

# A Comparison Study of Structural Changes During High-voltage Cycling Between Pristine and Al<sub>2</sub>O<sub>3</sub> Coated LiCoO<sub>2</sub>

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## Introduction

LiCoO<sub>2</sub> is the most widely used cathode material for commercial lithium ion batteries because of its high capacity, low self-discharge and excellent cycle life. When a Li/Li<sub>1-x</sub>CoO<sub>2</sub> cell is cycled within limited composition range (0 < x < 0.5, charge voltage limit below 4.2 V), LiCoO<sub>2</sub> shows reasonably good capacity retention. However, if the charge limit is raised above 4.2 V, its capacity fades rapidly [1]. If this capacity fading (together with the thermal stability problem) at higher voltage can be solved, more potential capacity will be utilized for LiCoO<sub>2</sub> type materials. Among the efforts to improve the electrochemical performance of LiCoO<sub>2</sub> at high voltage, one is to modify the cathode surface by coating LiCoO<sub>2</sub> with various metal oxides (such as LiMn<sub>2</sub>O<sub>4</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> [2,3], MgO, and ZrO<sub>2</sub> etc.). As one example, our recent study [3] shows that Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub> exhibits excellent capacity retention even when the material was charged to a voltage as high as 4.5V. Although various types of coatings have demonstrated the significant improvements in capacity retention, the mechanism of capacity fading at high voltage and the effects of surface coating is far from clear.

In this study, the *in situ* XRD data was collected on both coated and uncoated LiCoO<sub>2</sub> multiply cycled in the voltage range between 3 and 4.8 V. A 4.8 V high voltage limit was chosen for accelerating the structural damage of the uncoated sample. Clear differences in structural changes between the coated and uncoated LiCoO<sub>2</sub> cathode materials were observed. The mechanism of capacity fading of uncoated LiCoO<sub>2</sub> due to high voltage cycling has been proposed. These results will help us to understand how does the Al<sub>2</sub>O<sub>3</sub> surface coating improve the capacity retention and may shine some light on the effects of other metal oxide coatings such as ZrO<sub>2</sub> and TiO<sub>2</sub> coatings.

## Experimental

The LiCoO<sub>2</sub> used as starting material and reference samples were purchased from Nippon Chemical Industry. The detailed procedure of Al<sub>2</sub>O<sub>3</sub> coating on LiCoO<sub>2</sub> has been described in our previous work [3]. *In situ* XRD spectra were collected on beam line X18A (using  $\lambda=1.195$  Å wavelength) at the National Synchrotron Light Source (NSLS) located at Brookhaven National Lab. The step size of 2 $\theta$  scan was 0.02 degrees in the regions with Bragg reflections and 0.05 degrees in the regions without reflections. The XRD spectra were collected in transmission mode.

## Results and Discussion

Electrochemical performances and structural evolution of the modified cathode material were characterized and compared with that of pristine LiCoO<sub>2</sub>. A specific capacity of 190mAh/g was

obtained in Li/(Al<sub>2</sub>O<sub>3</sub>-coated LiCoO<sub>2</sub>) half-cells when charged to 4.5 V. The relationship between the structural evolution and the electrochemical performances in the overcharged state was investigated using *in situ* synchrotron X-ray diffraction. After charging the half-cell using uncoated LiCoO<sub>2</sub> as a cathode, the range of variation the “c” axis in hexagonal structure is severely reduced during the subsequent cycles. This reduction in “c” variation range is concurrently related to the capacity fading. In contrast, the variation range of “c” is preserved in the Al<sub>2</sub>O<sub>3</sub> coated cathodes, and so is capacity. Based on these results, a new capacity fading mechanism of LiCoO<sub>2</sub> type cathode materials after overcharge is proposed.

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