



## Suppression of Cobalt Dissolution from the LiCoO<sub>2</sub> Cathodes with Various Metal-Oxide Coatings

Yong Jeong Kim,<sup>a</sup> Jaephil Cho,<sup>b,\*</sup> Tae-Joon Kim,<sup>a</sup> and Byungwoo Park<sup>a,\*</sup>

<sup>a</sup>School of Materials Science and Engineering and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Korea

<sup>b</sup>Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

ZrO<sub>2</sub>-coated LiCoO<sub>2</sub> showed negligible capacity loss up to 70 cycles at the cutoff voltage of 4.4 V, while bare LiCoO<sub>2</sub> exhibited ~60% of its original capacity after only 30 cycles. The improved electrochemical behavior was caused by the suppression of cobalt dissolution by nanoscale metal-oxide coating. The amount of cobalt dissolution in the electrolyte from the charged LiCoO<sub>2</sub> held at 25 and 90°C, respectively, correlates well with the capacity retention, among coatings of various metal oxides. The trend of the open-circuit voltage reduction is again well correlated with both the cobalt dissolution and capacity retention.  
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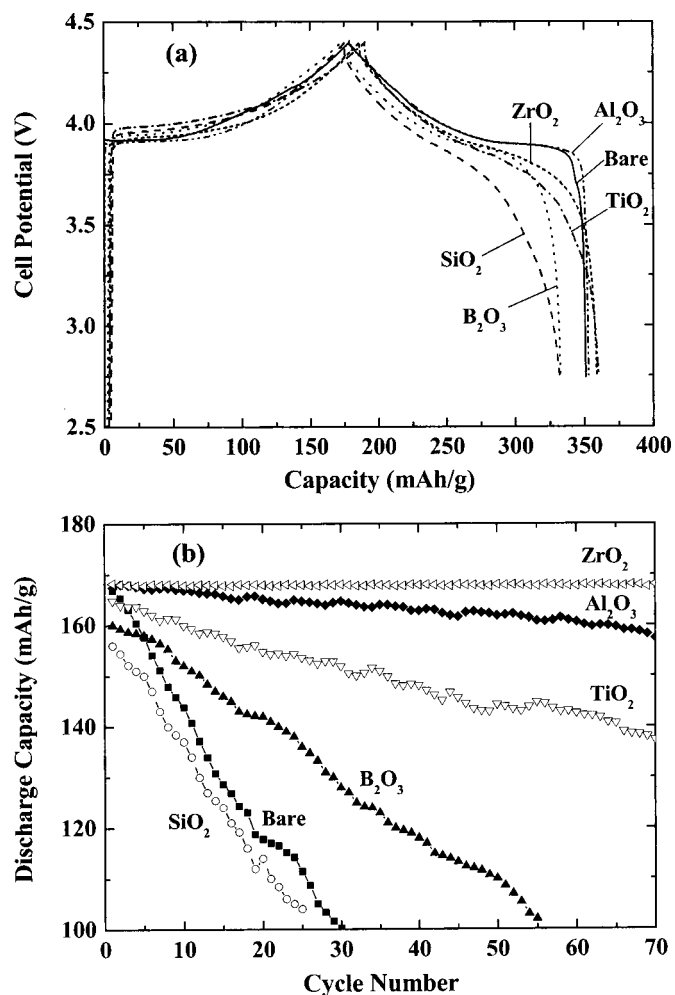
Commercial rechargeable lithium-ion batteries use LiCoO<sub>2</sub> cathodes extensively due to its high energy density and good cycling-life performance. However, even though the theoretical capacity is 274 mAh/g, only ~140 mAh/g of its capacity is used in practical cells. This capacity corresponds to the range  $0 < x < 0.5$  in Li<sub>1-x</sub>CoO<sub>2</sub>, with a cutoff voltage of approximately 4.2 V (with respect to a Li metal). To access more than 50% of its theoretical capacity, one must charge the Li<sub>1-x</sub>CoO<sub>2</sub> to above 4.2 V. However, cycling above 4.2 V leads to a dramatic deterioration in capacity retention, which is related to structural changes in the unit-cell volume,<sup>1-7</sup> and an increase in cobalt dissolution into the electrolyte.<sup>8</sup>

To improve the electrochemical performance of LiCoO<sub>2</sub> above 4.2 V, an innovative approach has been reported.<sup>5-7,9-19</sup> Recent reports by Cho *et al.* on the nanoscale coating of cathode materials with metal oxides (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, etc.) have shown that a surface coating is an effective approach for improving the electrochemical performances, by suppressing lattice-constant changes during the first charge.<sup>5-7</sup> However, Chen and Dahn reported that a ZrO<sub>2</sub> coating on the powder has no effect on the lattice-constant suppression, even though the cycling behavior is improved after coating.<sup>11</sup> This discrepancy may be due to the difference in the coating precursors. The coating solution used by Dahn's group was a zirconium-oxide polymeric precursor or an aqueous solution of ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O. In the thin-film geometry, the variation of lattice constants of LiCoO<sub>2</sub> thin films depends on the conditions of sputtering deposition, substrate, annealing, etc.<sup>18,20</sup> In this paper, with nanoscale coating of various metal oxides, the correlation between the electrochemical properties and cobalt dissolution is reported.

### Experimental

A sol-gel coating of metal oxides, which have a wide range of fracture toughness (ZrO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub> > B<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>),<sup>21-23</sup> were used on the LiCoO<sub>2</sub> particle surfaces. Metal ethylhexanate-diisopropoxide [M(OOC<sub>8</sub>H<sub>15</sub>)(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>] was dissolved in 2-propanol. The LiCoO<sub>2</sub> powder (with an average particle size of ~10 μm) was then mixed with the coating solution (such that the amount of metal-oxide precursor corresponded to 5, 10, and 20 wt % of the LiCoO<sub>2</sub> powders used), and annealed at 400°C for 10 h. Electron microscopy confirmed that the metal-oxide coating was continuous.<sup>7,17-19</sup> To test the cycle-life performance of each cathode material, a slurry was prepared by mixing the cathode materials, super P carbon black, and a poly(vinylidene fluoride) (PVDF) binder with a weight ratio of 92:4:4 in *N*-methyl-2-pyrrolidone (NMP). A coin-type half cell (2016-size) contained a test cathode, a lithium-metal counter-and-reference electrode, a 15

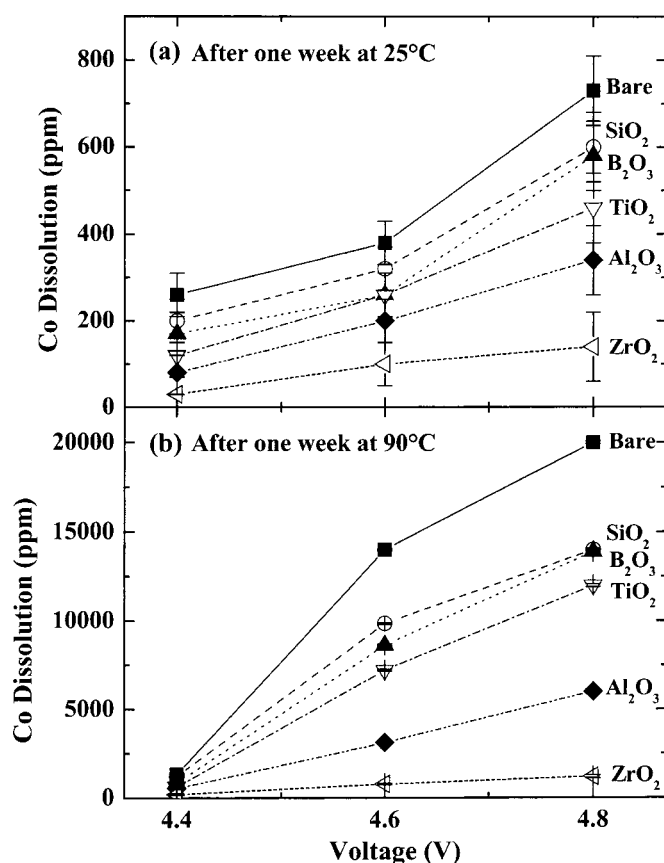
μm thick microporous polyethylene separator, and an electrolyte solution of 1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (1:1 vol %). Water content and HF level in the electrolyte solution determined by gas chromatography (GC) was 10 ppm and 20 ppm, respectively. The half cells in Li/LiCoO<sub>2</sub> were charged to the prede-



**Figure 1.** (a) The discharge curves of various metal-oxide coated LiCoO<sub>2</sub> (5 wt %), compared to the uncoated LiCoO<sub>2</sub>, for the first cycle. (b) Cycle-life performances for ZrO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>-, B<sub>2</sub>O<sub>3</sub>-, SiO<sub>2</sub>-coated, and uncoated LiCoO<sub>2</sub>. The cells were cycled at a rate of 0.1 C (14 mA/g) on the first two cycles, followed by a 0.5 C rate between 4.4 and 2.75 V at 21°C.

\* Electrochemical Society Active Member.

<sup>z</sup> E-mail: jphcho@kumoh.ac.kr

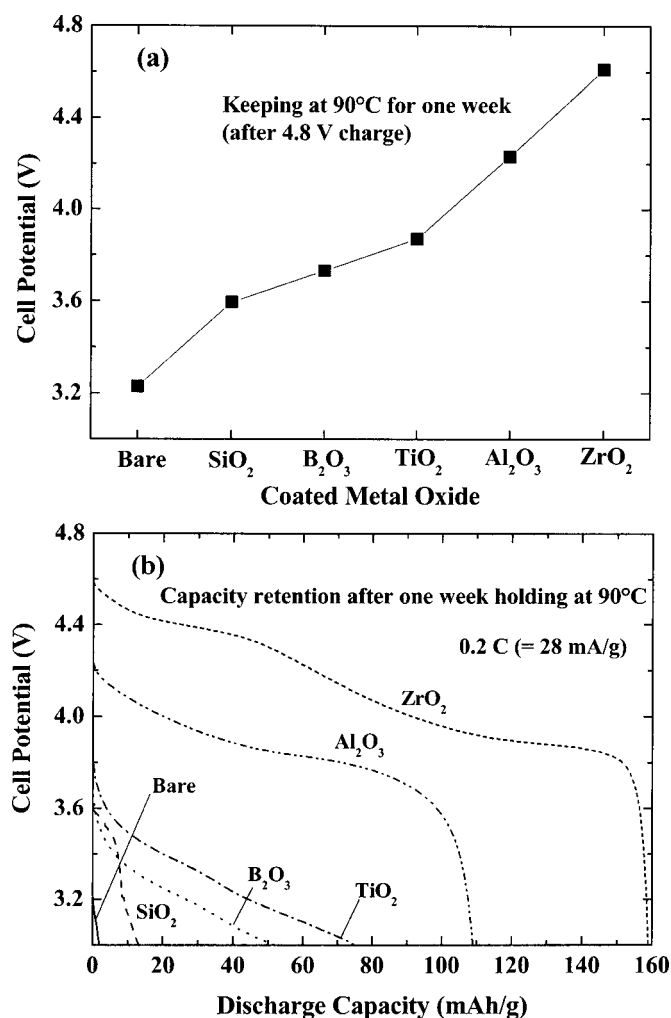


**Figure 2.** The amount of cobalt dissolution in the electrolyte, from various metal-oxide coated (5 wt %) and uncoated LiCoO<sub>2</sub>, after an initial charge and being immersed for one week at (a) 25°C and (b) 90°C, respectively.

terminated voltages (4.4, 4.6, and 4.8 V), and the charged cathodes (20 mg) were immersed in the electrolyte solution (4 mL) at 25°C and 90°C, respectively, for one week. The extent of cobalt dissolution from the bare and coated LiCoO<sub>2</sub> cathodes into the electrolyte was measured by inductively coupled plasma-mass spectroscopy (ICP-MS).

### Results and Discussion

X-ray diffraction (XRD) of the metal-oxide coated samples confirmed a single-phase  $R\bar{3}m$  structure. Auger electron spectroscopy and transmission electron microscopy showed that the metal-oxide coating layer was distributed continuously within  $\sim 10$  nm of the particle surface.<sup>6,7,17-19</sup> Figure 1a shows that the initial discharge capacities of the ZrO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-coated samples were similar to that of the uncoated one, while the discharge voltage profile in the case of the ZrO<sub>2</sub> coating was slightly lower. The trend of the cycle-life performance (Fig. 1b) was consistent with the fracture toughness of coated oxides, in the order of ZrO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > TiO<sub>2</sub> > B<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>. In addition, the ZrO<sub>2</sub>-coated sample exhibited negligible capacity fading over 70 cycles between 4.4 and 2.75 V, thereby retaining its original capacity. In contrast, the SiO<sub>2</sub>-coated LiCoO<sub>2</sub> exhibited  $\sim 65\%$  of its original capacity after only 25 cycles, which was similar to the bare samples. This correlation between the capacity retention and fracture toughness of coated metal oxides may have been because the fraction of the LiCoO<sub>2</sub> surface exposed to the electrolyte after the electrochemical cycling decreased with the higher fracture toughness of the coating layer. However, the actual fracture toughness of coated metal-oxide layer may have differed

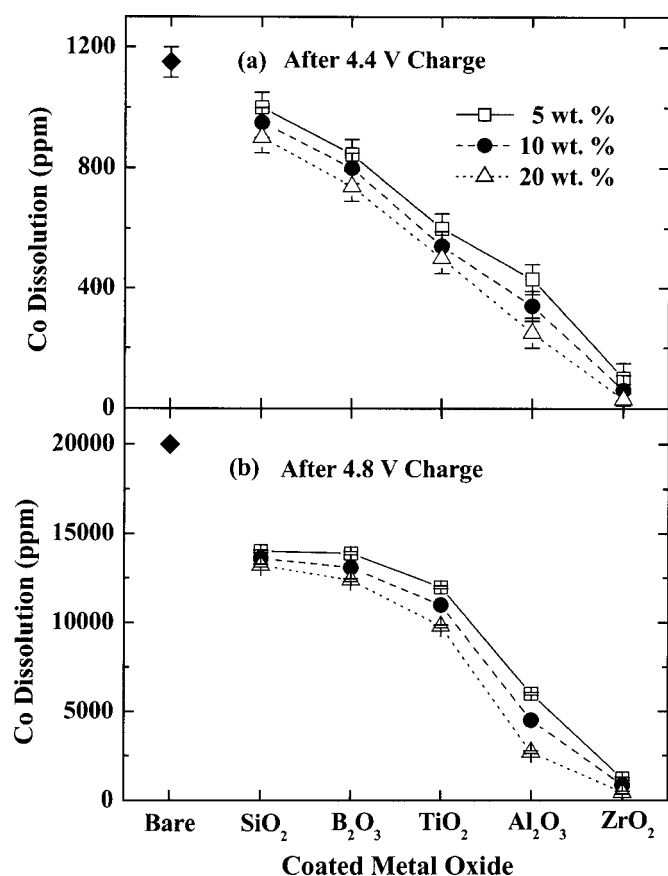


**Figure 3.** (a) OCV of the ZrO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>-, B<sub>2</sub>O<sub>3</sub>-, and SiO<sub>2</sub>-coated, (5 wt %), and the uncoated LiCoO<sub>2</sub>, and (b) the discharge curves at a rate of 0.2 C (28 mA/g). Both (a) and (b) are after charging to 4.8 V, then after standing at 90°C for one week.

from that of the pure phase due to some Li solutes in the metal-oxide layer, potential interdiffusion with LiCoO<sub>2</sub>, intrinsic stress from the interface, etc.

As shown in Fig. 2, the amount of cobalt dissolution determined by ICP-MS, after immersing the charged LiCoO<sub>2</sub> cathodes in the electrolyte for one week at 25 and 90°C, respectively, correlated well with the capacity retention (Fig. 1b). The amount of cobalt dissolution at 25°C from the uncoated LiCoO<sub>2</sub> powders was  $\sim 260$  ppm at 4.4 V, while that from the ZrO<sub>2</sub>-coated ones was  $\sim 30$  ppm (Fig. 2a). Cobalt dissolution from the uncoated samples at an elevated temperature largely increased up to  $\sim 1330$  ppm at 4.4 V, while that of ZrO<sub>2</sub>-coated ones was  $\sim 200$  ppm (Fig. 2b). Figure 2 also shows that cobalt dissolution increased with increasing the charge-cutoff voltage, which is because an increase in the fraction of Co<sup>4+</sup> in Li<sub>1-x</sub>CoO<sub>2</sub> augmented the reactivity with the acidic HF in the electrolyte.<sup>8</sup> Amatucci *et al.* reported that cobalt dissolution is closely related to a weakening of the crystal structure by the removal of the binding lithium.<sup>8</sup> However, cobalt dissolution of ZrO<sub>2</sub>-coated LiCoO<sub>2</sub> ( $\sim 1200$  ppm) was reduced by more than one order of magnitude, compared to that of an uncoated LiCoO<sub>2</sub> ( $\sim 20000$  ppm), charged to 4.8 V after one week storage at 90°C, as shown in Fig. 2b.

Figure 3a shows the open-circuit voltage (OCV) when the coated samples, first charged to 4.8 V, were immersed in the liquid electro-



**Figure 4.** Cobalt dissolution from the cathodes charged to (a) 4.4 V and (b) 4.8 V, depending on the weight percent of the metal-oxide precursors. All the charged cathodes were immersed for one week at 90°C.

lyte for one week at 90°C. The OCV of the ZrO<sub>2</sub>-coated cathode was ~4.61 V, indicating that the phenomenon of self-discharge was insignificant for one week. On the other hand, the OCV of the uncoated powders decreased to ~3.23 V. The trend of the OCV reduction is again well correlated with both cobalt dissolution and capacity retention. Reactions between the nucleophilic LiCoO<sub>2</sub> (negatively-charged oxygen) and the highly electrophilic solvents in the electrolytes led to a decrease in the OCV (spontaneous lithium intercalation).<sup>24,25</sup> In addition, cobalt dissolution also played a major role in decreasing the OCV during storage at 90°C.

When the LiCoO<sub>2</sub> cathode (first charged to 4.8 V) was discharged at a 0.2 C rate after one week storage at 90°C, the capacity retention correlated strongly with cobalt dissolution, *i.e.*, the capacity retention of ZrO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>-, B<sub>2</sub>O<sub>3</sub>-, SiO<sub>2</sub>-coated, and uncoated LiCoO<sub>2</sub> were approximately 80, 55, 38, 27, 7, and 1%, respectively (Fig. 3b), compared to the discharge capacity (~198 mAh/g) of the cell from the initial cycle at 25°C.

In addition, as the fraction of the metal-oxide-coating content increased from 5 to 20 wt %, cobalt dissolution of the LiCoO<sub>2</sub>

decreased (Fig. 4), charged to 4.4 and 4.8 V, respectively, after one week storage at 90°C. This is attributed to the formation of a more uniform coating layer on the LiCoO<sub>2</sub> and an enhanced fracture strength.

### Conclusions

The amount of cobalt dissolution correlated well with the capacity retention, among coatings of various metal oxides. The enclosing of LiCoO<sub>2</sub> powders by ZrO<sub>2</sub> can effectively inhibit cobalt dissolution, resulting in an excellent electrochemical behavior above 4.4 V. Further studies are currently underway to detail the microstructures of coated metal-oxide layer, and to identify the effect of metal-oxide coating on the oxygen loss from the cathode and the surface-film formation above 4.4 V.

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