIMENTAL DETAILS</b>	<b>85</b>
<b>5.6</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>87</b>
	5.6.1 Estimation of Electrolytes Concentration	87
	5.6.2 Effect of Constant Current Efficiency	89
	5.6.3 Proposed Potentiometric Measurement of the 25 cm <sup>2</sup> Unit Cell V-RFB	91
<b>5.7</b>	<b>CHAPTER CONCLUSION</b>	<b>93</b>
 <b>CHAPTER 6</b>		<b>94</b>
<b>CHARACTERISATION OF A VANADIUM REDOX FLOW BATTERY</b>		<b>94</b>
<b>6.1</b>	<b>CHAPTER OVERVIEW</b>	<b>94</b>
<b>6.2</b>	<b>INTRODUCTION</b>	<b>95</b>
	6.3.1 Chemicals	97
	6.3.2 V-RFB Experiments	97
<b>6.4</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>98</b>
	6.4.1 Formation Charge	98
	6.4.2 Effect of Current Density	103
	6.4.3 Effect of Temperature	105
	6.4.3.1 Charge-discharge Characteristics	105
	6.4.3.2 Discharge Cell Voltage at Different Temperatures and Current Densities	108
	6.4.4 Effect of Flow Rates	109
	6.4.5 Effect of Concentration	112
	6.4.6 Electrode Material	114
<b>6.5</b>	<b>CHAPTER CONCLUSION</b>	<b>118</b>
 <b>CHAPTER 7</b>		<b>120</b>
<b>ELECTRICAL CIRCUIT MODEL OF V-RFB USING EXTENDED KALMAN FILTER</b>		<b>120</b>
<b>7.1</b>	<b>CHAPTER OVERVIEW</b>	<b>120</b>

<b>7.1</b>	<b>INTRODUCTION</b>	<b>121</b>
<b>7.2</b>	<b>MODEL FORMULATION AND PARAMETERS IDENTIFICATION METHOD</b>	<b>123</b>
	7.2.1 Modeling the Battery	123
	7.2.2 Modeling Equations	124
	7.2.3 Model Parameters Identification	125
	7.2.4 EKF-based Parameters Identification for V-RFB	126
<b>7.3</b>	<b>EXPERIMENTAL DETAILS</b>	<b>128</b>
<b>7.4</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>129</b>
	7.4.1 Open-circuit Voltage and State-of-charge	129
	7.4.2 Ohmic Resistance	130
	7.4.3 Dynamic V-RFB Parameters Identification	134
	7.4.4 Model Verification and Validation	139
<b>7.5</b>	<b>CHAPTER CONCLUSIONS</b>	<b>146</b>
	<b>CHAPTER 8</b>	<b>147</b>
	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>147</b>
<b>8.1</b>	<b>CHAPTER OVERVIEW</b>	<b>147</b>
<b>8.2</b>	<b>CONCLUDING REMARKS</b>	<b>147</b>
<b>8.3</b>	<b>RECOMMENDATIONS FOR FUTURE WORK</b>	<b>150</b>
	<b>REFERENCES</b>	<b>152</b>
	<b>APPENDIX - LIST OF PUBLICATIONS</b>	<b>163</b>

## LIST OF TABLES

<b>Table</b>	<b>Caption</b>	<b>Page</b>
<b>Table 2.1:</b>	Typical power and energy rating for three main application sectors; portable devices, transport and stationary application (Swanbarton.Ltd, 2004)	<b>14</b>
<b>Table 2.2:</b>	Comparisons of selected energy storage technologies at different parameters (Gonzalez et al., 2004)	<b>20</b>
<b>Table 2.3:</b>	A comparison of RFBs and conventional batteries	<b>36</b>
<b>Table 3.1:</b>	Calculation for Preparation of Supporting Electrolyte H <sub>2</sub> SO <sub>4</sub>	<b>52</b>
<b>Table 3.2:</b>	Concentration Variant for 1.6 mol dm <sup>-3</sup> V(III)/V(IV) in 4 mol dm <sup>-3</sup> H <sub>2</sub> SO <sub>4</sub>	<b>52</b>
<b>Table 6.1:</b>	Summary of 25 cm <sup>2</sup> unit cell laboratory unit V-RFB performances under different operating parameters; obtained from charge-discharge characteristics. Unless mentioned, all electrolyte concentrations was at 1.6 mol dm <sup>-3</sup> V(III)/V(IV) in 4 mol dm <sup>-3</sup> H <sub>2</sub> SO <sub>4</sub> . All results exclude the auxiliary consumption	<b>114</b>
<b>Table 7.1:</b>	EKF-based identification model parameters for a 25 cm <sup>2</sup> V-RFB. Operating parameters are the same as in Figure 7.5.	<b>145</b>
<b>Table A:</b>	List of submitted or published in peer-reviewed Journals and Conferences for Experimental Characterisation and Modeling of a Vanadium Redox Flow Battery	<b>163</b>

## LIST OF FIGURES

<b>Figure</b>	<b>Caption</b>	<b>Page</b>
<b>Figure 2.1:</b>	Single stack flow circuit to describe the principles of operation, main components of a RFB system, and parts to establish the power and energy rating of the system	<b>21</b>
<b>Figure 2.2:</b>	RFB figures-of-merit for voltage-, coulombic-, power- and energy efficiencies	<b>21</b>
<b>Figure 2.3:</b>	Time-line for development redox flow battery (not limited to)	<b>22</b>
<b>Figure 2.4:</b>	Reconstructed figures from various authors for flow-through and flow-by configuration with different terminologies and layouts, (a) Zhou <i>et al.</i> (Zhou <i>et al.</i> , 2006); (b) Joerissen <i>et al.</i> (Joerissen <i>et al.</i> , 2004); and (c) Trainham <i>et al.</i> (Trainham <i>et al.</i> , 1981)	<b>25</b>
<b>Figure 2.5:</b>	Principle of operation of the bromide-polysulfide RFB	<b>27</b>
<b>Figure 2.6:</b>	Principle of operation of the iron-chromium RFB based on (a) cationic membrane (b) anionic membrane	<b>28</b>
<b>Figure 2.7:</b>	The principle of operation of zinc – bromine RFB	<b>29</b>
<b>Figure 2.8:</b>	The principle of operation of the zinc – cerium RFB	<b>31</b>
<b>Figure 2.9:</b>	The principle of operation of the soluble lead – acid flow battery	<b>32</b>
<b>Figure 2.10:</b>	Principle of operation of the vanadium-vanadium RFB	<b>34</b>
<b>Figure 4.1:</b>	Single stack flow circuit to describe the principles of operation, main components of a V-RFB system, and parts to establish the power and energy rating of the system (adapted from (Mohamed <i>et al.</i> , 2009))	<b>56</b>
<b>Figure 4.2:</b>	Charge Logger v2.1 developed by Re-Fuel Technology Ltd capable of recording 3 V-RFB cell parameters i.e. Cell	

	potential, Reference Cell Potential and Shunt current; including controls charge-discharge cycle according to preset on-load cell potential threshold	58
<b>Figure 4.3:</b>	Electrical schematic for charge-discharge mode of V-RFB system with details connection of relay control circuit	59
<b>Figure 4.4:</b>	A unit cell laboratory unit, un-optimised 100 cm <sup>2</sup> V-RFB. Modified from a laboratory system by Re-Fuel Technology Ltd (Mohamed <i>et al.</i> , 2009)	59
<b>Figure 4.5:</b>	Specification of the cell stack of a laboratory, un-optimised 100 cm <sup>2</sup> unit cell laboratory V-RFB system	60
<b>Figure 4.6:</b>	Experimental processes of 25 – 100 cm <sup>2</sup> unit cell laboratory unit V-RFB	61
<b>Figure 4.7:</b>	Overview of 10 cm x 10 cm x 2 cm half-cell of divided, open-circuit cell (known as reference cell)	62
<b>Figure 4.8:</b>	A typical voltage charge-discharge characteristic of 100 cm <sup>2</sup> laboratory V-RFB at maximum charge and discharge currents of 10 A (100 mA cm <sup>-2</sup> ) vs. time (Mohamed <i>et al.</i> , 2009)	64
<b>Figure 4.9:</b>	Single-cycle of voltage charge and discharge characteristic of 100 cm <sup>2</sup> laboratory V-RFB at maximum charge and discharge currents of 10 A operating under a failure mode vs. time	65
<b>Figure 4.10:</b>	Shaded area (~ 5 cm x 5 cm) illustrates the corroded 10 cm x 10 cm x 0.6 cm carbon current collector affected by side reaction within the V-RFB cell during charge-discharge cycles	66
<b>Figure 4.11:</b>	Assembly of cells compartments (a) 18 cm x 18 cm x 2 cm cell's frame (b) 15 cm x 15 cm x 0.1 cm copper plates placed on the cell's frame (c) 15 cm x 15 cm x 0.6 cm carbon current collector on top of copper plate	68
<b>Figure 4.12:</b>	Affected V-RFB component (a) deteriorated 15 cm x 15 cm x 0.15 cm (outer), 10 cm x 10 cm x 0.15 cm (inner) PTFE layers due to compression during series of cell assembly (b) corroded silver wire exposed to vanadium electrolyte (c) disconnected silver wire	70

- Figure 4.13:** Alternative of cell compartments (a) 15 cm x 15 cm x 0.6 cm flow-through electrode compartment made of PVC (b) flow-through electrode compartment made of rubber (c) graphite electrode dipped-into vanadium electrolyte for measuring cell's equilibrium **72**
- Figure 4.14:** New un-optimised V-RFB system of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB **74**
- Figure 4.15:** A divided, open-circuit potentiometric cell (a) reference and working electrode (b) graphite rod as working electrode **75**
- Figure 4.16:** New 12.5 cm x 12.5 cm x 2 cm cell design (a) new cell frame with copper plate slot and rubber seal (b) 4 new holes at each corner with PTFE rod to hold carbon current collector and electrode compartments (c) comparison of carbon current collector (d) comparison of grafoil **75**
- Figure 4.17:** New PVC 5 cm x 5 cm x 0.4 cm electrode cell compartment enclosed by rubber seal **76**
- Figure 4.18:** Experimental charge-discharge characteristic of previous design, 100 cm<sup>2</sup> and newly implemented design, 25 cm<sup>2</sup> of V-RFB at 100 mA cm<sup>-2</sup>, 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> used at constant volumetric flow rate 3 cm<sup>3</sup> s<sup>-1</sup> and constant temperature of 298 ± 2 K vs. time. **77**
- Figure 4.19:** Experimental charge-discharge characteristic of 25 cm<sup>2</sup> of V-RFB at 100 mA cm<sup>-2</sup>, with half-cell potentials and contact resistance potential vs. time. **78**
- Figure 5.1:** Overview of electrical wiring and tubing system for un-optimised 25 - 100 cm<sup>2</sup> unit cell laboratory unit V-RFB system **86**
- Figure 5.2:** Reference cell for potentiometric measurement for the new 25 cm<sup>2</sup> unit cell V-RFB **87**
- Figure 5.3:** Concentration of vanadium species changes exponentially over period of time during charge-discharge cycle **89**
- Figure 5.4:** Manual estimation of V(III) / V(IV) concentrations at the start of redox reaction based on  $E_{cell(ORP)}$  recorded using experiment of 100 cm<sup>2</sup> unit cell V-RFB during charging cycle **89**

- Figure 5.5:** Comparison of experimental  $E_{cell(ORP)}$  and estimated  $E_{cell(ORP)}$  at constant current efficiency vs. time (a) experimental curve obtained from potential different across two working electrodes of reference cell during charging of 100 cm<sup>2</sup> unit cell laboratory unit V-RFB of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at 10 A (100 mA cm<sup>-2</sup>) (b) estimated  $E_{cell(ORP)}$  at  $\phi=1.0$  (c) estimated  $E_{cell(ORP)}$  at  $\phi=0.7$  (d) estimated  $E_{cell(ORP)}$  at  $\phi=0.5$  90
- Figure 5.6:** Comparison of experimental  $E_{cell(ORP)}$  and estimated  $E_{cell(ORP)}$  (a) experimental curve obtained from potential different across two working electrodes of reference cell during charging cycle of 100 cm<sup>2</sup> unit cell laboratory unit V-RFB of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at constant current density of 100 mA cm<sup>-2</sup> (b) estimated  $E_{cell(ORP)}$  when the current efficiency is varied,  $\phi=0.1-1.0$  91
- Figure 5.7:** Comparison of experimental  $E_{cell(ORP)}$  and estimated  $E_{cell(ORP)}$  (a) experimental curve obtained using a divided, open-circuit potentiometric cell, through Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrodes and graphite rod working electrodes separated by ion exchange membrane (DuPont Nafion NF115/H<sup>+</sup>) during charging cycle of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at constant current density of at 100 mA cm<sup>-2</sup> (b) estimated  $E_{cell(ORP)}$  when current efficiency is varied,  $\phi=0.1-1.0$  92
- Figure 5.8:** Comparison of estimated SOC with respect to SOC obtained through experimental of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at constant current density of at 100 mA cm<sup>-2</sup> 92
- Figure 6.1:** Cell voltage vs. time for formation charge of unit cell, laboratory unit vanadium redox flow battery for 250 cm<sup>3</sup> (each half reservoir) of 1.6 mol dm<sup>-3</sup> V(III) / V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, at current density (a) 20 mA cm<sup>-2</sup>, and (b) 80 mA cm<sup>-2</sup> indicating  $E_{cell(ORP)}$ ,  $E_{V(IV)/V(V)}$  and  $E_{V(III)/V(II)}$ , respectively. Both

positive and negative electrolytes were circulated at volumetric flow rate of  $3\text{ cm}^3\text{ s}^{-1}$  (linear flow rate  $1.11\text{ cm s}^{-1}$ ) assisted by peristaltic pump and maintained at temperature of  $298 \pm 2\text{ K}$  by water bath.

100

**Figure 6.2:**  $E_{cell(ORP)}$  vs. percentage of formation charge for  $250\text{ cm}^3$  (half reservoir) of  $1.6\text{ mol dm}^{-3}\text{ V(III) / V(IV)}$  in  $4\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ , at current density  $20\text{ mA cm}^{-2}$  and  $80\text{ mA cm}^{-2}$ , volumetric flow rate of  $3\text{ cm}^3\text{ s}^{-1}$  (linear flow rate  $1.11\text{ cm s}^{-1}$ ) and temperature of  $298 \pm 2\text{ K}$

102

**Figure 6.3:**  $E_{V(IV)/V(V)}$ ,  $E_{V(III)/V(II)}$  vs. percentage of formation charge with respect to  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode for  $250\text{ cm}^3$  (half reservoir) of  $1.6\text{ mol dm}^{-3}\text{ V(III) / V(IV)}$  in  $4\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ , at current density  $20\text{ mA cm}^{-2}$  and  $80\text{ mA cm}^{-2}$ , volumetric flow rate of  $3\text{ cm}^3\text{ s}^{-1}$  (linear flow rate  $1.11\text{ cm s}^{-1}$ ) and temperature of  $298 \pm 2\text{ K}$

103

**Figure 6.4:** Cell voltage vs. time representing charge-discharge characteristics of  $25\text{ cm}^2$  unit cell laboratory unit V-RFB under controlled current density ( $20$ ,  $60$  and  $100\text{ mA cm}^{-2}$ ) for  $250\text{ cm}^3$  (half reservoir) of  $1.6\text{ mol dm}^{-3}\text{ V(III) / V(IV)}$  in  $4\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  at constant linear flow rate and temperature,  $1.11\text{ cm s}^{-1}$  and  $298 \pm 2\text{ K}$  respectively

104

**Figure 6.5:** Performance efficiencies vs. current density of  $25\text{ cm}^2$  unit cell laboratory unit V-RFB at different current density ( $20$ ,  $60$  and  $100\text{ mA cm}^{-2}$ ) for  $250\text{ cm}^3$  (half reservoir) of  $1.6\text{ mol dm}^{-3}\text{ V(III) / V(IV)}$  in  $4\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  at linear flow rate of  $1.11\text{ cm s}^{-1}$  and constant temperature of  $298 \pm 2\text{ K}$  (●) coulombic (X) voltage (▲) energy

105

**Figure 6.6:** Cell voltage vs. time representing charge-discharge characteristics of  $25\text{ cm}^2$  unit cell laboratory unit V-RFB under controlled temperatures ( $288$ ,  $298$  and  $308\text{ K} \pm 2\text{ K}$ ) for  $250\text{ cm}^3$  (half reservoir) of  $1.6\text{ mol dm}^{-3}\text{ V(III) / V(IV)}$  in  $4\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  at constant linear flow rate of  $1.11\text{ cm s}^{-1}$  and constant current density of  $60\text{ mA cm}^{-2}$

107



- Figure 6.7:** Performance efficiencies *vs.* temperature of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB at different constant temperatures (288, 298 and 308 K). Electrolyte compositions and operating conditions were the same as in Figure 6.6. (●) coulombic (X) voltage (▲) energy **107**
- Figure 6.8:** Discharge cell voltage *vs.* temperature of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB at different constant temperature (288, 298 and 308 mA cm<sup>-2</sup>) and current densities (20 - 100 mA cm<sup>-2</sup>). Electrolyte compositions and operating conditions were similar to that in as Figure 6.6 **109**
- Figure 6.9:** Cell voltage *vs.* time representing charge-discharge characteristics of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB at controlled flow rate (1, 3 and 5 cm<sup>3</sup> s<sup>-1</sup>) for 250 cm<sup>3</sup> (half reservoir) of 1.6 mol dm<sup>-3</sup> V(III) / V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at constant temperature 298 ± 2K and constant current density of 60 mA cm<sup>-2</sup> **110**
- Figure 6.10:** Discharge cell voltages *vs.* volumetric flow rate representing effect of flow condition of 25 cm<sup>2</sup> unit cell V-RFB at controlled flow rate (1 - 7 cm<sup>3</sup> s<sup>-1</sup>). Electrolyte compositions and operating conditions were similar as Figure 6.9 **111**
- Figure 6.11:** Cell voltages *vs.* time representing charge-discharge characteristics of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB at constant volumetric flow rate at 3 cm<sup>3</sup> s<sup>-1</sup>, constant temperature 298 ± 2 K and constant current density of 60 mA cm<sup>-2</sup>. The 250 cm<sup>3</sup> (half reservoir) electrolyte composition was varied as follows (a) 0.8 mol dm<sup>-3</sup> V(III) / V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (b) 1.6 mol dm<sup>-3</sup> V(III) / V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> (c) 0.8 mol dm<sup>-3</sup> V(III) / V(IV) in 3 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> **113**
- Figure 6.12:** Effect of electrolyte flow velocities on the electrochemical behaviour of a 25 cm<sup>2</sup> unit cell laboratory unit V-RFB during the discharge reaction. Electrodes: 2-d planar carbon polyvinyl-ester. Electrolyte: 1.6 mol dm<sup>-3</sup> V(III)/V(IV) at 90 % SOC **115**

- Figure 6.13:** Scanning electron microscope (SEM) images of 5 cm x 5 cm x 0.4 cm Sigratherm GFA5, a porous and layered carbon felt electrodes (effective volumetric porosity of  $0.68 \pm 0.07$ ) (a) before immersion into vanadium electrolyte (b) positive electrode after operation of the V-RFB; immersed into vanadium electrolyte (c) negative electrode after operation of the V-RFB; immersed into vanadium electrolyte. Vanadium electrolyte:  $1.6 \text{ mol dm}^{-3} V(III)/V(IV)$  in  $4 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  **117**
- Figure 6.14:** Linear sweep voltammograms of a  $25 \text{ cm}^2$  unit cell laboratory unit V-RFB using two types of electrode materials at 298 K (i) two-dimensional planar carbon polyvinylester (ii) three-dimensional porous carbon-felt. Electrolyte  $1.6 \text{ mol dm}^{-3} V(III)/V(IV)$  in  $4 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  at 90 % SOC; Electrolyte volumetric flow velocity  $3 \text{ cm}^3 \text{ s}^{-1}$  **118**
- Figure 7.1:** Equivalent electrical circuit of a unit cell, laboratory unit V-RFB system **124**
- Figure 7.2:** Operation of EKF in estimating the optimal or quasi-optimal value of V-RFB parameters. **126**
- Figure 7.3:** Configuration of V-RFB test bank with schematic of the overall experimental arrangement including electrolyte flow-tube, nitrogen and oxygen flows, and electrical connection circuits. **129**
- Figure 7.4:** Open-circuit cell potential  $E_{cell(ORP)}$  of a  $25 \text{ cm}^2$  unit cell, laboratory unit V-RFB as a function of state-of-charge; comparison of estimated SOC with respect to SOC obtained through experiments for  $250 \text{ cm}^3$  (half reservoir) of  $1.6 \text{ mol dm}^{-3} V(III) / V(IV)$  in  $4 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$  at linear flow rate of  $1.11 \text{ cm s}^{-1}$ , constant temperature of  $298 \pm 2 \text{ K}$  and constant current density of  $100 \text{ mA cm}^{-2}$  (adapted from (Mohamed *et al.*, 2013)). **130**
- Figure 7.5:** V-RFB cell voltage characteristic of a  $25 \text{ cm}^2$  unit cell, laboratory unit V-RFB during pulse-relaxation test at SOC = 0.8 of  $250 \text{ cm}^3$  (half reservoir) of  $1.6 \text{ mol dm}^{-3} V(III) / V(IV)$  in  $4 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ , with specific current density of  $60 \text{ mA cm}^{-2}$

<sup>2</sup>, constant linear flow rate of  $1.11 \text{ cm s}^{-1}$  and controlled temperature of  $298 \pm 2 \text{ K}$ , simulated through a refrigerated circulators bath (Grant LTD 6/20 – LTD6G).

132

**Figure 7.6:** V-RFB cell voltage characteristic of a  $25 \text{ cm}^2$  unit cell, laboratory unit V-RFB during pulse-relaxation test at different SOC from 10 % SOC to 90 % SOC for  $250 \text{ cm}^3$  (half reservoir) of  $1.6 \text{ mol dm}^{-3} \text{ V(III) / V(IV)}$  in  $4 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at linear flow rate of  $1.11 \text{ cm s}^{-1}$ , constant temperature of  $298 \pm 2 \text{ K}$  and current density of at  $60 \text{ mA cm}^{-2}$ . For simplicity, except 10 % and 90 % SOC, no odd percentage SOCs are shown

133

**Figure 7.7:** Ohmic resistance of a  $25 \text{ cm}^2$  unit cell, laboratory unit V-RFB at different SOC from 10 % SOC to 90 % SOC for  $250 \text{ cm}^3$  (half reservoir) of  $1.6 \text{ mol dm}^{-3} \text{ V(III) / V(IV)}$  in  $4 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at linear flow rate of  $1.11 \text{ cm s}^{-1}$ , constant temperature of  $298 \pm 2 \text{ K}$  and current density of at  $60 \text{ mA cm}^{-2}$ .

134

**Figure 7.8:** Comparison of EKF-based estimated  $E_{cell}$  and experimental  $E_{cell}$  vs. time of a  $25 \text{ cm}^2$  unit cell, laboratory unit V-RFB during pulse-relaxation test at 80 % SOC (a) pulse-relaxation test at 80 % SOC (b) Estimated error

135

**Figure 7.9:** Degree of uncertainties of the state estimation covariance which depicts all the state estimation smoothly approaching steady state at the end of pulse-relaxation test.

136

**Figure 7.10:** Identification parameters of the V-RFB based on the implemented EKF model vs. time / seconds (a) Ohmic activation polarisation, (b) Ohmic concentration polarisation, (c) Capacitance activation polarisation, (d) Capacitance concentration polarisation, and (e) Cell voltage estimation error. All data are captured at discharging mode.

139

**Figure 7.11:** Performance consistency of the tuned covariance matrix of  $Q$ ,  $P$  and  $R$  at different SOC; 20 % SOC (a) Comparison of EKF-based estimated  $E_{cell}$  and experimental  $E_{cell}$  vs. time of the V-RFB during pulse-relaxation test at 20 % SOC, (b) Ohmic

activation polarisation, (c) Ohmic concentration polarisation, (d) Capacitance activation polarisation, (e) Capacitance concentration polarisation, and (f) Cell voltage estimation error. All data, except (a), are captured at discharging mode.

143

**Figure 7.12:** Validation of EKF-based estimation model with respect to the experimental data *vs.* time (a) comparison of the  $E_{cell}$  EKF-based estimation and  $E_{cell}$  experiment, (b) comparison of the  $E_{cell(ORP)}$  EKF-based estimation and  $E_{cell(ORP)}$  experiment, and (c) mean-error of the EKF-based estimation with respect to the experimental data. Operating parameters are the same as in Figure 7.5.

145

## LIST OF SYMBOLS

Symbol	Meaning	Units
$C_{V(II)}$	Concentration of V(II) species	Mol dm <sup>-3</sup>
$C_{V(III)}$	Concentration of V(III) species	Mol dm <sup>-3</sup>
$C_{V(IV)}$	Concentration of V(IV) species	Mol dm <sup>-3</sup>
$C_{V(V)}$	Concentration of V(V) species	Mol dm <sup>-3</sup>
$\emptyset$	Current efficiency	
$C_{oxd}$	Concentration of oxidised species	Mol dm <sup>-3</sup>
$C_{red}$	Concentration of reduced species	Mol dm <sup>-3</sup>
$C_{ap}$	Activation polarisation capacitance (transient response)	F
$C_{cp}$	Concentration polarisation capacitance (transient response)	F
$E_{cell}$	Cell potential; measured across unit cell stack	V
$E_{cell(ORP)}$	Open-circuit cell potential across two electrode or Oxidation-reduction redox potential; measured across two working electrode at reference cell (otherwise $E_{V(IV)/V(V)} - E_{V(III)/V(II)}$ )	V
$E_{drop}$	Cell potential after $IR_o$ effect	V
$E_{cell,oc}$	Open-circuit cell potential	V
$E^{\circ}_{cell}$	Standard cell potential; potential different across the two half-cells with respect to the standard hydrogen electrode (SHE) (otherwise $E^{\circ}_{cell,+} - E^{\circ}_{cell,-}$ )	V

$E_{cell,+}^{\circ}$	Standard positive half-cell potential; standard electrode potentials of positive half-reactions with respect to the standard hydrogen electrode (SHE)	V
$E_{cell,-}^{\circ}$	Standard negative half-cell potential; standard electrode potentials of negative half-reactions with respect to the standard hydrogen electrode (SHE)	V
$E_{V(IV)/V(V)}$	Positive half-cell potential for V-RFB; measured at positive half-cell reference cell across working electrode and Hg/Hg <sub>2</sub> SO <sub>4</sub> reference electrode	V
$E_{V(III)/V(II)}$	Negative half-cell potential for V-RFB; ; measured at negative half-cell reference cell across working electrode and Hg/Hg <sub>2</sub> SO <sub>4</sub> reference electrode	V
$E$	Energy	Wh
$E_d$	Energy density	Wh L <sup>-1</sup>
$F$	Faraday's constant	Ah mol <sup>-1</sup>
$I$	Current	A
$IR_o$	Drop of cell potential due to internal resistance of V-RFB cell	V
$I_{shunt}$	Shunt current; measured at positive terminal of dc supply and load during charge-discharge cycle at range 100 mV/A	A
$I-V$	Electrical power	P
$j$	Current density	mA cm <sup>-2</sup>
$K, L, M, N$	Concentrations of oxidation and reduction species in Nernst equation	Mol dm <sup>-3</sup>
$k,l,m,n$	Stoichiometric factors in Nernst equation	-

$M_m$	Molar mass of the reactant	$\text{g mol}^{-1}$
$P$	Power	W
$P_d$	Power density	$\text{W L}^{-1}$
$P_p$	Percentage purity	
$p$	Pressure	Pa
$q$	Charge	C
$q/V$	Volumetric charge density	$\text{Ah L}^{-1}$
$Q$	Equilibrium constant	-
$R_o$	Ohmic polarisation	$\Omega$
$R_{ap}$	Activation polarisation resistance (Reaction rate loss)	$\Omega$
$R_{cp}$	Concentration polarisation resistance (Mass transport loss)	$\Omega$
$S_g$	Specific gravity of $\text{H}_2\text{SO}_4$	-
$t$	Time	second
$T$	Temperature	$^{\circ}\text{C}$
$\% \eta_V$	Voltage efficiency	%
$\% \eta_C$	Charge efficiency	%
$\% \eta_E$	Energy efficiency	%
$\Delta c$	Change in the reactant concentration	$\text{mol L}^{-1}$
$V$	Volume of electrolyte	L
$W_{cell}$	Amount of work in electrochemical cell	Joules, J
$z$	No. of electrons transferred during the redox reaction	-

## LIST OF ABBREVIATIONS

AER	–	All electric range
BEV	–	Battery electric vehicle
EGM	–	Electric generator/motor
EKF	–	Extended Kalman filter
EV	–	Electric vehicle
FC	–	Fuel cell
FCEV	–	Fuel cell electric vehicle
HEV	–	Hybrid electric vehicle
HR	–	Hybridization ratio
ICE	–	Internal combustion engine
PHEV	–	Plug-in HEV
OCV	–	Open-circuit voltage
ORP	–	Oxidation-reduction redox potential
PVC	–	Polyvinyl chloride polymer
RESS	–	Rechargeable energy storage system
RFB	–	Redox flow battery
SHE	–	Standard hydrogen electrode
SOC	–	State-of-charge
UNSW	–	The University of New South Wales, Australia
V-RFB	–	Vanadium RFB



## ABSTRACT

This thesis presents the summarization of work on experimental characterisation and modeling of a vanadium redox flow battery (V-RFB). This thesis presents background material and motivation factors of the studies; research goals, a review of previous work and discussion on related issues with respect to energy storage technologies, emphasising on V-RFB system. The aim of the study is to investigate the performance of V-RFB through experimental characterisation of V-RFB at different operating parameters and develop electrical circuit modeling of V-RFB. Preliminary experiment on 100 cm<sup>2</sup> unit cell laboratory unit V-RFB has helped in familiarising with V-RFB setup and its design weaknesses and factors leading the cell into failure mode are highlighted. Based on observation on 100 cm<sup>2</sup> unit cells, new design of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB has been proposed with an improvement of efficiency and reduction of contact resistance are observed. Theoretically studies by using Faraday's law of electrolysis and Nernst equation are used to relate the equilibrium cell's potential with the concentration changes in vanadium species, back-up with experimental data from a divided, open-circuit potentiometric cell approach. Two different approaches has been presented, with newly proposed approach of a divided, open-circuit potentiometric cell, via Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrodes and graphite rod working electrodes present superiorities in estimating the state-of-charge (SOC) of V-RFB. System characterisation has been carried-out for the new 25 cm<sup>2</sup> unit cell laboratory unit V-RFB under different of operating parameters such as current densities, temperatures, flow rates, concentrations and material properties. The cell exhibits highest energy efficiency at 82.1 %, operating at 308 K, 60 mA cm<sup>-2</sup> current density and 3 cm<sup>3</sup> s<sup>-1</sup> volumetric flow rate for 250 cm<sup>3</sup> (each reservoir) of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Formation charge of mixture of vanadium species into single electro-active species at positive and negative electrodes are highlighted. A method for estimating the V-RFB to complete its formation charge using electrochemical calculation of Faraday's constant are also presented. New equivalent electric circuit model for V-RFB has been proposed which consists of an open-circuit cell potential in series of ohmic internal resistance and the parallel n-RC network. Extended Kalman filter is used for parameter identification of dynamic characterisation of V-RFB. Numerical simulations are compared to experimental data at different pulse voltages at few SOCs and experimental charge-discharge characterisation of V-RFB system, demonstrating good agreement.

## ABSTRAK

Tesis ini membentangkan ringkasan hasil kerja lapangan mencirikan dan memodelkan vanadium redox bateri teralir (V-RFB). Tesis ini membentangkan latar belakang dan faktor yang memotivasikan untuk pengajian, matlamat kajian, penilaian hasil kerja yang lepas dan perbincangan berkaitan dengan teknologi penyimpanan tenaga, dengan penekanan kepada sistem V-RFB. Tujuan pengajian ini adalah untuk mengkaji prestasi V-RFB melalui pencirian eksperimen V-RFB pada parameter operasi yang berbeza dan membangunkan model litar elektrik V-RFB. Eksperimen awal pada 100 cm<sup>2</sup> sel unit makmal yang membantu membiasakan dengan pembinaan V-RFB dan juga kelemahan rekaannya dan faktor yang menyebabkan bateri gagal berfungsi ada dinyatakan. Berdasarkan pemerhatian pada 100 cm<sup>2</sup> sel unit makmal, satu rekaan baru iaitu 25 cm<sup>2</sup> sel unit makmal dicadangkan dengan peningkatan tahap kecekapan dan penurunan rintangan sentuhan dapat diperhatikan. Kajian secara teori hukum Faraday elektrolisis dan persamaan Nernst digunakan untuk mengaitkan potensi sel keseimbangan dengan perubahan kepekatan spesies vanadium, dibantu dengan data eksperimen dari litar terbuka-terbahagi-sel pendekatan potentiometrik. Dua pendekatan yang berbeza telah dikemukakan, dengan pendekatan baru dari litar terbuka-terbahagi-sel pendekatan potentiometrik, melalui Hg/Hg<sub>2</sub>SO<sub>4</sub> elektrod rujukan dan rod grafit bekerja-elektrod memberikan pendekatan terbaik dalam menganggarkan tahap caj (SOC) V-RFB. Pencirian sistem telah diberikan untuk sistem baru 25 cm<sup>2</sup> sel unit makmal V-RFB di bawah variasi parameter operasi seperti kepadatan arus, suhu, kadar aliran, kepekatan dan sifat bahan. Sel telah mencatatkan kecekapan tenaga tertinggi pada 82.1%, beroperasi pada 308 K, 60 mA cm<sup>-2</sup> ketumpatan arus dan 3 cm<sup>3</sup> s<sup>-1</sup> kadar aliran isipadu 250 cm<sup>3</sup> (setiap satu takungan) 1.6 mol dm<sup>-3</sup> V (III) / V (IV) dalam 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Cas pembentukan campuran spesies vanadium ke spesies elektro-aktif tunggal pada elektrod positif dan negatif telah diketengahkan. Satu kaedah untuk menganggarkan V-RFB untuk melengkapkan cas pembentukan campuran spesies vanadium ke spesies elektro-aktif tunggal menggunakan pengiraan elektrokimia pemalar Faraday juga dibentangkan. Litar setara model elektrik yang baru untuk V-RFB telah dicadangkan yang terdiri daripada voltan terbuka litar sel sesiri dengan rintangan dalaman dan selari dengan rangkaian n-RC. Penapis Lanjutan Kalman digunakan untuk mengenalpasti parameter pencirian dinamik V-RFB. Simulasi berangka berbanding dengan data eksperimen pada voltan nadi berbeza pada beberapa SOCs dan eksperimen cas-discas pencirian sistem V-RFB, menunjukkan penemuan yang baik.

## REFERENCES

- Aaron, D.S., Liu, Q., Tang, Z., Grim, G.M., Papandrew, A.B., Turhan, A., Zawodzinski, T.A. and Mench, M.M. 2012. Dramatic performance gains in vanadium redox flow batteries through modified cell architecture. *Journal of Power Sources* **206** (0): 450-453.
- Abu-Sharkh, S. and Doerffel, D. 2004. Rapid test and non-linear model characterisation of solid-state lithium-ion batteries. *Journal of Power Sources* **130** (1-2): 266-274.
- Abu Sharkh, S.M. and Griffiths, G. 2002. Energy storage systems for unmanned underwater vehicles. *Underwater Technology* **25** (3): 143-148.
- Al-Fetlawi, H., Shah, A.A. and Walsh, F.C. 2009. Non-isothermal modelling of the all-vanadium redox flow battery. *Electrochimica Acta* **55** (1): 78-89.
- Al-Fetlawi, H., Shah, A.A. and Walsh, F.C. 2010. Modelling the effects of oxygen evolution in the all-vanadium redox flow battery. *Electrochimica Acta* **55** (9): 3192-3205.
- Al-Karaghoul, A., Renne, D. and Kazmerski, L.L. 2010. Technical and economic assessment of photovoltaic-driven desalination systems. *Renewable Energy* **35** (2): 323-328.
- Aymé-Perrot, D., Walter, S., Gabelica, Z. and Valange, S. 2008. Evaluation of carbon cryogels used as cathodes for non-flowing zinc-bromine storage cells. *Journal of Power Sources* **175** (1): 644-650.
- Bae, C.H., Roberts, E.P.L. and Dryfe, R.A.W. 2002. Chromium redox couples for application to redox flow batteries. *Electrochimica Acta* **48** (3): 279-287.
- Barote, L., Marinescu, C. and Georgescu, M. 2009. VRB modeling for storage in stand-alone wind energy systems. *PowerTech, 2009 IEEE Bucharest*: 1-6.
- Barrado, E., Pardo, R., Castrillejo, Y. and Vega, M. 1997. Electrochemical behaviour of vanadium compounds at a carbon paste electrode. *Journal of Electroanalytical Chemistry* **427** (1-2): 35-42.
- Bartolozzi, M. 1989. Development of redox flow batteries: a historical bibliography. *Journal of Power Sources* **27** (3): 219-234.
- Baxter, R. 2006. *Energy storage: a nontechnical guide*. illustrated. Oklahoma: PennWell Books.
- Blanc, C. 2009. Modeling of a vanadium redox flow battery electricity storage system. Laboratoire d'Electronique Industrielle Lausanne, Ecole Polytechnique Federale De Lausanne. **PhD Thesis**: 263.
- Blanc, C. and Rufer, A. 2008. Multiphysics and energetic modeling of a vanadium redox flow battery. *IEEE International Conference on Sustainable Energy Technologies, ICSET2008*, Singapore, IEEE: 696-701.
- Brady, J.E. 1990. *General chemistry : principles & structure*. 5th. New York: John Wiley & Sons.
- Broman, A.Z.B.M. 2004. Redox flow battery and method of operating it. US Patent. US, Squirrel Holdings Ltd. **US 6692862 B1**: 1-10.
- Burke, A.F. 2007. Batteries and ultracapacitors for electric, hybrid, and fuel cell vehicles. *Proceedings of the IEEE*. **95**: 806-820.
- Cathro, K.J. 1988. Performance of zinc/bromine cells having a propionitrile electrolyte. *Journal of Power Sources* **23** (4): 365-383.

- Cathro, K.J., Constable, D.C. and Hoobin, P.M. 1988. Performance of porous plastic separators in zinc/bromine cells. *Journal of Power Sources* **22** (1): 29-57.
- Chahwan, J., Abbey, C. and Joos, G. 2007. VRB modelling for the study of output terminal voltages, internal losses and performance. *IEEE Canada Electrical Power Conference, 2007. EPC 2007.*: 387-392.
- Chan, H.L. 2000. A new battery model for use with battery energy storage systems and electric vehicles power systems. *IEEE Power Engineering Society Winter Meeting, 2000.* **1**: 470-475 vol.471.
- Charlot, G. 2007. *Qualitative inorganic analysis*. US: Thomas Press.
- Chen, H., Cong, T.N., Yang, W., Tan, C., Li, Y. and Ding, Y. 2009. Progress in electrical energy storage system: a critical review. *Progress in Natural Science* **19** (3): 291-312.
- Chen, J., Zhu, S., Wang, B. and Yang, J. 2009. Model of open-circuit voltage for all-vanadium redox flow battery. *Huagong Xuebao / CIESC Journal* **61** (1): 211-215.
- Chen, M. and Rincon-Mora, G.A. 2006. Accurate electrical battery model capable of predicting runtime and I-V performance. *IEEE Transactions on Energy Conversion* **21** (2): 504-511.
- Cheng, J., Zhang, L., Yang, Y.-S., Wen, Y.-H., Cao, G.-P. and Wang, X.-D. 2007. Preliminary study of single flow zinc-nickel battery. *Electrochemistry Communications* **9** (11): 2639-2642.
- Clarke, R.L., Dougherty, B., Harrison, S., Millington, P.J. and Mohanta, S. 2006. Battery with bifunctional electrolyte. PatentStorm. Patent, U.S. USA, Plurion Systems, Inc. **6986966**.
- Clarke, R.L., Dougherty, B., Harrison, S., Millington, P.J. and Mohanta, S. 2009. Cerium batteries FreePatentsOnline. Patent, U.S. USA, Plurion Limited Company (GB). **7625663**.
- Collins, J., Kear, G., Li, X., Low, C.T.J., Pletcher, D., Tangirala, R., Stratton-Campbell, D., Walsh, F.C. and Zhang, C. 2010. A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II) Part VIII. The cycling of a 10 cm × 10 cm flow cell. *Journal of Power Sources* **195** (6): 1731-1738.
- Collins, J., Li, X., Pletcher, D., Tangirala, R., Stratton-Campbell, D., Walsh, F.C. and Zhang, C. A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II). Part IX: Electrode and electrolyte conditioning with hydrogen peroxide. *Journal of Power Sources* **In Press, Corrected Proof**.
- Cook, B. 2002. Introduction to fuel cells and hydrogen technology. *Engineering Science And Education Journal*: 205-216.
- Dai, H., Wei, X., Sun, Z., Wang, J. and Gu, W. 2012. Online cell SOC estimation of Li-ion battery packs using a dual time-scale Kalman filtering for EV applications. *Applied Energy* **95** (0): 227-237.
- Dees, D.W., Battaglia, V.S. and Bélanger, A. 2002. Electrochemical modeling of lithium polymer batteries. *Journal of Power Sources* **110** (2): 310-320.
- Deguchi, H., Shigematsu, T. and Tokuda, N. 2010. Method for designing redox flow battery system. US Patent. US, Sumitomo Electric Industries, Ltd.
- The Kansai Electric Power Co, Inc. **7704634**: 1-18.
- Dhameja, S. 2002. *Electric vehicle battery systems*. Woburn: Newnes Press.

- Dillon, T.S., Martin, R.W. and Sjelvgren, D. 1980. Stochastic optimization and modelling of large hydrothermal systems for long-term regulation. *International Journal of Electrical Power & Energy Systems* **2** (1): 2-20.
- Dürr, M., Cruden, A., Gair, S. and McDonald, J.R. 2006. Dynamic model of a lead acid battery for use in a domestic fuel cell system. *Journal of Power Sources* **161** (2): 1400-1411.
- Eckroad, S. 2007. Vanadium redox flow batteries : an in-depth analysis. Palo Alto, CA, Electric Power Research Institute.
- Fabjan, C., Garche, J., Harrer, B., Jörissen, L., Kolbeck, C., Philippi, F., Tomazic, G. and Wagner, F. 2001. The vanadium redox-battery: an efficient storage unit for photovoltaic systems. *Electrochimica Acta* **47** (5): 825-831.
- Fedkiw, P.S. and Watts, R.W. 1984. A mathematical model for the iron/chromium redox battery. *Journal of The Electrochemical Society* **131** (4): 701-709.
- Feng, X. and Sun, Z. 2008. A battery model including hysteresis for state-of-charge estimation in Ni-MH battery. *IEEE Vehicle Power and Propulsion Conference, 2008. VPPC '08.*: 1-5.
- Gaku Oriji, Y.K., Takashi Miura. 2004. Investigation on V(IV)/V(V) species in a vanadium redox flow battery. *Electrochimica Acta* **49** (19): 3091-3095.
- Gattrell, M., Park, J., MacDougall, B., Apte, J., McCarthy, S. and Wu, C.W. 2004. Study of the Mechanism of the Vanadium 4+/5+ Redox Reaction in Acidic Solutions. *Journal of The Electrochemical Society* **151** (1): A123-A130.
- Ge, B., Wang, W., Bi, D., Rogers, C.B., Peng, F.Z., de Almeida, A.T. and Abu-Rub, H. 2013. Energy storage system-based power control for grid-connected wind power farm. *International Journal of Electrical Power & Energy Systems* **44** (1): 115-122.
- Gonzalez-Garcia, J., Bonete, P., Exposito, E., Montiel, V., Aldaz, A. and Torregrosa-Macia, R. 1999. Characterization of a carbon felt electrode: structural and physical properties. *Journal of Materials Chemistry* **9** (2): 419-426.
- Gonzalez, A., Gallachóir, B.Ó., McKeogh, E. and Lynch, K. 2004. Study of electricity storage technologies and their potential to address wind energy intermittency in Ireland.  
Available:<<http://www.sei.ie/uploadedfiles/FundedProgrammes/REHC03001FinalReport.pdf>>, (15 June 2009)
- Hazza, A., Pletcher, D. and Wills, R. 2004. A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II). Part I. Preliminary studies. *Physical Chemistry Chemical Physics* **6** (8): 1773-1778.
- Hazza, A., Pletcher, D. and Wills, R. 2005. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): IV. The influence of additives. *Journal of Power Sources* **149**: 103-111.
- He, H., Xiong, R., Zhang, X., Sun, F. and Fan, J. 2011. State-of-Charge Estimation of the Lithium-Ion Battery Using an Adaptive Extended Kalman Filter Based on an Improved Thevenin Model. *IEEE Transactions on Vehicular Technology* **60** (4): 1461-1469.
- He, H., Zhang, X., Xiong, R., Xu, Y. and Guo, H. 2012. Online model-based estimation of state-of-charge and open-circuit voltage of lithium-ion batteries in electric vehicles. *Energy* **39** (1): 310-318.
- He, X., Maxwell, T. and Parten, M. 2006. Development of a hybrid electric vehicle with a hydrogen-fueled IC engine. *IEEE Transactions on Vehicular Technology* **55** (6): 1693-1703.

- Hebner, R., Beno, J. and Walls, A. 2002. Flywheel batteries come around again. *Spectrum, IEEE* **39** (4): 46-51.
- Hu, Y., Yurkovich, S., Guezennec, Y. and Bornatico, R. 2008. Model-based calibration for battery characterization in HEV applications. *American Control Conference, 2008*: 318-325.
- Hu, Y., Yurkovich, S., Guezennec, Y. and Yurkovich, B.J. 2009. A technique for dynamic battery model identification in automotive applications using linear parameter varying structures. *Control Engineering Practice* **17** (10): 1190-1201.
- Husain, I. 2003. *Electric and hybrid vehicles: design fundamentals*. Boca Raton, Florida: CRC Press.
- Ivakin, A.A. and Voronova, E.M. 1973. A spectrophotometric study of vanadium (IV) sulfate complexes. *Russian Journal of Inorganic Chemistry* **18** (7): 956.
- J. A. Smith, M. H. Nehrir, V. Gerez and Shaw, a.S.R. 2002. A broad look at the workings, types, and applications of fuel cells. *Power Engineering Society Summer Meeting 2002, IEEE* **1**: 70-75.
- J. Larminie and Lowry, J. 2003. *Electric vehicle technology explained*. West Sussex: John Wiley & Sons, Ltd.
- Jia, C., Liu, J. and Yan, C. 2010. A significantly improved membrane for vanadium redox flow battery. *Journal of Power Sources* **195** (13): 4380-4383.
- Joerissen, L., Garche, J., Fabjan, C. and Tomazic, G. 2004. Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems. *Journal of Power Sources*, Ulm, Germany, Elsevier. **127**: 98-104.
- Kaizuka, T. and Sasaki, T. 2001. Evaluation of control maintaining electric power quality by use of rechargeable battery system. *IEEE Power Engineering Society Winter Meeting, 2001*. **1**: 88-93 vol.81.
- Kaneko, H., Nozaki, K., Wada, Y., Aoki, T., Negishi, A. and Kamimoto, M. 1991. Vanadium redox reactions and carbon electrodes for vanadium redox flow battery. *Electrochimica Acta* **36** (7): 1191-1196.
- Kangro, W. 1969. Couples redox liquides. *Proceeding 6th ESRO Summer Srhobf Noordwijk Space Power Systems Energy Storage*., The Nertherlands, ESRO. **X**.
- Karki, R. 2006. Reliability Focused and Market Driven Growth of Wind Power in Electric Power Systems. *International Review of Electrical Engineering* **1** (1): 170-177.
- Kazacos, M. and Skyllas-Kazacos, M. 1989. Performance characteristics of carbon plastic electrodes in the all-vanadium redox cell. *Journal of The Electrochemical Society* **136** (9): 2759-2760.
- Kazmerski, L.L. 2006. Solar photovoltaics R&D at the tipping point: A 2005 technology overview. *Journal of Electron Spectroscopy and Related Phenomena* **150** (2-3): 105-135.
- Kiessling, R. and Mills, J. 1995. A battery model for the monitoring of, and corrective action on, lead/acid electric-vehicle batteries. *Journal of Power Sources*. **53**: 339-340.
- Kinoshita, K. and Leach, S.C. 1982. Mass-transfer study of carbon felt, flow-through electrode. *Journal Electrochemical Society* **129** (09/1982): 1993-1997.
- Kondoh, J., I. Ishii, H. Yamaguchi, A. Murata, K. Otani, K. Sakuta, N. Higuchi, Sekine, S. and Kamimoto, M. 2000. Electrical energy storage systems for energy networks. *Energy Conversion and Management* **41** (17): 1863-1874.

- Koshizuka, N., Ishikawa, F., Nasu, H., Murakami, M., Matsunaga, K., Saito, S., Saito, O., Nakamura, Y., Yamamoto, H., Takahata, R., Itoh, Y., Ikezawa, H. and Tomita, M. 2003. Progress of superconducting bearing technologies for flywheel energy storage systems. *Physica C: Superconductivity* **386**: 444-450.
- Kroeze, R.C. and Krein, P.T. 2008. Electrical battery model for use in dynamic electric vehicle simulations. *IEEE Power Electronics Specialists Conference, 2008. PESC 2008.* : 1336-1342.
- Lam, L.T., Ozgun, H., Lim, O.V., Hamilton, J.A., Vu, L.H., Vella, D.G. and Rand, D.A.J. 1995. Pulsed-current charging of lead/acid batteries — a possible means for overcoming premature capacity loss? *Journal of Power Sources* **53** (2): 215-228.
- Laughton, M.A. 1982. Power and energy systems planning. *International Journal of Electrical Power & Energy Systems* **4** (1): 42-50.
- Laughton, M.A., Barak, M.M. and Inman, D. 2003. 29 - Batteries. *Electrical Engineer's Reference Book (Sixteenth Edition)*. Oxford, Newnes: 1-19.
- Lavelaine, H. and Allanore, A. 2008. Optimized design of an iron electrowinning cell. *Proceedings of the 4th Ulcos seminar*, Essen: 1-12.
- Lazarou, S., Pyrgioti, E. and Alexandridis, A.T. 2009. A simple electric circuit model for proton exchange membrane fuel cells. *Journal of Power Sources* **190** (2): 380-386.
- Lee, S., Kim, J., Lee, J. and Cho, B.H. 2008. State-of-charge and capacity estimation of lithium-ion battery using a new open-circuit voltage versus state-of-charge. *Journal of Power Sources* **185** (2): 1367-1373.
- Leung, P.K., Ponce-de-León, C., Low, C.T.J., Shah, A.A. and Walsh, F.C. 2011. Characterization of a zinc–cerium flow battery. *Journal of Power Sources* **196** (11): 5174-5185.
- Lex, P. 2009. Demonstration of a 2-MWh Peak Shaving Z-BESS Available: <[http://www.zbbenergy.com/pdf/Techpapers\\_%20Demonstrationproject.pdf](http://www.zbbenergy.com/pdf/Techpapers_%20Demonstrationproject.pdf)>, (20 November 2009)
- Li, M.H., Funaki, T. and Hikiyama, T. 2007. A study of output terminal voltage modeling for redox flow battery based on charge and discharge experiments. *Power Conversion Conference - Nagoya, 2007. PCC '07*: 221-225.
- Li, X., Pletcher, D. and Walsh, F.C. 2009. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): part VII. Further studies of the lead dioxide positive electrode. *Electrochimica Acta* **54** (20): 4688-4695.
- Li, X.G., Huang, K.L., Liu, S.Q., Tan, N. and Chen, L.Q. 2007. Characteristics of graphite felt electrode electrochemically oxidized for vanadium redox battery application. *Transactions of Nonferrous Metals Society of China* **17** (1): 195-199.
- Lone, S.A. and Mufti, M.u.-D. 2006. Integrating a redox flow battery system with a wind-diesel power system. *International Conference on Power Electronics, Drives and Energy Systems, 2006. PEDES '06.* : 1-6.
- Luo, Q., Zhang, H., Chen, J., Qian, P. and Zhai, Y. 2008. Modification of Nafion membrane using interfacial polymerization for vanadium redox flow battery applications. *Journal of Membrane Science* **311** (1-2): 98-103.
- Lynch, W.A. and Salameh, Z.M. 2006. Electrical component model for a nickel-cadmium electric vehicle traction battery. Piscataway, NJ, USA, 2006 IEEE Power Engineering Society General Meeting: 5 pp.

- M. Kazacos, M. Cheng and Skyllas-Kazacos, M. 1990. Vanadium redox cell electrolyte optimization studies. *Journal of Applied Electrochemistry* **20**: 463-467.
- M. Skyllas-Kazacos, C. Menictas and Kazacos, M. 1996. Thermal stability of concentrated V(V) electrolytes in the vanadium redox cell. *Journal of the Electrochemical Society* **143** (No. 4): L86–L88.
- Ma, X., Zhang, H., Sun, C., Zou, Y. and Zhang, T. 2012. An optimal strategy of electrolyte flow rate for vanadium redox flow battery. *Journal of Power Sources* **203** (0): 153-158.
- Malleo, D., Nevill, J.T., van Ooyen, A., Schnakenberg, U., Lee, L.P. and Morgan, H. 2010. Note: Characterization of electrode materials for dielectric spectroscopy. *Review of Scientific Instruments* **81** (1): 016104-016104-016103.
- Medora, N.K. and Kusko, A. 2005. Dynamic battery modeling of lead-acid batteries using manufacturers' data. *27<sup>th</sup> International Telecommunications Conference, 2005. INTELEC '05.* : 227-232.
- Menictas, C., Hong, D.R., Yan, Z.H., Wilson, Y.J., Kazacos, M. and Skyllas-Kazacos, M. 1994. Status of the vanadium redox battery development program. *National Conference Publication - Institution of Engineers, Australia, Sydney, USA, IE Aust, Crows Nest, NSW, Aust.* **1**: 299-303.
- Miyake, S. and Tokuda, N. 2001. Vanadium redox-flow battery for a variety of applications. *IEEE Power Engineering Society Summer Meeting, 2001.* . **1**: 450-451 vol.451.
- Mohamed, M.R., Ahmad, H. and Abu Seman, M.N. 2012. State-of-the-art of vanadium redox flow battery: A review on research prospects. *International Review of Electrical Engineering (IREE)* **7** (5): 5610-5622.
- Mohamed, M.R., Ahmad, H. and Abu Seman, M.N. 2013. Estimating the State-of-Charge of all-Vanadium Redox Flow Battery using a Divided, Open-circuit Potentiometric Cell. *Elektronika Ir Elektrotechnika* **19** (3): 37-42.
- Mohamed, M.R., Ahmad, H. and Abu Seman, M.N. In Press. Estimating State-of-Charge of all-Vanadium Redox Flow Battery using a Divided, Open-circuit Potentiometric Cell. *Elektronika ir elektrotechnika* **Accepted for publication on Nov. 18, 2012.**
- Mohamed, M.R. and Li, S. 2010. Charge-discharge of 25 cm<sup>2</sup> V-RFB unit cell laboratory unit. Southampton, Unpublished.
- Mohamed, M.R., Sharkh, S.M., Ahmad, H., Abu Seman, M.N. and Walsh, F.C. 2012. Design and development of unit cell and system for vanadium redox flow batteries (V-RFB). *International Journal of the Physical Sciences* **7** (7): 1010 - 1024.
- Mohamed, M.R., Sharkh, S.M. and Walsh, F.C. 2009. Redox flow batteries for hybrid electric vehicles: progress and challenges. *The 5th International IEEE Vehicle Power and Propulsion Conference (VPPC'09)*, Dearborn, Michigan, IEEE: 551-557.
- Mohammadi, F., Timbrell, P., Zhong, S., Padeste, C. and Skyllas-Kazacos, M. 1994. Overcharge in the vanadium redox battery and changes in electrical resistivity and surface functionality of graphite-felt electrodes. *Journal of Power Sources* **52** (1): 61-68.
- Mohammadi, T., Chieng, S.C. and Skyllas Kazacos, M. 1997. Water transport study across commercial ion exchange membranes in the vanadium redox flow battery. *Journal of Membrane Science* **133** (2): 151-159.



- Mohammadi, T. and Skyllas-Kazacos, M. 1995. Characterisation of novel composite membrane for redox flow battery applications. *Journal of Membrane Science* **98** (1-2): 77-87.
- Mohammadi, T. and Skyllas-Kazacos, M. 1995. Preparation of sulfonated composite membrane for vanadium redox flow battery applications. *Journal of Membrane Science* **107** (1-2): 35-45.
- N. Tokuda, T. Kanno, T. Hara, T. Shigematsu, Y. Tsutsui, A. Ikeuchi, T. Itou and Kumamoto., T. 2000. Development of redox flow battery system. *SEI Technical Review June 2000 No. 50*: 88-94.
- Nakaishi, H., Kanno, T., Ogino, S., Ito, T., Shigematsu, T. and Tokyda, N. 2008. Cell frame for redox flow battery, and redox flow battery. US Patent. US, Sumitomo Electric Industries, Ltd.
- The Kansai Electric Power Co, Inc. **US2008/0081247 A1**: 1-7.
- Noack, J.N., Vorhauser, L., Pinkwart, K. and Tuebke, J. 2008. Vanadium redox flow batteries : an in-depth analysis. Society. California, Electric Power Research Institute. **3**: 2010-2010.
- Ottewill, G.A. and Walsh, F.C. 1992. Electrode potential measurements. *Transactions of the Institute of Metal Finishing* **70** (3): 141-143.
- P. Bhusal, A.Z., M. Eloholma, L. Halonen. 2007. Energy-efficient Innovative Lighting and Energy Supply Solutions in Developing Countries. *International Review of Electrical Engineering* **2** (1): 665-670.
- P. Zhao, H. Zhang, H. Zhou, J. Chen, S. Gao and Yi, B. 2006. Characteristics and performance of 10 kW class all-vanadium redox-flow battery stack. *Journal of Power Sources* **162** (2): 1416-1420.
- Pan, J., Sun, Y., Cheng, J., Wen, Y., Yang, Y. and Wan, P. 2008. Study on a new single flow acid Cu-PbO<sub>2</sub> battery. *Electrochemistry Communications* **10** (9): 1226-1229.
- Parasuraman, A., Lim, T.M., Menictas, C. and Skyllas-Kazacos, M. 2012. Review of material research and development for vanadium redox flow battery applications. *Electrochimica Acta* (0).
- Pathak, S., Das, J.N., Rangarajan, J., Choudhury, S.R. and Prakash, R. 2006. Development of prototype phosphoric acid fuel cell pick-up electric vehicle. *IEEE Conference ICEHV '06*. : 1-4.
- Pawar, S., Madhale, R., Patil, P. and Lokhande, C. 1988. Studies on iron-chromium redox storage system. *Bulletin of Materials Science* **10** (4): 367-372.
- Pellegrini, A. and Broman, B.M. 2002. Redox flow battery system and cell stack. US Patent. US, Squirrel Holding Ltd. **6475661 B1**: 1-16.
- Pera, M.C., Hissel, D. and Kauffmann, J.M. 2002. Fuel cell systems for electrical vehicles. *IEEE 55th Vehicular Technology Conference, 2002. VTC Spring 2002*. **4**: 2097-2102 vol.2094.
- Piller, S., Perrin, M. and Jossen, A. 2001. Methods for state-of-charge determination and their applications. *Journal of Power Sources* **96** (1): 113-120.
- Ping Zhao, H.Z., Hantao Zhou, Baolian Yi. 2005. Nickel foam and carbon felt applications for sodium polysulfide/bromine redox flow battery electrodes. *Electrochimica Acta* **51** (6): 1091-1098.
- Pletcher, D., Hantao, Z., Kear, G., Low, C.T.J., Walsh, F.C. and Wills, R.G.A. 2008. A novel flow battery - a lead-acid battery based on an electrolyte with soluble lead

- (II). Part VI. studies of the lead dioxide positive electrode. *Journal of Power Sources* **180** (1): 630-634.
- Pletcher, D. and Wills, R. 2004. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II). Part II. Flow cell studies. *Physical Chemistry Chemical Physics* **6** (8): 1779-1785.
- Pletcher, D. and Wills, R. 2005. A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): III. The influence of conditions on battery performance. *Journal of Power Sources* **149**: 96-102.
- Pletcher, D., Zhou, H., Kear, G., Low, C.T.J., Walsh, F.C. and Wills, R.G.A. 2008. A novel flow battery : a lead-acid battery based on an electrolyte with soluble lead(II): Part VI. Studies of the lead dioxide positive electrode. *Journal of Power Sources* **180** (1): 630-634.
- Pletcher, D., Zhou, H., Kear, G., Low, C.T.J., Walsh, F.C. and Wills, R.G.A. 2008. A novel flow battery : a lead-acid battery based on an electrolyte with soluble lead(II): V. Studies of the lead negative electrode. *Journal of Power Sources* **180** (1): 621-629.
- Plurion. Accessed 25 Nov 2009. Technology. Available,
- Ponce-de-León, C., Frías-Ferrer, A., González-García, J., A.Szánto, D. and Walsh, F.C. 2006. Redox flow cells for energy conversion. *Journal of Power Sources* **160** (1): 716-732.
- Ponce-de-Leon, C., Reade, G.W., Whyte, I., Male, S.E. and Walsh, F.C. 2007. Characterization of the reaction environment in a filter-press redox flow reactor. *Electrochimica Acta* **52** (19): 5815-5823.
- Ponce de León, C., Frías-Ferrer, A., González-García, J., Szánto, D.A. and Walsh, F.C. 2006. Redox flow cells for energy conversion. *Journal of Power Sources* **160** (1): 716-732.
- Pop, V., Bergveld, H.J., Notten, P.H.L. and Regtien, P.P.L. 2005. State-of-the-art of battery state-of-charge determination. *Measurement Science and Technology* **16** (12): R93.
- Price, A. 2005. Electrical energy storage - a review of technology options. *Proceedings of the Institution of Civil Engineers: Civil Engineering* **158** (SPEC. ISS. 2): 52-58.
- Qian, P., Zhang, H., Chen, J., Wen, Y., Luo, Q., Liu, Z., You, D. and Yi, B. 2008. A novel electrode-bipolar plate assembly for vanadium redox flow battery applications. *Journal of Power Sources* **175** (1): 613-620.
- Radford, G.J.W., Cox, J., Wills, R.G.A. and Walsh, F.C. Electrochemical characterisation of activated carbon particles used in redox flow battery electrodes. *Journal of Power Sources* **In Press, Accepted Manuscript**.
- Rahman, F., Habiballah, I.O. and Skyllas-Kazacos, M. 2004. Electrochemical behavior of vanadium electrolyte for vanadium redox battery - a new technology for large scale energy storage systems. *Cigre 2004 Session Proceedings* - (Session): 1-8.
- Rahman, F., Rehman, S. and Abdul-Majeed, M.A. 2012. Overview of energy storage systems for storing electricity from renewable energy sources in Saudi Arabia. *Renewable and Sustainable Energy Reviews* **16** (1): 274-283.
- Rahman, F. and Skyllas-Kazacos, M. 1998. Solubility of vanadyl sulfate in concentrated sulfuric acid solutions. *Journal of Power Sources* **72** (2): 105-110.
- Rahman, F. and Skyllas-Kazacos, M. 2009. Vanadium redox battery: Positive half-cell electrolyte studies. *Journal of Power Sources* **189** (2): 1212-1219.

- Rao, R., Vrudhula, S. and Rakhmatov, D.N. 2003. Battery modeling for energy aware system design. *Computer* **36** (12): 77-87.
- Ridley, P. 2010. Cell data. Mohamed, M.R. Southampton, email communication with Peter Ridley (Re-Fuel Technology Ltd, Finchampstead, Wokingham, UK) on 15 July 2010.
- Romm, J.J. 2004. *The hype about hydrogen: fact and fiction in the race to save the climate*. 1-55963-703-X, I. Washington DC: Island Press.
- Rychcik, M. and Skyllas-Kazacos, M. 1988. Characteristics of a new all-vanadium redox flow battery. *Journal of Power Sources* **22** (1): 59-67.
- S. G. Chalk and Miller, J.F. 2006. Key challenges and recent progress in batteries, fuel cells, and hydrogen storage for clean energy systems. *Journal of Power Sources* **159** (1): 73-80.
- Sahu, S.K. 2011. Redox flow cell. US Patent. US, Deeya Energy, Inc. **7927731B2**: 1-14.
- Salman, M., Chang, M.F. and Chen, J.Y. 2005. Predictive energy management strategies for hybrid vehicles. *IEEE Vehicle Power and Propulsion Conference, VPPC 2005. VPPC'05*.
- Sanabria, L.A. and Dillon, T.S. 1998. Power system reliability assessment suitable for a deregulated system via the method of cumulants. *International Journal of Electrical Power & Energy Systems* **20** (3): 203-211.
- Scamman, D.P., Reade, G.W. and Roberts, E.P.L. 2009. Numerical modelling of a bromide-polysulphide redox flow battery: Part 1: Modelling approach and validation for a pilot-scale system. *Journal of Power Sources* **189** (2): 1220-1230.
- Shah, A.A., Al-Fetlawi, H. and Walsh, F.C. 2010. Dynamic modelling of hydrogen evolution effects in the all-vanadium redox flow battery. *Electrochimica Acta* **55** (3): 1125-1139.
- Shah, A.A., Watt-Smith, M.J. and Walsh, F.C. 2008. A dynamic performance model for redox-flow batteries involving soluble species. *Electrochimica Acta* **53** (27): 8087-8100.
- Singh, P. 1984. Application of non-aqueous solvents to batteries. *Journal of Power Sources* **11** (1-2): 135-142.
- Singh, P. and Jonshagen, B. 1991. Zinc---bromine battery for energy storage. *Journal of Power Sources* **35** (4): 405-410.
- Skyllas-Kazacos, M. 2003. Novel vanadium chloride/polyhalide redox flow battery. *Journal of Power Sources* **124**: 299-302.
- Skyllas-Kazacos, M. 2008. Recent progress with the USNW vanadium battery. Available: [http://www.arizonaenergy.org/Analysis/FuelCell/Vanadium%20Battery/recent\\_progress\\_with\\_the\\_unsw\\_va.htm](http://www.arizonaenergy.org/Analysis/FuelCell/Vanadium%20Battery/recent_progress_with_the_unsw_va.htm), (07 July 2008)
- Skyllas-Kazacos, M., Chakrabarti, M.H., Hajimolana, S.A., Mjalli, F.S. and Saleem, M. 2011. Progress in Flow Battery Research and Development. *Journal of The Electrochemical Society* **158** (8): R55-R79.
- Skyllas-Kazacos, M. and Grossmith, F. 1987. Efficient vanadium redox flow cell. *Journal of The Electrochemical Society* **134** (12): 2950-2953.
- Skyllas-Kazacos, M., Kasherman, D., Hong, D.R. and Kazacos, M. 1991. Characteristics and performance of 1 kW UNSW vanadium redox battery. *Journal of Power Sources* **35** (4): 399-404.

- Skyllas-Kazacos, M., Kazacos, G., Poon, G. and Verseema, H. 2010. Recent advances with UNSW vanadium-based redox flow batteries. *International Journal of Energy Research* **34** (2): 182-189.
- Skyllas-Kazacos, M. and Kazacos, M. 2011. State of charge monitoring methods for vanadium redox flow battery control. *Journal of Power Sources* **196** (20): 8822-8827.
- Skyllas-Kazacos, M. and Limantari, Y. 2004. Kinetics of the chemical dissolution of vanadium pentoxide in acidic bromide solutions. *Journal of Applied Electrochemistry* **34** (7): 681-685.
- Skyllas-Kazacos, M. and Menictas, C. 1997. The vanadium redox battery for emergency back-up applications. *19th International Telecommunications Energy Conference, 1997. INTELEC 97.*, : 463-471.
- Skyllas-Kazacos, M. and Robins, R.G. 1988. All vanadium redox battery. US Patent, Unisearch Limited, AUS. **4786567 (Abandoned pattern No. 849094, 07 April 1986)**: 1-16.
- Snihir, I., Rey, W., Verbitskiy, E., Belfadhel-Ayeb, A. and Notten, P.H.L. 2006. Battery open-circuit voltage estimation by a method of statistical analysis. *Journal of Power Sources* **159** (2): 1484-1487.
- Sukkar, T. and Skyllas-Kazacos, M. 2003. Water transfer behaviour across cation exchange membranes in the vanadium redox battery. *Journal of Membrane Science* **222** (1-2): 235-247.
- Sukkar, T. and Skyllas-Kazacos, M. 2004. Membrane stability studies for vanadium redox cell applications. *Journal of Applied Electrochemistry* **34** (2): 137-145.
- Sun, C., Chen, J., Zhang, H., Han, X. and Luo, Q. 2010. Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery. *Journal of Power Sources* **195** (3): 890-897.
- Swanbarton.Ltd 2004. Status of electrical energy storage systems. DTI.Technology. UK, Crown Copyright 2004. **DG/DTI/00050/00/00**.
- Tang, A., Bao, J. and Skyllas-Kazacos, M. 2011. Dynamic modelling of the effects of ion diffusion and side reactions on the capacity loss for vanadium redox flow battery. *Journal of Power Sources* **196** (24): 10737-10747.
- Tang, A., Bao, J. and Skyllas-Kazacos, M. 2012. Thermal modelling of battery configuration and self-discharge reactions in vanadium redox flow battery. *Journal of Power Sources* **216** (0): 489-501.
- Tao, H. and Fangqin, X. 2009. Investigation on manganese ( $Mn^{2+}/Mn^{3+}$ ) - vanadium ( $V^{2+}/V^{3+}$ ) redox flow battery. *Power and Energy Engineering Conference, 2009. APPEEC 2009. Asia-Pacific*: 1-4.
- Thaller, L.H. 1976. Electrically rechargeable redox flow cells. Patent, U.S. **3996064**.
- Tian, B., Yan, C.W. and Wang, F.H. 2004. Proton conducting composite membrane from Daramic/Nafion for vanadium redox flow battery. *Journal of Membrane Science* **234** (1-2): 51-54.
- Trainham, J.A. and Newman, J. 1981. A comparison between flow-through and flow-by porous electrodes for redox energy storage. *Electrochimica Acta* **26** (4): 455-469.
- Tremblay, O., Dessaint, L.-A. and Dekkiche, A.-I. 2007. A generic battery model for the dynamic simulation of hybrid electric vehicles. *IEEE Vehicle Power and Propulsion Conference, 2007. VPPC 2007.*: 284-289.

- Trinidad, P., de León, C.P. and Walsh, F.C. 2008. The use of electrolyte redox potential to monitor the Ce(IV)/Ce(III) couple. *Journal of Environmental Management* **88** (4): 1417-1425.
- V. Isastia and Meo, S. 2009. Overview on Automotive Energy Storage Systems. *International Review of Electrical Engineering (IREE)* **4** (6): 1122-1144.
- Van Mierlo, J., Van den Bossche, P. and Maggetto, G. 2004. Models of energy sources for EV and HEV: fuel cells, batteries, ultracapacitors, flywheels and engine-generators. *Journal of Power Sources* **128** (1): 76-89.
- Walsh, F.C. 1991. Electrochemical cell reactions in metal finishing. *Transactions of the Institute of Metal Finishing* **69** (pt 3): 111-116.
- Walsh, F.C. 1993. *A first course in electrochemical engineering*. Romsey: The Electrochemical Consultancy (Romsey) Ltd.
- Walsh, F.C. 2010. Electrode materials and membranes. Southampton, Southampton Electrochemistry Group.
- Walsh, F.C. 2010. Principles of redox flow batteries for large scale energy storage. Southampton, Southampton Electrochemistry Group.
- Wang, W.H. and Wang, X.D. 2007. Investigation of Ir-modified carbon felt as the positive electrode of an all-vanadium redox flow battery. *Electrochimica Acta* **52** (24): 6755-6762.
- Will, F.G. and Spacil, H.S. 1980. Performance analysis of zinc--bromine batteries in vehicle and utility applications. *Journal of Power Sources* **5** (2): 173-188.
- Williamson, S.S. and Emadi, A. 2005. Comparative assessment of hybrid electric and fuel cell vehicles based on comprehensive well-to-wheels efficiency analysis. *IEEE Transactions on Vehicular Technology* **54** (3): 856-862.
- Wu, T., Wang, M., Xiao, Q. and Wang, X. 2012. The SOC Estimation of Power Li-Ion Battery Based on ANFIS Model. *Smart Grid and Renewable Energy* **3**: 51-55.
- Yang, M.Z., Wu, H. and Selman, J.R. 1989. A model for bipolar current leakage in cell stacks with separate electrolyte loops. *Journal of Applied Electrochemistry* **19**: 247-254.
- Yang, S.-C. 1994. An approximate model for estimating the faradaic efficiency loss in zinc/bromine batteries caused by cell self-discharge. *Journal of Power Sources* **50** (3): 343-360.
- You, D., Zhang, H. and Chen, J. 2009. A simple model for the vanadium redox battery. *Electrochimica Acta* **54** (27): 6827-6836.
- Yu, D. and Yuvarajan, S. 2005. Electronic circuit model for proton exchange membrane fuel cells. *Journal of Power Sources* **142** (1-2): 238-242.
- Zhang, C.P., Liu, J.Z., Sharkh, S.M. and Zhang, C.N. 2010. Identification of dynamic model parameters for lithium-ion batteries used in hybrid electric vehicles. *International Symposium on Electric Vehicles (ISEV)*, Beijing, China: 11.
- Zhang, H. and Chow, M.Y. 2010. Comprehensive dynamic battery modeling for PHEV applications *2010 IEEE Power and Energy Society General Meeting* Minneapolis, IEEE: 1-6.
- Zhang, L., Cheng, J., Yang, Y.-s., Wen, Y.-h., Wang, X.-d. and Cao, G.-p. 2008. Study of zinc electrodes for single flow zinc/nickel battery application. *Journal of Power Sources* **179** (1): 381-387.
- Zhou, H., Zhang, H., Zhao, P. and Yi, B. 2006. A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery. *Electrochimica Acta* **51** (28): 6304-6312.

## APPENDIX - LIST OF PUBLICATIONS

Table A presents the entire articles that have been submitted or published in peer-reviewed Journals and Conferences as progressive contributions of this research work.

**Table A:** List of submitted or published in peer-reviewed Journals and Conferences for Experimental Characterisation and Modeling of a Vanadium Redox Flow Battery

No	Journals Publication Details	Impact Factor	Status	Thesis Chapter
1	<b>Mohamed, M.R.</b> , Ahmad, H. and Abu Seman, M.N. 2012. State-of-the-art of vanadium redox flow battery: A review on research prospects. <i>International Review of Electrical Engineering (IREE)</i> <b>7</b> (5): 5610-5622.	1.364	Published	Chapter 2
2	<b>Mohamed, M.R.</b> , Sharkh, S.M., Ahmad, H., Abu Seman, M.N. and Walsh, F.C. 2012. Design and development of unit cell and system for vanadium redox flow batteries (V-RFB). <i>International Journal of the Physical Sciences</i> <b>7</b> (7): 1010 - 1024.	0.540	Published	Chapter 3
3	<b>Mohamed, M.R.</b> , Ahmad, H. and Abu Seman, M.N. In Press. Estimating State-of-Charge of Vanadium Redox Flow Battery using a Divided, Open-circuit Potentiometric Cell. <i>Elektronika Ir Elektrotechnika</i> <b>19</b> (3): 37-42	0.913	Published	Chapter 4
3	<b>Mohamed, M.R.</b> , Leung, P.K., Ahmad, H., Abu Seman, M.N., <i>Renewable &amp; Sustainable Energy Reviews</i> , Submitted on 29 Oct 2012 (RSER-D-12-01127).	6.619	Under Review	Chapter 5
4	<b>Mohamed, M.R.</b> , Ahmad, H., Abu Seman, M.N., Razali, S., Najib, M.S. <i>Journal of Power Sources</i> , In Press, Accepted Manuscript, Available online 3 April 2013	4.951	Published	Chapter 6
No	Conferences Publication Details			Thesis Chapter
1	<b>Mohamed, M.R.</b> , Sharkh, S.M., Ahmad, H., Abu Seman, M.N. and Walsh, F.C., In : Malaysian Postgraduate Conference on Electrical, Electronic and Control Technology (MCEECT 2012) 16-17 February 2012, Universiti Malaysia Pahang.			Chapter 2
2	<b>Mohamed, M.R.</b> , Ahmad, H., Abu Seman, M.N. (2012) In: International Conference on Green Technology & Ecosystems for Global Sustainable Development 2012 (ICGTEC2012), 28-30			Chapter 2

May 2012, University of Tuzla, Bosnia.

- 3 **Mohamed, M.R.**, Sharkh, S.M., Walsh, F.C., in: The 5th International IEEE Vehicle Power and Propulsion Conference (VPPC'09), IEEE, Dearborn, Michigan, 2009, pp. 551-557.
-