Design of Nanostructured Materials for Advanced Lithium Ion Batteries

A thesis submitted in fulfilment of the requirements

for the award of the degree

Doctor of Philosophy

from

University of Technology, Sydney

by

Ying Wang (B.Eng., M.Eng.)

Principal supervisor: Guoxiu Wang
Co-supervisor: Alison Ung
Centre for Clean Energy Technology
Faculty of Science
2012

DECLARATION

I, Ying Wang, declare that the work presented in this thesis is original unless otherwise referenced or acknowledged and has not been submitted for qualifications at any other academic institution. This thesis is in fulfilment of the requirements for the award of Doctor of Philosophy in the Centre for Clean Energy Technology, Faculty of Science, University of Technology, Sydney.

Ying Wang

Sydney, Australia

December, 2012

DEDICATION

This dissertation is dedicated to my parents and my husband. Thank you for all of your love and support.

(Translation from English to Chinese)

致谢

本论文献给我的父亲，母亲和我的丈夫。感谢你们给予我的爱与支持。这份爱我将铭记于心。

ACKNOWLEDGEMENTS

This dissertation is based on the results of my PhD project during the past four years, which were conducted in the Institute for Superconducting and Electronic Materials (ISEM) at the University of Wollongong (UOW) and the Centre for Clean Energy Technology, School of Chemistry and Forensic Science, Faculty of Science, University of Technology, Sydney (UTS). I would like to acknowledge all the staff and students in both organizations for sharing such an enjoyable and unforgettable period with me.

I would like express my deepest gratitude to my principle supervisor, Prof. Guoxiu Wang and co-supervisor, Assoc. Prof. Alison Ung, for their invaluable advice and supervision throughout this research work. Their innovative research ideas and inspiration enlightened and encouraged me during my PhD study.

I appreciate the technical and administrative support and assistance I received from Dr Ronald Shimmon, Dr Linda Xiao, Dr Jane Yao, Mrs Rochelle Seneviratne, Mrs Era Koirala, and staff in MAU. They have provided me with tremendous help.

I also would like to thank my colleagues Dr Hao Liu, Dr Bing Sun, Mr Bei Wang, Mrs Huimin Wu, Mr Dawei Su, Mr Kefei Li, Mr Shuangqiang Chen, Mr Anjon K. Mondal, Mr Jinqiang Zhang and Mr Yiying Wei for their encouragement and brilliant ideas during the period of this research.

Finally, I would like to express my sincere gratitude to my husband, Mr Zhou Tan, and my parents. Without their encouragement and support, it would have been impossible for me to complete the research. Their love is the mental strength that supported me while achieving my study abroad and it will hold a special place in my heart forever.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Among currently available rechargeable battery systems, Lithium-ion (Li-ion) batteries feature high energy density and operating voltage, and long cycle life. Since the 1990s, the development of Li-ion battery technology has been ongoing, owing to the ever-growing demand in portable electronics, electric vehicles (EV), hybrid electric vehicles (HEV) and stationary energy storage devices. Although the improvements in battery technology rely on achievements in electrode materials, separators, electrolytes and external management systems, electrode materials play the most important role as they control the electrochemical reaction and determine the properties of a battery system. Based on extensive literature reviews, the electrochemical performances of electrode materials are size- and morphology-dependent. In this study, several nanostructured materials with specifically designed morphologies were synthesized, characterized, and used as electrode materials for Li-ion battery applications.

First, spherical over-lithiated transition metal oxide was chosen as the high capacity cathode material. Through a modified co-precipitation method, this material exhibited relatively low irreversible capacity loss, high specific capacity, satisfactory cyclability and rate capability. These are suitable for large-scale application.

Secondly, two different carbon coating techniques were designed and applied in the synthesis of $LiFePO_4$ and Li_2FeSiO_4 cathode materials through *in-situ* polymerization and modified ball-milling methods respectively. Carbon-coated $LiFePO_4$ consists of primary particles (40-50 nm) and agglomerated secondary particles (100-110 nm). Each particle is evenly coated with an amorphous carbon layer, which has a thickness around 3-5 nm. Meanwhile, Li_2FeSiO_4/C nanoparticles

were coated with an amorphous carbon layer, owing to the carbonization of glycolic acid. Both materials exhibited much higher specific capacity, better capacity retention, and better rate capability than their pristine counterparts.

After that, a hydrothermal method was chosen and applied to synthesize hollow-structured $CoFe_2O_4$ nanospheres and $CoFe_2O_4$/mutiwalled carbon nanotubes (MWCNTs) hybrid material. The significant improvements in the electrochemical performances of these two materials, including high capacities, excellent capacity retentions and satisfactory rate capabilities could benefit from their unique nano architectures. $CoFe_2O_4$ demonstrated uniform hollow nanosphere architecture, with an outer diameter of 200-300 nm and the wall thickness of about 100 nm. Hybrid material resembled wintersweet flower “buds on branches”, in which $CoFe_2O_4$ nanoclusters, consisting of nanocrystals with a size of 5-10 nm, were anchored along carbon nanotubes. Both materials could be a promising high capacity anode material for lithium ion batteries.