Synthesis and characterization of nanostructured electrode materials for rechargeable lithium ion batteries

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Synthesis and Characterization of Nanostructured Electrode Materials for Rechargeable Lithium Ion Batteries

A thesis submitted in fulfillment of the requirements

for the award of

DOCTOR OF PHILOSOPHY

By

MIN SIK PARK

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Declaration

I, Min-Sik Park declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, in the Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.

Wollongong, Australia

March 2008
“Anybody who has been seriously engaged in scientific work of any kind realizes that over the entrance to the temple of science are written the words: ‘You must have faith.’ It is a quality which the scientist cannot dispense with.”

-Max Planck (The Nobel Prize in Physics, 1918)-
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Abstract

State-of-the-art rechargeable lithium-ion battery technology has now paved the way for advanced energy storage systems to take their place in a variety of portable electronics. High cell voltage, good cycle life, and an attractive combination of energy and power generation are on the verge of being guaranteed for high-power and large-scale applications, such as plug-in hybrid vehicles. This investigation examines the circumstances attending the development of the rechargeable lithium-ion battery, to seek a better understanding of the factors affecting its electrochemical performance. The major objective of this work is to determine the advantages and drawbacks of tin dioxide (SnO$_2$) nanostructured materials as alternative anode materials and to suggest promising structural modifications in order to improve their electrochemical properties. Another important objective is to identify the correlation between electrochemical performance and particle size minimization in the lithium iron phosphate (LiFePO$_4$) system, a promising cathode material, and to give further evidence supporting the incomplete room-temperature reaction mechanism.

The selection and assembly of nanostructured materials have been considered as central issues in the development of alternative anode materials that possess higher capacity and better cyclic retention compared to commercial graphite. SnO$_2$ has shown high capacity and a relatively low reaction potential with Li$^+$, and is thus under consideration as a possible candidate for high-power and high-energy applications. We have synthesized various types of SnO$_2$ nanostructured materials, such as nanopowders, nanowires, and nanotubes in this work, and their electrochemical properties have been carefully compared in order to demonstrate the effects of their morphological differences on the electrochemical performance, based on
thermodynamic and kinetic considerations. By incorporating structural modifications into the SnO$_2$ nanostructured materials, we have formed Carbon encapsulated SnO$_2$ nanopowders and nanowires by simple decomposition of malic acid (C$_4$H$_6$O$_5$) at low temperature, which effectively improved specific capacity and cyclic performance. Combining surfactant mediated synthesis and the sol–gel vacuum suction method, SnO$_2$–mesoporous organo-silica nano-array (MOSN) nanocomposites were prepared for controlling the large volume variation of SnO$_2$ during cycling, where the MOSN could act as a mechanical buffer, resulting in a strong enhancement of cyclic retention.

On the other hand, the reaction mechanism and phase transition of LiFePO$_4$ at room temperature have not been fully understood yet. In pursuit of extending our understanding, we have prepared LiFePO$_4$/C nanocomposites with different particle sizes and characterized their fundamental crystal structure, which is directly related to the electrochemical behavior. Considering the fact that the room temperature phase diagram is essential to understand the facile electrode reaction of Li$_x$FePO$_4$ (0 < $x$ < 1), here, we have suggested experimental evidence for isolation of an intermediate solid solution phase at around $x = 0.93$ at room temperature, which strongly supports the incomplete miscibility gap model. More interestingly, the impacts of air exposure on the LiFePO$_4$/C nanocomposites have been systematically investigated as a function of temperature. We found that Li$^+$ could be spontaneously extracted from the host structure, even at room temperature under air atmosphere. This finding also can explain the room temperature phase transition of LiFePO$_4$ and provide the reason for the undesirable Li$^+$ loss that is induced by external factors at room temperature.
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