SYNTHESE, CHARACTERIZATION AND IMPROVEMENT OF Li-EXCESS SPINEL AND LAYERED Mn-BASED CATHODE MATERIALS FOR LITHIUM ION BATTERIES

XI LIUJIANG

DOCTOR OF PHILOSOPHY
CITY UNIVERSITY OF HONG KONG
AUGUST 2013
Synthesis, Characterization and Improvement of Li-excess Spinel and Layered Mn-based Cathode Materials for Lithium Ion Batteries

Submitted to
Department of Physics and Materials Science
in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

by

XI Liujiang

August 2013
二零一三年八月
Abstract

Rechargeable lithium ion batteries (LIBs) are among the most promising energy storage devices for electric vehicles (EV) and hybrid electric vehicles (HEV) due to their higher energy density, lower cost and longer cycling lifespan in comparison with other secondary battery system. However, their wide application in EV or HEV has been largely hindered due to low power, insufficient specific energy and extravagant price. To solve these problems, the development of cathode material with high rate capability and energy density is one of the key factors for LIBs. This dissertation develops Li-excess spinel LiMn$_2$O$_4$ porous spheres with high rate capability and Li-excess layered Li$_2$MnO$_3$.3LiNi$_{0.5-x}$Mn$_{0.5-x}$Co$_{2x}$O$_2$ spheres with high energy density to promote the application of LIBs in EV or HEV to some extent.

Li-excess spinel LiMn$_2$O$_4$ cathode material with novel porous spherical morphology exhibiting excellent electrochemical performance was successfully prepared by using α-MnO$_2$ urchin-like structure as a self-sacrificial template. This cathode material possessed outstanding high rate capability and extremely high cycling stability at room temperature as well as elevated temperature. When tested at 10 C and 20 C rates, the first discharge capacities were up to 93.7 and 76.0 mAh·g$^{-1}$. After 1000 cycles, the corresponding retention rates of capacities were more than 71% and 62% at room temperature. When cycled at 60 °C and 10 C rate, the first discharge capacity was 61.1 mAh·g$^{-1}$ between 3–4.5 V. After tested for 250 cycles at 60 °C and 10 C rate, the retention rate of capacity was still over 76%. This makes the present LiMn$_2$O$_4$ cathode a promising candidate for high rate capability LIBs, which can greatly reduce the charge time and improve the power.
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Furthermore, high rate capability LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_{12}$ full cells have been made using Li-excess spinel LiMn$_2$O$_4$ porous spheres as the positive electrode and Li$_4$Ti$_5$O$_{12}$ nanorods as the negative electrode, which displayed superior cycling stability at high rate. The discharge capacity and the mass energy density sequentially reached 40 mAh·g$^{-1}$ and 86.4 Wh·kg$^{-1}$ at 10 C rate, while the capacity retention was about 60% after 1000 cycles, suggesting that the LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_{12}$ full cells as promising candidates for the power of HEV.

Spherical Li-excess layered Li$_2$MnO$_3$·3LiNi$_{0.5-x}$Mn$_{0.5-x}$Co$_{2x}$O$_2$ (x=0, 0.05, 0.1, 0.165) cathode materials with Mn-rich core were successfully synthesized for LIBs using a simple two-step precipitation calcination method. The charge/discharge evolution revealed that the capacity was markedly improved by adding Co. The activation of as-prepared products containing Co element became easier and can be accomplished completely when charged to 4.6 V at the 0.025 C rate in the initial cycle. Better electrochemical performances were obtained for samples with x=0.05 and 0.1. The corresponding initial discharge capacities were up to 281 and 285 mAh·g$^{-1}$ at 0.025 C between 2–4.6 V at room temperature. After 250 cycles at 0.5 C, the respective capacity retentions of them were 71.2% and 70.4%, which were higher than the sample with uniformly distributed Mn elecment delivering capacity retention of 62.9%, revealing better cycling stability. Moreover, the samples were investigated by electrochemical impedance spectroscopy (EIS) at room and elevated temperature, revealing that the key factor affecting electrochemical performance might be the charge transfer resistance of the particles.

The electrochemical performance of Li-excess layered Li$_2$MnO$_3$·3LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ cathode material has been improved significantly by surface modification with Eu$_2$O$_3$, Bi$_2$O$_3$, Al$_2$O$_3$ and CuO. After modification by Al$_2$O$_3$, the initial coulombic
efficiency was improved from 84.7% to 87.1%, and the capacity retention was raised from 43.5% to 86.3% after 300 cycles at 0.5 C rate. After modification by Eu$_2$O$_3$, the rate capability of pristine Li$_2$MnO$_3$·3LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ material was enhanced. Moreover, the CuO modified Li$_2$MnO$_3$·3LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ material was further treated by hydrazine hydrate water solution, and the electrochemical performance data revealed that the rate capability and cycling stability can be further improved, delivering the capacity retention about 96.8% after 300 cycles when treated by hydrazine hydrate water solution.
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