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Investigation on advanced active materials for lithium-ion batteries

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Investigation on Advanced Active Materials for Lithium-ion Batteries

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Doctor of Philosophy

from

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by

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Institute for Superconducting & Electronic Materials, Faculty of Engineering

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Dedicated to

My Parents, Shaoying Diao and Shanliang Chen

My husband, Jiangfeng Wu

My lovely Son, David Sichen Wu

Candidate's Certificate

I hereby declare that the research work presented in this thesis is original and was performed by the candidate in the laboratories in Institute for Superconducting & Electronic Materials and in the Faculty of Engineering at the University of Wollongong, New South Wales, Australia. This thesis has not been submitted for a degree to any other University or Institution.

Yao Chen

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CONTENTS

ABSTRACT

The objectives of the Ph.D project were: (1) to prepare and study advanced active materials with high capacity and long cycle life for rechargeable lithium ion batteries; (2) to understand the relationship between the structural, physical, and electrochemical properties of the electrode materials; (3) to identify the main parameters which are responsible for the differences in electrochemical behaviour. In this study, several methods have been used to improve the performance of electrodes, including element substitution, synthesis methods, carbon-enriching, etc.

A starting point for the study was a survey of the literature pertaining to the cathode and anode materials for lithium ion batteries. Many different electrode materials are described. The thesis provides a detailed description of the status of current research and development in electrode materials for lithium ion batteries.

A variety of cathode materials have been investigated. Some of them have shown good electrochemical performance when used in lithium ion cells. Electroactive $LiCo_xMn_yNi_{1-x-y}O_2$ powders were prepared from lithium compounds and $Co_xMn_yNi_{1-x-y}(OH)_2$ precursor by heating at 850-900 °C.

High density spherical $LiCo_{0.25}Ni_{0.75}O_2$ compounds were synthesized from lithium compounds and spherical $Co_{0.25}Ni_{0.75}$ $(OH)_2$ precursor by heating in oxygen at 750°C and 800°C for 12 hrs. The structural characteristics of the compounds were determined by x-ray diffraction. The best sintering temperature was found to be 800 °C, in terms of

stabilising the layered structure and improving the cycle life. It was found that the spherical $LiCo_{0.25}Ni_{0.75}O_2$ compounds sintered at 800 °C have a highly ordered layered structure with reduced cation mixing.

Carbon-enriched nanocrystalline $LiFePO_4$ compounds were prepared by the sol-gel method and the R/F carbon gel method, respectively. A layer of carbon was laid down as a coating on the surface of the lithium crystals, which dramatically enhanced the electronic conductivity of the $LiFePO_4$ compounds. A high capacity of 160 mAh/g at the C/5 rate has been demonstrated for the $LiFePO_4$ electrode. These electrodes also exhibited good cyclability at different charge/discharge rates.

A variety of anode materials have also been investigated to search out alternative anode materials to replace graphite for lithium ion batteries. Five types of cobalt oxides were prepared by high temperature decomposition, low temperature decomposition, high energy ball-milling, and the chemical decomposition of cobalt octacarbonyl in toluene, respectively. The LT-Co_3O_4, the CoO, and the nanosize Co_3O_4 powders prepared by decomposing organo-cobalt compounds at low temperature show good capacity retention on charge/discharge cycling, which is promising for their use as anode materials in Li-ion cells. It was found that the electrochemical properties of cobalt oxides are sensitive to the crystallinity, morphology, and particle size.

Nanosize Ag powders were prepared via a reverse micelle approach. The size of Ag nanoparticles can be influenced by the concentration of the reduction agent. In addition, SnO_2 nanopowders were synthesized by using the same method. 1D structured SnO_2

nanorods were observed in the SnO_2 nanopowders. The SnO_2 nanopowder electrodes show high electrochemical reactivity toward lithium in Li-ion cells.

The synthesized materials were characterized by x-ray diffraction, SEM and TEM, through which the phase composition and microstructure were observed. The capacity and cycle life of the cathode materials were obtained from charge/discharge cycling tests. The kinetic characteristics and kinetic parameters of lithium ion insertion and extraction within the electrode materials were determined by a.c. impedance spectroscopy and cyclic voltammograms.

In summary, the investigations in this project have produced several types of electrode materials with high capacity and long cycle life. In particular, the study focuses on the preparation of cathode materials with high density and ordered structure, and anode materials with ultrafine particles. Analysis of the electrochemical processes in lithium ion cells was conducted by various techniques. All of these studies provide a fundamental basis for the development of high energy density electrode materials.