Effects of Nano-Crystalline ZnO Coating on Electrochemical Performance of LiCoO₂
cycled to 4.5 V

Ting Fang,(1) Jenq-Gong Duh,(1)* Su-Yueh Tsai,(2)
(1) Department of Material Science and Engineering
National Tsing Hua University
Hsinchu, Taiwan 300, R.O.C.
(2) Instrument Center
National Tsing Hua University
Hsinchu, Taiwan 300, R.O.C.

Serious capacity fading is the main limitation for LiCoO₂ in battery applied at high upper cut-off voltage. It may be caused by several factors, such as structural instability, and impedance growth during cycling. Recently, it is discovered that to improve the capacity retention of cells, coating metal oxide on the LiCoO₂ surfaces is a more effective way than doping metal ion into the LiCoO₂ crystals. Even though surface modification is verified to be beneficial to enhance cycleability of LiCoO₂, the role of metal-oxide films played during cycling is not yet understood. In this work, Zn²⁺ ions were uniformly coated on commercial LiCoO₂ particles by a chemical method and then calcined to form ZnO crystallites. The morphology of modified LiCoO₂ powders is shown in Fig. 1. From the TEM images and SAD patterns, it was confirmed that during heat treatment, deposited Zn²⁺ ions not only oxidized, but a part of them would diffuse into the surface region of LiCoO₂ crystals to form Li-Co-Zn-O solid solution. The X-ray diffraction pattern shown in Fig. 2 indicates that ZnO-coated samples maintained the hexagonal LiCoO₂ structure. To investigate the effects of ZnO on cycling behavior of LiCoO₂, as-coated powders were calcined at different temperature to modify the fraction of diffused Zn²⁺ ions. Fig. 3 confirms that the capacity retention of LiCoO₂ is significantly enhanced by surface modification with ZnO. Although it was reported that ZnO can react with HF to prevent the transition metal ions from dissolving into the electrolyte, this is not the major cause for the improvement, since the best electrochemical performance is corresponding to an optimal proportion of ZnO to Li-Co-Zn-O solid solution, rather than the most amount of ZnO. In addition, detailed microstructural evaluation and IR spectra of bare and ZnO-coated LiCoO₂ after testing for 30 cycles are discussed to provide alternative evidences for the role of ZnO played in the Li-ion battery modification.

*Corresponding author
Telephone: 886-3-5712686
Fax: 886-3-5712686
E-mail:jgd@mx.nthu.edu.tw