

Design of Nanostructured Materials for Advanced Lithium Ion Batteries

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by

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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。

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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 $\text{Li}_2\text{FeSiO}_4$ 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, $\text{Li}_2\text{FeSiO}_4/\text{C}$ 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 /multiwalled 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.