

ELECTRODE MATERIALS FOR RECHARGEABLE LITHIUM AND SODIUM BATTERIES

A thesis presented for the award of the degree of doctor of philosophy

By

Kefei Li

B. Eng., M. Eng., M. Sci.

University of Technology, Sydney

Faculty of Science

2016

Certificate of original authorship

This thesis is the result of a research candidature conducted jointly with another University as part of a collaborative Doctoral degree. I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of student

A handwritten signature in black ink, appearing to read 'Li Kufei', written in a cursive style.

15 December 2016

Acknowledgements

I would like to express my deep appreciation to my principal supervisor Prof. Guoxiu Wang and co-supervisor Dr. Hao Liu for their persistent guidance and support throughout my study at University of Technology, Sydney.

I also owe my thanks to staff members and research students including Dr. Ronald Shimmon, Dr. Yueping Yao, Dr. Linda Xiao, Dr. Bing Sun, Dr. Xiaodan Huang, Dr. Dawei Su, Dr. Zhimin Ao, Dr. Shuangqiang Chen, Dr. Ying Wang, Dr. Anjon Kumar Mondal, Mr. Jinqiang Zhang, Mr. Xiuqiang Xie, Ms. Katja Kretschmer, Mr. Xin Guo, Mr. Weizhai Bao, Mr. Jianjun Song, Ms. Yufei Zhao and Ms. Jin Xu who have work with me during my study at University of Technology, Sydney. Those brilliant people helped me build up a friendly research environment which is essential for my research project. In addition, I would like to give special thanks to Dr. Dawei Su and Dr. Hao Liu for their assists on transmission electron microscopy analysis. Finally, I would like to give special thanks to Dr. Steve Bewlay for his efforts on the thesis proofreading.

Table of contents

List of figures and tables	i
List of abbreviations	iii
Abstract	iv
Chapter 1 Introduction	1
1.1 Research motivations	1
1.2 Objectives	2
1.3 Research methodology	3
1.4 Contributions	4
1.5 Thesis Outline	5
Chapter 2 Literature Review	6
2.1 Brief history of lithium-ion battery development	6
2.2 Intercalation cathode materials	14
2.3 Intercalation type negative materials	20
2.4 Alloy type negative electrode materials	23
2.5 Conversion type negative electrode materials	28
2.6 Key indices of electrode materials for lithium-ion batteries	32
2.7 Electrolytes for lithium-ion batteries	36
2.8 Lithium secondary batteries beyond intercalation chemistry	38
2.9 Revival of research interest in room-temperature rechargeable sodium batteries	45
Chapter 3 Research strategy and experimental design	50
3.1 Electrospinning technique for material synthesis	51
3.2 Solvothermal synthesis route	55
3.3 Material characterizations	56
3.3.1 Scanning electron microscopy	57
3.3.2 Transmission electron microscopy	60

Table of Contents

3.3.3 Powder X-ray diffraction	65
3.3.4 Thermogravimetric analysis	69
3.3.5 Raman spectroscopy	72
3.3.6 Gas adsorption surface area analysis	74
3.4 Electrochemical Characterizations	77
3.4.1 Electrode preparation and cell configurations	77
3.4.2 Cyclic voltammetry	81
3.4.3 Charge-discharge cycling test	81
3.4.4 Cell impedance	83
Chapter 4 One dimensional carbon fiber synthesis by electrospinning	86
4.1 Introduction	86
4.2 Experimental	88
4.3 Results and discussion	90
4.3.1 Solution Concentration	90
4.3.2 Applied voltage	93
4.3.3 Change of PAN fibers after thermal treatment	95
4.3.4 Galvanostatic cycle tests carbon fiber electrode	101
4.4 Conclusion	103
Chapter 5 Antimony - carbon alloy type negative electrodes	104
5.1 Introduction	104
5.2 Experimental	106
5.2.1 Material synthesis	106
5.2.2 Material characterization	108
5.2.4 Electrochemical characterization	109
5.3 Results and discussion	110
5.3.1 X-ray diffraction	110
5.3.2 Thermogravimetric analysis	112

Table of Contents

5.3.3 Raman spectroscopy	112
5.3.4 Morphological features of Sb-CF/RGO composite	114
5.3.5 Electrochemical characteristics in lithium half-cells	115
5.3.6 Electrochemical characteristics in sodium half-cells	118
5.4 Conclusion	123
Chapter 6 Application of porous carbon sheet in lithium-sulfur battery	124
6.1 Introduction.....	124
6.2 Experimental	128
6.2.1 Material synthesis	128
6.2.2 Material characterization.....	129
6.2.3 Electrochemical characterization	130
6.3 Results and Discussion.....	132
6.3.1 Morphology and composition of synthesized material	132
6.3.2 Electrochemical characteristics in lithium sulfur cells	135
6.4 Conclusions	140
Chapter 7 Antimony sulfide – graphene composite anode materials.....	141
7.1 Introduction.....	141
7.2 Experimental	143
7.2.1 Material synthesis	143
7.2.2 Material characterization.....	144
7.2.3 Electrochemical characterization	144
7.3 Results and discussion	145
7.3.1 Compositions and morphologies of synthesized materials	145
7.3.2 Electrochemical characteristics in lithium half-cells	151
7.3.3 Electrochemical characteristics in sodium half-cells	156
7.4 Conclusion	161
Chapter 8 Conclusions.....	162

Table of Contents

8.1 Conclusions	162
8.2 Future perspectives	166
Bibliography	168

List of figures and tables

Figure 2.1 Schematic view of a “rocking chair” cell configuration.	11
Figure 2.2 Schematic illustration of high voltage lithium intercalation compounds with layered, spinel, olivine and tavorite crystal structures.	16
Table 2.1 Electrochemical characteristics of the major intercalation cathode materials for lithium-ion batteries.	19
Figure 2.3 Schematic illustration of the solid-electrolyte interphase (SEI) on graphite anode in lithium-ion batteries.	21
Figure 2.4. Capacity retention rates with coulombic efficiencies of 99%, 99.6%, and 99.9% after 100 cycles of charge-discharge.	34
Figure 2.5. Average operating potentials versus volumetric capacity of selected cathode materials for intercalation type lithium or sodium secondary batteries.	48
Figure 3.1 Schematic illustration of standard material synthesis procedures involving electrospinning and post thermal treatment.	52
Figure 4.1 SEM images of electrospun polyvinyl alcohol and polyacrylonitrile fibers.	92
Figure 4.2 SEM images of polyacrylonitrile fibers at different voltages.	94
Figure 4.3 SEM images of polyvinyl alcohol and polyacrylonitrile fibers after thermal treatments.	97
Figure 4.4 XRD patterns and Raman spectra of PAN-derived carbon fibers.	99
Figure 4.5 Nitrogen adsorption-desorption isotherms and the BET plot from PAN-derived carbon fibers.	100
Figure 4.6 Galvanostatic profiles of PAN-derived carbon fibers electrode in lithium and sodium cells.	102
Figure 5.1 XRD patterns of Sb-CF/RGO composite after hydrogen reduction at 600°C and pyrolysis in air at 600°C	111
Figure 5.2 Thermogravimetric curve and Raman spectra of Sb-CF/RGO composite.	113
Figure 5.3 SEM and TEM images of Sb-CF/RGO composite.	115
Figure 5.4 Electrochemical characterization results for lithium cells.	116
Figure 5.5 Electrochemical characterization results for sodium cells.	120
Figure 6.1 The image of catholyte solution.	128

List of figures and tables

Figure 6.2 Schematic illustration of components in the assembled Li-S coin cells.	130
Figure 6.3 SEM images of PAN fibers and carbon fiber electrodes.	132
Figure 6.4 XRD pattern and Raman spectrum of PAN derived carbon fibers.	134
Figure 6.5 Electrochemical characterization results for lithium-sulfur cells.	136
Figure 7.1 XRD patterns of synthesized GO and $\text{Sb}_2\text{S}_3@\text{RGO}$ composite.	145
Figure 7.2 SEM images and TEM images of GO, $\text{Sb}_2\text{S}_3@\text{GO}$, $\text{Sb}_2\text{S}_3@\text{RGO}$ composite.	147
Figure 7.3 Thermogravimetric curves and Raman spectra of $\text{Sb}_2\text{S}_3@\text{GO}$ and $\text{Sb}_2\text{S}_3@\text{RGO}$ composites.	134
Figure 7.4 Nitrogen adsorption-desorption isotherms and the BET plot from $\text{Sb}_2\text{S}_3@\text{RGO}$ composite.	150
Figure 7.5 Cyclic voltammograms of $\text{Sb}_2\text{S}_3@\text{RGO}$ composite in lithium cells.	152
Figure 7.6 Electrochemical characterization results for lithium cells.	155
Figure 7.7 Cyclic voltammograms of $\text{Sb}_2\text{S}_3@\text{RGO}$ composite in sodium cells.	157
Figure 7.8 Electrochemical characterization results for sodium cells.	159

List of abbreviations

Abbreviation	Full name
a.u.	arbitrary unit
BET	Brunauer, Emmett and Teller
CF	carbon fiber
CMC	carboxymethyl cellulose
DMC	dimethyl carbonate
DME	1,2-dimethoxyethane
DMF	N,N-Dimethylformamide
DOL	1,3-dioxolane
EIS	electrochemical impedance spectroscopy
EC	ethylene carbonate
FEC	fluoroethylene carbonate
FESEM	field emission scanning electron microscopy
GO	graphene oxide
JCPDS	Joint Committee On Powder Diffraction Standards
NMP	1-methyl-2-pyrrolidinone
PAN	polyacrylonitrile
PVA	polyvinyl alcohol
PVDF	polyvinylidene fluoride
RGO	reduced graphene oxide
SEI	solid electrolyte interphase
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
USABC	United States Advanced Battery Consortium
VC	vinylene carbonate
XRD	X-ray diffraction

Abstract

The development of lithium-ion batteries with higher power, higher energy, longer cycle life and lower cost is the focus of battery research at present, and the situation will remain the same in the foreseeable future. The research of rechargeable batteries may lead to better understanding on interfacial chemistries, the discovery of new battery chemistries and ultimately more powerful energy storage systems. This project aims at the application of carbon based composite materials as electrode materials in rechargeable lithium or sodium batteries and potential improvement in the performance of batteries via novel design of electrode materials. The electrospinning technique, microwave-assisted solvothermal synthesis process and inert gas thermal treatment have been utilized for material preparations. A series of experiments were designed to screen the most important factors that dominates the structural features of electrospun polymer fibers. One-dimensional carbon fibers and composite materials with desired structural features have been synthesized. The carbon fiber converted from electrospun polyacrylonitrile membranes are used as negative electrode materials in lithium and sodium cells, which showed stable reversible capacities of 118 mAh/g and 84 mAh/g for lithium and sodium, respectively. The antimony-carbon fiber composite materials were synthesized as alloy type negative electrodes for lithium-ion and sodium-ion batteries. The obtained material exhibited high reversible capacities of 562 mAh/g and 371 mAh/g in lithium and sodium cells, respectively. Due to the homogeneous distribution of nanosized antimony particles within the interconnected carbon fiber networks, this materials also exhibited good rate capabilities in sodium cells as it cycled at high current rates up to 1000 mA/g without severe capacity fading. The binder-free carbon electrode was used for the synthesis of composite sulfur cathode in a novel

Abstract

lithium-sulfur cell design, the resulted lithium-sulfur battery demonstrated a high reversible capacity of 1101 mAh/g at a high charge-discharge current of 1000 mA/g. In addition, a two dimensional graphene-based composite material containing antimony sulfide nanoparticles synthesized via microwave-assisted solvothermal approach was also investigated as potential negative electrode materials for rechargeable lithium or sodium batteries. High reversible capacities of 595 mAh/g in lithium cells and 560 mAh/g in sodium cells from this electrode materials were achieved. The material design with graphene nanosheets as the conductive substrate was proved effective for high rate charge-discharge as this composite material showed good rate capabilities under various current rates up to 1000 mA/g.