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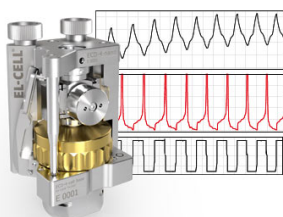
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## High Capacity Surface-Modified LiCoO<sub>2</sub> Cathodes for Lithium-Ion Batteries

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The surface of LiCoO<sub>2</sub> cathodes was modified with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> by a chemical processing procedure followed by heat treatment at 300°C in air for 4 h. The surface-modified LiCoO<sub>2</sub> samples show much better capacity retention at both 25 and 60°C than the unmodified LiCoO<sub>2</sub> cathode to higher cutoff charge voltages of as high as 4.7 V vs. lithium. For example, Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub> shows approximately 180 mAh/g at 4.5 to 3.2 V with a capacity fade of only 8% in 100 cycles, compared to 32% for the unmodified LiCoO<sub>2</sub>. Transmission electron microscopic studies reveal that the guest materials are present as loose oxides (Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>) or as monolayers (TiO<sub>2</sub>) on the surface of LiCoO<sub>2</sub> particles. The improved capacity retention and the higher reversible capacity (180 mAh/g) of the surface-modified LiCoO<sub>2</sub> compared to the unmodified LiCoO<sub>2</sub> (140 mAh/g) could be due to a suppression of the chemical and structural instabilities of the charged Li<sub>1-x</sub>CoO<sub>2</sub> cathodes and/or reduction of interparticle stresses and strains.

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Lithium-ion batteries have become attractive power sources for portable electronic devices due to their higher energy density compared to other rechargeable systems. Currently, most of the commercial lithium-ion cells use layered LiCoO<sub>2</sub> as the cathode material.<sup>1,2</sup> However, only 50% of the theoretical capacity of LiCoO<sub>2</sub> can be practically utilized (140 mAh/g), which corresponds to a reversible extraction/insertion of 0.5 lithium per cobalt. Extraction of more than 0.5 lithium per cobalt, which corresponds to voltages > 4.2 V vs. metallic lithium, leads to capacity fade due to chemical and structural instabilities. Li<sub>1-x</sub>CoO<sub>2-δ</sub> phases obtained by both chemical lithium extraction and electrochemical charging have been found to lose oxygen from the lattice for (1 - x) < 0.5 due to the interaction of the highly oxidizing cathode surface with the chemical oxidizing agent or the electrolyte.<sup>3-6</sup>

One way to suppress the chemical instability in contact with the electrolyte and thereby increase the capacity of the LiCoO<sub>2</sub> cathodes is to modify their surface with materials that are chemically more stable or inert. For example, surface modifications of LiMnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, and LiCoO<sub>2</sub> cathodes have been found recently to improve capacity retention.<sup>7-14</sup> We present here the study of surface modification of LiCoO<sub>2</sub> cathodes with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> by simple chemical routes, and the characterization of these surface-modified cathodes by electrochemical discharge/charge cycling and transmission electron microscopy. The surface-modified LiCoO<sub>2</sub> cathodes show superior performance to higher cutoff charge voltage (4.7 V) with high capacities of around 200 mAh/g compared to the unmodified LiCoO<sub>2</sub> cathode.

### Experimental

A commercially available LiCoO<sub>2</sub> powder was used as the host material for our study. Surface modification of LiCoO<sub>2</sub> was carried out by chemical processes so that the amount of the modifying material Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or ZrO<sub>2</sub> in the final product is 3 wt %. The surface modifications were achieved by dispersing the LiCoO<sub>2</sub> powders in aluminum nitrate(aqueous), titanium propoxide, or zirconium propoxide solutions followed by precipitating the hydrous aluminum, titanium, or zirconium oxide with ammonium hydroxide (in the case of aluminum) or controlled hydrolysis (in the cases of titanium and zirconium) and heating the products at 300°C in air for 4 h. Although we designate the modifying materials as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or ZrO<sub>2</sub> in this paper, they could be present as hydrous oxides even after firing at 300°C. For example, bulk samples obtained under

similar conditions, but without dispersing the LiCoO<sub>2</sub> powders, were found from X-ray diffraction (XRD) line broadening techniques after firing at 300°C to be nanocrystalline AlOOH, TiO<sub>2</sub>, and ZrO<sub>2</sub> with crystallite sizes of, respectively, 3, 6, and 2 nm. However, the hydrous oxides such as AlOOH present in small quantities could undergo electrochemical decomposition to produce Al<sub>2</sub>O<sub>3</sub> during the charge/discharge process.

Cathodes were fabricated with the surface-modified and unmodified LiCoO<sub>2</sub> powders, Denka black carbon, and polytetrafluoroethylene (PTFE) binder in weight ratios of 75:20:5. The electrochemical performances were evaluated with CR2032 coin cells assembled with the cathodes thus fabricated, metallic lithium anodes, polyethylene separators, and a 1 M LiPF<sub>6</sub> in ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte at C/5 rate. The morphology of the surface-modified LiCoO<sub>2</sub> samples were examined using a JEOL 2010 transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometry (EDS) for elemental analysis. TEM specimens were prepared by dispersing the samples in isopropyl alcohol and applying drops of the dispersion onto lacey carbon support films.

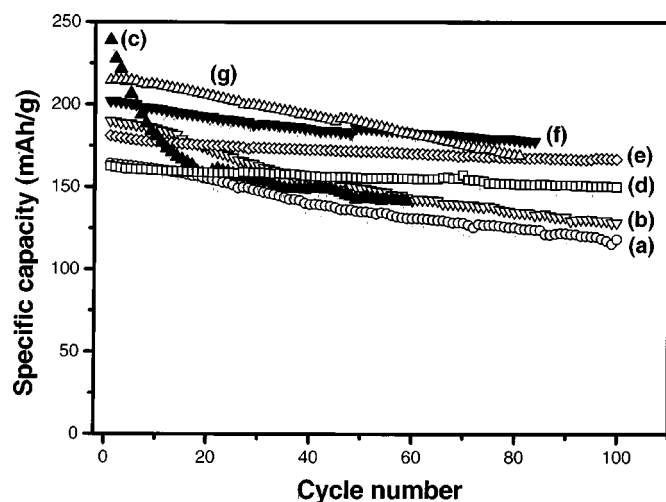
### Results and Discussion

Figure 1 compares the cyclability data of Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub> and the unmodified LiCoO<sub>2</sub> cathodes in the voltage ranges of 4.3 to 3.2, 4.5 to 3.2, 4.6 to 3.2, and 4.7 to 3.2 V at 25°C. Table I gives the first discharge capacity and the percent of capacity fade per cycle. LiCoO<sub>2</sub> is known to show good cyclability in lithium-ion cells when the cutoff charge voltage is limited to 4.2 V vs. lithium. Above 4.2 V, LiCoO<sub>2</sub> exhibits severe capacity fade as seen in Fig. 1 and Table I. In contrast, the Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub> shows superior cycling performance to much higher cutoff charge voltages. While the unmodified LiCoO<sub>2</sub> exhibits severe capacity fades of 0.28, 0.32, and 0.71% per cycle, respectively, for the cutoff voltages of 4.3, 4.5, and 4.7 V, the Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub> exhibits 0.07, 0.08, 0.14, and 0.25% per cycle, respectively, for 4.3, 4.5, 4.6, and 4.7 V (Table I). The reversible capacity of approximately 180 mAh/g, achieved at a cutoff voltage of 4.5 V with excellent cyclability, corresponds to a reversible extraction/insertion of 0.65 lithium per cobalt, compared to 0.5 lithium per cobalt for unmodified LiCoO<sub>2</sub> at 4.2 V (140 mAh/g). The Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub> also exhibits excellent cyclability at 60°C as seen in Table I. The inferior performance of the unmodified LiCoO<sub>2</sub> cathode at higher voltages is related to the development of larger impedance (polarization losses) as seen in Fig. 2.

Figure 3 compares the cyclability data of both the TiO<sub>2</sub>- and ZrO<sub>2</sub>-modified LiCoO<sub>2</sub> with that of unmodified LiCoO<sub>2</sub>. The data in Table I reveal that the TiO<sub>2</sub>- and ZrO<sub>2</sub>-modified samples also

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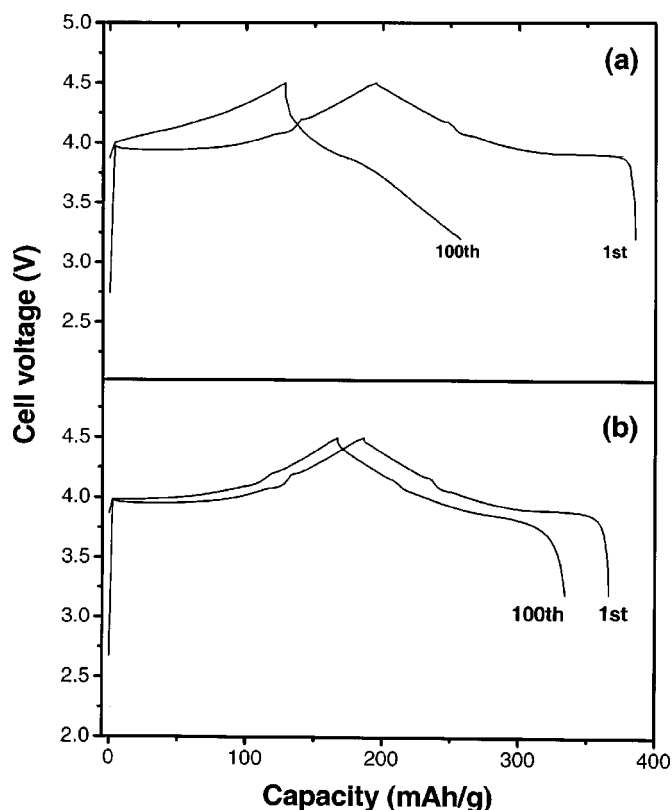
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**Figure 1.** Comparison of the cyclability data of unmodified and  $\text{Al}_2\text{O}_3$  modified  $\text{LiCoO}_2$  cathodes in different voltage ranges at C/5 rate: (a) unmodified  $\text{LiCoO}_2$  (4.3 to 3.2 V), (b) unmodified  $\text{LiCoO}_2$  (4.5 to 3.2 V), (c) unmodified  $\text{LiCoO}_2$  (4.7 to 3.2 V), (d)  $\text{Al}_2\text{O}_3$  modified  $\text{LiCoO}_2$  (4.3 to 3.2 V), (e)  $\text{Al}_2\text{O}_3$  modified  $\text{LiCoO}_2$  (4.5 to 3.2 V), (f)  $\text{Al}_2\text{O}_3$  modified  $\text{LiCoO}_2$  (4.6 to 3.2 V), and (g)  $\text{Al}_2\text{O}_3$  modified  $\text{LiCoO}_2$  (4.7 to 3.2 V).

exhibit superior cycling performance compared to the unmodified sample. The  $\text{ZrO}_2$ -modified sample exhibits slightly lower capacity than the  $\text{Al}_2\text{O}_3$ -modified sample (176 vs. 181 mAh/g at 4.5 V), but with a slightly better capacity retention (0.067 vs. 0.080% fade per cycle). The  $\text{TiO}_2$  modified sample, on the other hand, exhibits much higher capacity (193 mAh/g) than the other two systems, but with a faster fade rate of 0.113% per cycle.

Figure 4 compares the TEM photographs of the surface-modified and unmodified  $\text{LiCoO}_2$ . In all the cases, the  $\text{LiCoO}_2$  particles were found to be nodular single crystals of around 5  $\mu\text{m}$  in diam and the specimens were sensitive to the electron beam. It was, therefore, necessary to reduce the intensity and record the photographs quickly. The unmodified sample particles exhibit smooth surfaces with no apparent facets or shape anisotropy as indicated by the smoothly contoured edge in Fig. 4a. In the case of  $\text{Al}_2\text{O}_3$ - and  $\text{ZrO}_2$ -modified samples, nanocrystalline aluminum or zirconium oxide are present as loose flakes or clusters of flakes, occasionally attached to the surfaces of  $\text{LiCoO}_2$  (Fig. 4b and c); the aluminum



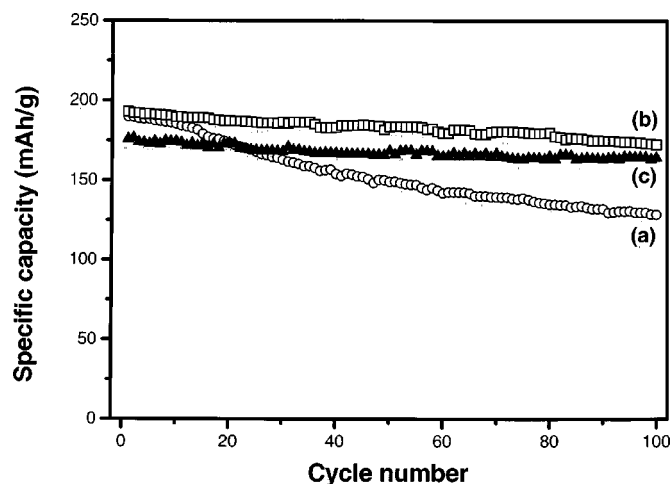
**Figure 2.** Comparison of the first and hundredth discharge/charge profiles of (a) unmodified  $\text{LiCoO}_2$  and (b)  $\text{Al}_2\text{O}_3$ -modified  $\text{LiCoO}_2$  cathodes at C/5 rate (4.5 to 3.2 V).

oxide appeared to be partially crystalline, possibly due to its hydrous nature ( $\text{AlOOH}$ ). In the case of  $\text{TiO}_2$ -modified sample, the only evidence of  $\text{TiO}_2$  was a roughening of the particle surface (Fig. 4d). EDS analysis consistently detected very small amounts of Ti near the edges of the particles (*i.e.*, beam at glancing angle to particle surface) and the Ti signal was reduced greatly when the beam was placed in the center of a particle, suggesting that  $\text{TiO}_2$  is possibly present as a monolayer on the surface of the  $\text{LiCoO}_2$  particles.

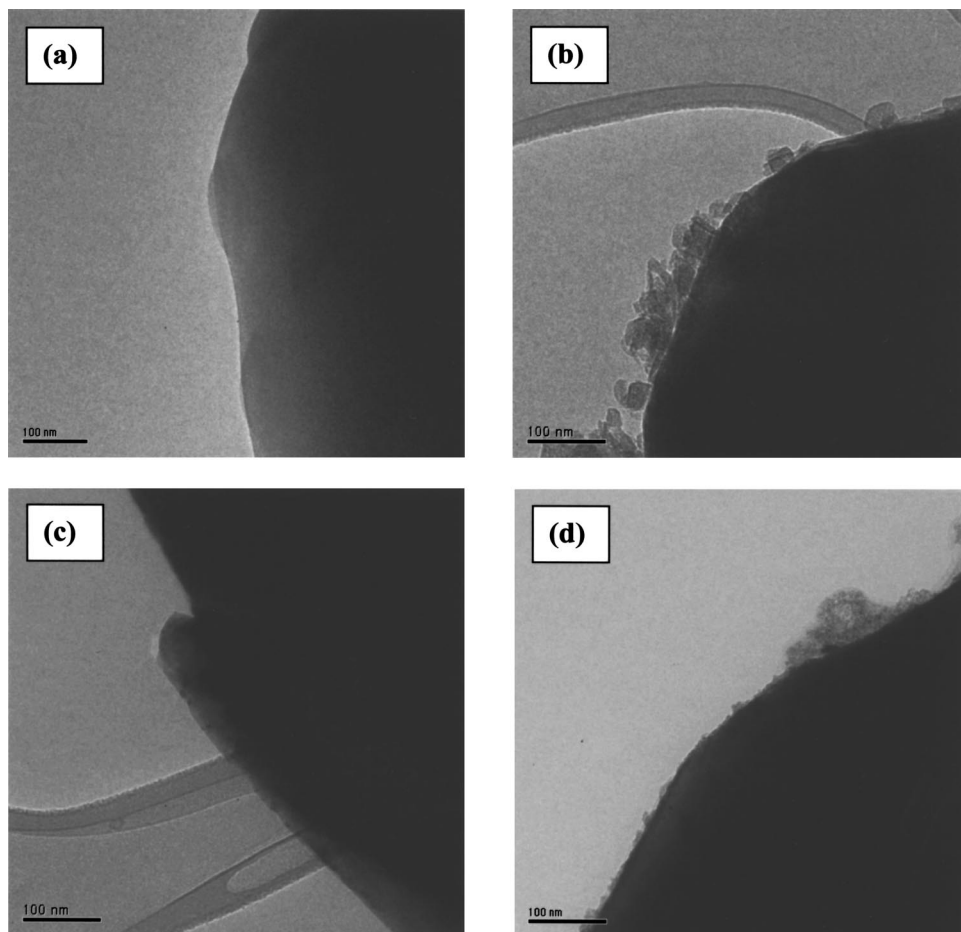
**Table I. Comparison of the capacity and capacity fading of surface-modified  $\text{LiCoO}_2$  and unmodified  $\text{LiCoO}_2$  cathodes at C/5 rate.**

Sample	1st discharge capacity (mAh/g)	Capacity fade per cycle (%)
$\text{LiCoO}_2$ (4.3-3.2 V)	164	0.28
$\text{LiCoO}_2$ (4.5-3.2 V)	190	0.32
$\text{LiCoO}_2$ (4.7-3.2 V)	239	0.71
$\text{Al}_2\text{O}_3$ modified $\text{LiCoO}_2$ (4.3-3.2 V)	163	0.07
$\text{Al}_2\text{O}_3$ modified $\text{LiCoO}_2$ (4.5-3.2 V)	181	0.08
$\text{Al}_2\text{O}_3$ modified $\text{LiCoO}_2$ (4.5-3.2 V) <sup>a</sup>	189	0.10
$\text{Al}_2\text{O}_3$ modified $\text{LiCoO}_2$ (4.6-3.2 V)	202	0.14
$\text{Al}_2\text{O}_3$ modified $\text{LiCoO}_2$ (4.7-3.2 V)	215	0.25
$\text{TiO}_2$ -modified $\text{LiCoO}_2$ (4.5-3.2 V)	193	0.113
$\text{TiO}_2$ -modified $\text{LiCoO}_2$ (4.7-3.2 V)	250	1.06
$\text{ZrO}_2$ -modified $\text{LiCoO}_2$ (4.5-3.2 V)	176	0.067
$\text{ZrO}_2$ -modified $\text{LiCoO}_2$ (4.7-3.2 V)	212	0.65

<sup>a</sup> Data collected at 60°C. All other data were collected at 25°C.



**Figure 3.** Comparison of the cyclability data of unmodified and  $\text{TiO}_2$ - and  $\text{ZrO}_2$ -modified  $\text{LiCoO}_2$  cathodes in the range of 4.5 to 3.2 V at C/5 rate: (a) unmodified  $\text{LiCoO}_2$ , (b)  $\text{TiO}_2$  modified  $\text{LiCoO}_2$ , and (c)  $\text{ZrO}_2$  modified  $\text{LiCoO}_2$ .



**Figure 4.** TEM photographs of (a) unmodified LiCoO<sub>2</sub>, (b) Al<sub>2</sub>O<sub>3</sub>-modified LiCoO<sub>2</sub>, (c) TiO<sub>2</sub>-modified LiCoO<sub>2</sub>, and (d) ZrO<sub>2</sub>-modified LiCoO<sub>2</sub>.

The improved cyclability (and reduced polarization losses) of the surface-modified LiCoO<sub>2</sub> cathodes to higher cutoff voltages compared to the unmodified LiCoO<sub>2</sub> cathodes could be due to the suppression of the chemical instability of the charged Li<sub>1-x</sub>CoO<sub>2</sub> cathodes. The surface modification by chemically inert or more stable aluminum, titanium, or zirconium oxide can minimize the chemical interaction between the highly oxidized Li<sub>1-x</sub>CoO<sub>2</sub> and the electrolyte and thereby suppress the tendency of Li<sub>1-x</sub>CoO<sub>2</sub> to lose oxygen<sup>3-6</sup> and cobalt<sup>15,16</sup> from the lattice. Alternatively, the presence of loose nanocrystalline oxides on the surface of LiCoO<sub>2</sub> particles might help to reduce interparticle stresses and microstrain<sup>17</sup> arising from structural and volume changes occurring at higher voltages and thereby improve the capacity retention.

### Conclusions

The practical capacity of the LiCoO<sub>2</sub> cathode has been increased significantly from the current levels of 140 mAh/g to around 180 mAh/g by modifying its surface with chemically stable materials such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>. The surface-modified LiCoO<sub>2</sub> shows excellent cyclability both at room temperature and at 60°C. The superior performance of the surface modified LiCoO<sub>2</sub> cathodes could be due to an improvement in the chemical and structural stabilities of the cathode/electrolyte interface and/or a suppression of the interparticle stresses and strains.

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