

**Effects of Nano-Crystalline ZnO Coating on Electrochemical Performance of LiCoO<sub>2</sub> cycled to 4.5 V**

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Serious capacity fading is the main limitation for LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub> surfaces is a more effective way than doping metal ion into the LiCoO<sub>2</sub> crystals. Even though surface modification is verified to be beneficial to enhance cycleability of LiCoO<sub>2</sub>, the role of metal-oxide films played during cycling is not yet understood. In this work, Zn<sup>2+</sup> ions were uniformly coated on commercial LiCoO<sub>2</sub> particles by a chemical method and then calcined to form ZnO crystallites. The morphology of modified LiCoO<sub>2</sub> powders is shown in Fig. 1. From the TEM images and SAD patterns, it was confirmed that during heat treatment, deposited Zn<sup>2+</sup> ions not only oxidized, but a part of them would diffuse into the surface region of LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub> structure. To investigate the effects of ZnO on cycling behavior of LiCoO<sub>2</sub>, as-coated powders were calcined at different temperature to modify the fraction of diffused Zn<sup>2+</sup> ions. Fig. 3 confirms that the capacity retention of LiCoO<sub>2</sub> 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 LiCoO<sub>2</sub> after testing for 30 cycles are discussed to provide alternative evidences for the role of ZnO played in the Li-ion battery modification.

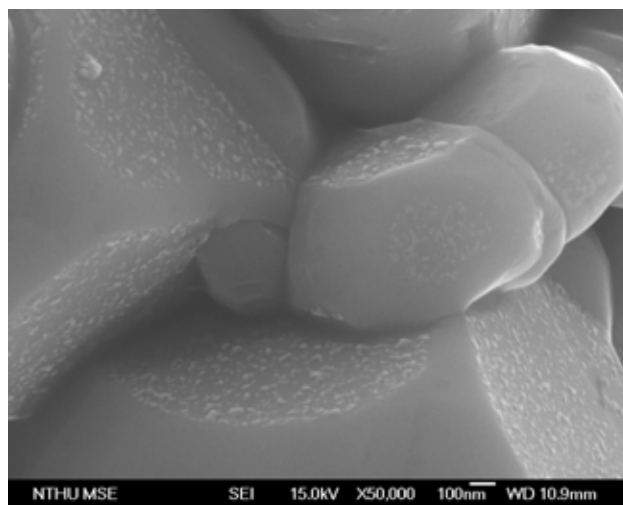


Fig. 1. FE-SEM image of ZnO-coated LiCoO<sub>2</sub> powders.

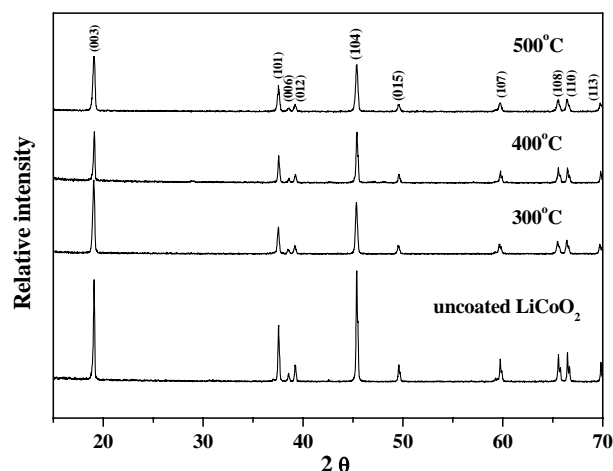


Fig. 2. XRD patterns of bare and ZnO-coated LiCoO<sub>2</sub> powders calcined at various temperatures.

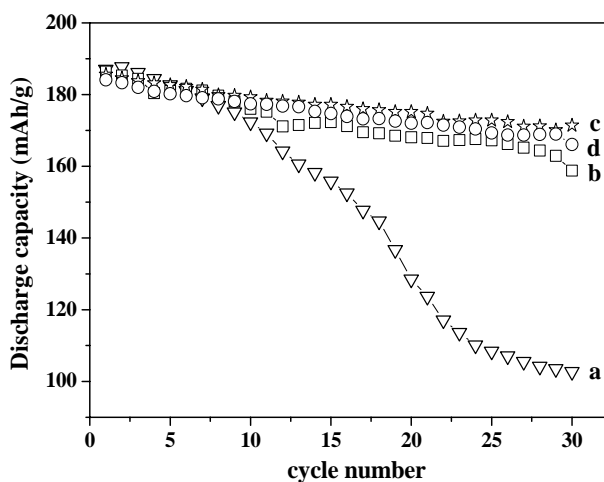


Fig. 3. Cycling behavior of LiCoO<sub>2</sub> powders (a) bare, and ZnO-coated calcined at (b) 300 °C, (c) 400 °C, and (d) 500 °C (scan rate: 0.1C at the 1st cycle and 0.2C after the 2nd cycle, cut-off voltage: 3.0V-4.5V).

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