



Annealing-Temperature Effect on Various Cutoff-Voltage Electrochemical Performances in AlPO_4 -Nanoparticle-Coated LiCoO_2

Jaephil Cho,^{a,*} Byoungsoo Kim,^b Joon-Gon Lee,^b Young-Woon Kim,^b
and Byungwoo Park^{b,*z}

^aDepartment of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

^bSchool of Materials Science and Engineering and Research Center for Energy Conversion and Storage, Seoul National University, Seoul, Korea

The electrochemical properties of AlPO_4 -coated LiCoO_2 cathodes were found to be superior to those of bare cathodes at various charge-cutoff voltages (4.3, 4.6, and 4.8 V), and depended on the annealing temperature. The AlPO_4 -coated cathodes annealed at 600 and 700°C retained a discharge capacity of ~ 150 mAh/g even with a 4.8 V charge-cutoff voltage (after 46 cycles at 1 C = 140 mA/g). The bare cathode showed zero capacity retention at the same condition after only 20 cycles. The enhanced electrochemical performance and rate capability in the coated cathodes were attributed to the inhibition of structural degradation during cycling. The AlPO_4 -nanoparticle coating layer on the LiCoO_2 effectively suppressed cobalt dissolution and a nonuniform distribution of local strain in the cathode.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1825387] All rights reserved.

Manuscript submitted April 22, 2004; revised manuscript received June 1, 2004. Available electronically November 17, 2004.

LiCoO_2 cathode material has a hexagonal α - NaFeO_2 layered structure ($R\bar{3}m$) based on a close-packed network of oxygen atoms with alternating lithium and cobalt planes. This material is mainly used as a cathode material in commercial Li-ion batteries as a result of its excellent electrochemical properties. However, it has been reported that LiCoO_2 exhibited abrupt capacity fading during cycling above 4.3 V.^{1,2} Recently, there has been a great deal of effort made on improving the electrochemical properties of LiCoO_2 . Tukamoto and West reported that the substitution of a small amount of Co^{3+} by Mg^{2+} could improve the electronic conductivity of LiCoO_2 .³ Jang *et al.* proposed that a microfracture in the cathode powders during cycling led capacity loss.⁴ Through transmission electron microscopy (TEM) studies, they showed that substitution of Co^{3+} by Al^{3+} in LiCoO_2 restrained the evolution of a microfracture in the powder, and reduced the capacity fading, compared to the unsubstituted LiCoO_2 . However, the cation-substituted LiCoO_2 had a lower initial discharge capacity than LiCoO_2 . Recently, Cho *et al.* reported that a metal-oxide coating by a sol-gel method significantly improved the electrochemical properties of LiCoO_2 without significant specific-capacity loss, and that the metal-oxide-coating layer acted as a solid electrolyte with a reasonably high Li-ion conductivity.⁵⁻⁹ Similarly, other groups reported that ZrO_2 - and TiO_2 -coated LiCoO_2 improved the capacity retention with high charge-cutoff voltages (≥ 4.4 V).^{10,11} Recently, Chen and Dahn reported that the cycle-life performance of LiCoO_2 was improved by a simple heat-treatment, due to the elimination of surface contamination on the cathode, for example, moisture, organic species, etc.^{12,13} However, we found that the thermal history of bare powders did not improve the electrochemical properties. The powder size in Ref. 13 is smaller than the conventional ~ 10 μm sized powders.

Until now, most studies on cathode materials have concentrated on improving the electrochemical properties. However, even metal-oxide-coated LiCoO_2 with an excellent electrochemical performance shows thermal instability at the overcharged state, which is similar to the bare LiCoO_2 . This safety problem of Li-ion cells is mainly related to the exothermic thermal decomposition of the cathode, electrolyte, and anode.^{14,15} Among these, the exothermic reaction of the flammable electrolyte with the cathode material is a well-known trigger for thermal runaway. To enhance the safety of Li-ion cells, some studies on more stable electrolytes at overcharged states have

been reported.¹⁶ Recently, it was reported that a novel AlPO_4 -nanoparticle coating on the LiCoO_2 surface improved both the thermal stability and electrochemical properties of the LiCoO_2 cathodes at high cutoff voltages.¹⁷⁻¹⁹ TEM showed that a nanoscale layer (~ 20 nm) was coated homogeneously over the LiCoO_2 surface, and consisted of randomly-oriented AlPO_4 nanoparticles with an average diameter of ~ 3 nm.¹⁷ In addition, it was reported that the coating material affected the electrochemical and thermal behaviors of the coated LiCoO_2 .¹⁸

In this paper, the effect of annealing temperature of the AlPO_4 -nanoparticle coating was examined from the viewpoint of the electrochemical properties of LiCoO_2 with various charge-cutoff voltages of 4.3, 4.6, and 4.8 V.

Experimental

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ (3 and 1 g, respectively) were dissolved in distilled water until a white AlPO_4 -nanoparticle suspension was observed. Subsequently, the LiCoO_2 powders (with an average size of ~ 10 μm) was slowly added to the coating solution, and mixed until the final viscosity of the slurry reached ~ 100 poise. The slurry was then dried in an oven for 6 h at 130°C, and annealed at 400, 600, and 700°C, respectively, for 5 h in air.

To test the electrochemical properties of the cathodes, coin-type half cells (2016 size) were fabricated in an Ar-filled glove box. The assembly and preparation of the coin-type half cells are described elsewhere.⁵⁻⁸ The electrolyte used was 1 M LiPF_6 with ethylene carbonate/diethyl carbonate/ethyl-methyl carbonate (EC/DEC/EMC: 30/30/40 vol %). Cycling tests of the coin-type half cells (with a Li-metal anode) were performed with the charge-cutoff voltages of 4.3, 4.6, and 4.8 V (with a fixed discharge-cutoff voltage of 3 V). The tests were proceeded by charging and discharging at 0.1 C for the first and second cycles, 0.2 C for the third cycle, 0.5 C for the fourth cycle, and finally at 1 C (=140 mA/g) for the remaining cycles. For the galvanostatic intermittent titration technique (GITT),^{20,21} the test cells were allowed to reach their equilibrium states after each incremental charge step using a constant current of 0.1 C by allowing an open-circuit period of 10 h. The cells for the diffusivity measurements were precycled for each cycle at 0.1, 0.2, 0.5, and 1 C between 4.4 and 3 V. To measure cobalt dissolution from the bare and coated LiCoO_2 cathodes, the electrolyte in the cycled cells was collected by a centrifugal separation method, and the amount of dissolved Co in the electrolyte was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-

* Electrochemical Society Active Member.

^z E-mail: byungwoo@snu.ac.kr

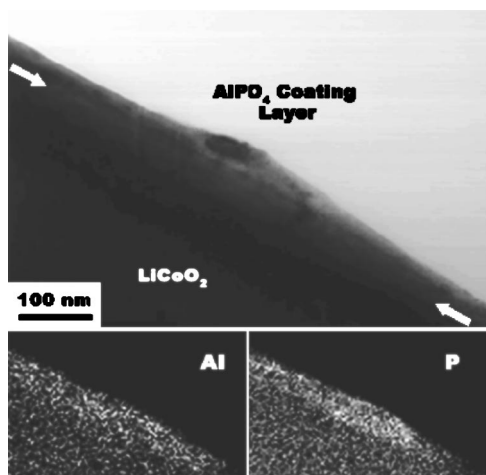


Figure 1. TEM bright-field image of the AlPO_4 -coated LiCoO_2 annealed at 400°C . EDS confirms the presence of Al and P in the nanoscale-coating layer. The arrows indicate the interface between the AlPO_4 nanoscale-coating layer and LiCoO_2 .

AES). The lattice constants and local strains were characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation.

Results and Discussion

Figure 1 shows a TEM image of AlPO_4 -coated LiCoO_2 sample annealed at 400°C . Energy-dispersive X-ray spectroscopy (EDS) confirms Al and P components in the ~ 30 nm coating layer. Similar TEM results were reported for the nanoscale AlPO_4 -coating layer on the cathode surface after annealing at 700°C for 5 h.¹⁷ Figure 2 shows the *ex situ* XRD patterns of the bare and coated LiCoO_2 at different charge voltages up to 4.7 V. Van der Ven *et al.* proposed that a stage-two phase (H1-3) exists at $x = 0.16$ (~ 4.6 V) in Li_xCoO_2 ,^{22,23} and Chen *et al.* experimentally confirmed the presence of a H1-3 phase in the Al_2O_3 -coated LiCoO_2 .²⁴ Similarly, the phase transition from O3 to H1-3 is confirmed between 4.5 and 4.6 V (as shown in Fig. 2). However, only the bare LiCoO_2 shows a minor peak corresponding to the O1 phase, not the AlPO_4 -coated cathode. In addition, at the 4.6 V-charged state, an unidentified peak,

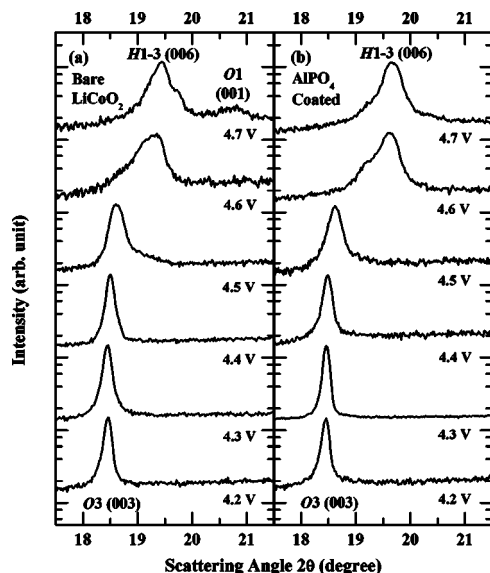


Figure 2. XRD patterns of (a) bare LiCoO_2 and (b) AlPO_4 -coated LiCoO_2 (annealed at 700°C), with different voltages during the first charge.

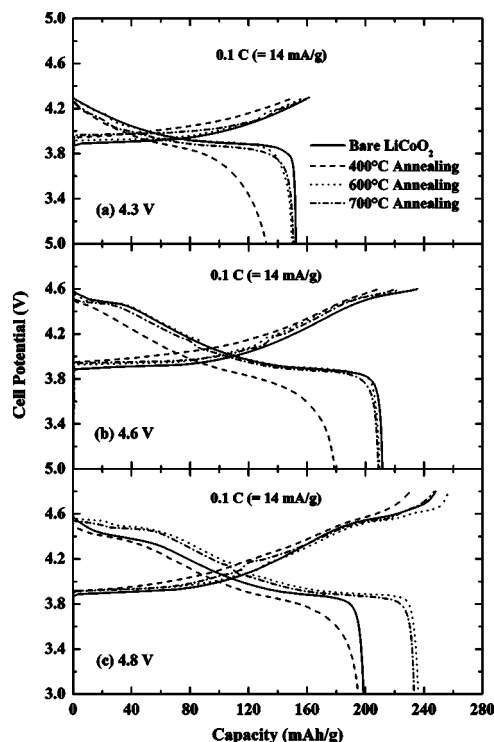


Figure 3. Initial charge and discharge curves of the bare and AlPO_4 -coated LiCoO_2 cathodes with various charge-cutoff voltages of (a) 4.3, (b) 4.6, and (c) 4.8 V. The discharge-cutoff voltage in Li/LiCoO_2 was fixed at 3 V.

which was first mentioned by Chen *et al.*, is observed at $\sim 19.1^\circ$.²⁴ They suggested that other staging phases may exist during the phase transition from O3 to H1-3. However, more systematic studies are needed to confirm the effect of the AlPO_4 coating on the phase transitions.

The annealing temperature has an influence on the electrochemical properties of the coated LiCoO_2 upon cycling. Figure 3 shows the initial charge and discharge curves of the bare and AlPO_4 -coated LiCoO_2 cathodes with various charge-cutoff voltages. The 400°C annealed LiCoO_2 cathodes have much less initial discharge capacities (at all the charge-cutoff voltages) than the 600 and 700°C annealed cathodes. For example, the initial discharge capacities of the 600°C -annealed cathodes with 4.3, 4.6, and 4.8 V charge-cutoff voltages are ~ 150 , ~ 210 , and ~ 235 mAh/g, while those of the 400°C annealed cathodes are ~ 130 , ~ 180 , and ~ 195 mAh/g at the same condition, respectively. Although the bare cathode has similar initial discharge capacity to the 600 and 700°C -annealed cathodes at 4.3 and 4.6 V charge-cutoff voltages, the bare cathode at the 4.8 V charge-cutoff voltage has only ~ 200 mAh/g of the initial discharge capacity, like the 400°C annealed cathode. This suggests that the AlPO_4 nanoparticle coating layer should be in the optimum condition to improve the electrochemical performance of LiCoO_2 . Moreover, the capacity drop in the 600 and 700°C annealed cathodes is ~ 40 mAh/g at a 4.8 V charge-cutoff voltage at the fifth cycle, while the drop in the bare and 400°C annealed cathodes is ~ 70 mAh/g (Fig. 4c). Although the 400°C annealed cathodes have a relatively low initial discharge capacity, they also show good capacity retention, compared with the bare ones. It is clear that the coated cathodes with various charge-cutoff voltages show superior cycle-life performance to the bare ones after 50 cycles.

The lithium diffusivities of the cathodes after the pre-cycles were measured by GITT. As shown in Fig. 5, the 600 and 700°C annealed cathodes effectively prevent the degradation of Li diffusivities during the cycles, in comparison to the bare and 400°C annealed cathode. To test the rate capability of the cathodes, Li-ion cells (graphite/

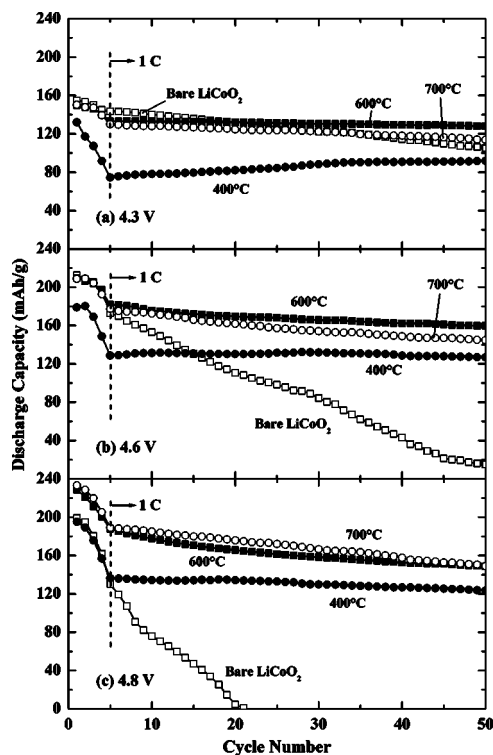


Figure 4. Cycle-life performance of the bare and AlPO₄-coated LiCoO₂ cathodes at a 0.1 C rate for the first and second cycles, the third cycle at 0.2 C rate, the fourth cycle at 0.5 C rate, and finally at 1 C (=140 mA/g) rate for the rest of cycles, with various charge-cutoff voltages of (a) 4.3, (b) 4.6, and (c) 4.8 V.

LiCoO₂) using the bare, 400 and 700°C annealed cathodes were fabricated and cycled between 4.2 and 2.75 V with a discharge rate from 0.2 to 2 C (Fig. 6). While the 700°C annealed cathode shows an excellent rate capability up to 2 C, the 400°C annealed cathode exhibits an inferior rate capability to the bare one. The AlPO₄ coating layer annealed at 600 and 700°C may have better crystallinity and adhesion (by interdiffusion) on LiCoO₂, in comparison to the coating layer annealed at 400°C. It is reported that the electrochemical properties of LiCoO₂ depends on the crystallinity of AlPO₄ coating layer.²⁵ These results explain why the AlPO₄-coating layer, which is annealed at 600 or 700°C, is suitable for enhancing the electrochemical performance of LiCoO₂ in comparison to the sample annealed at 400°C.

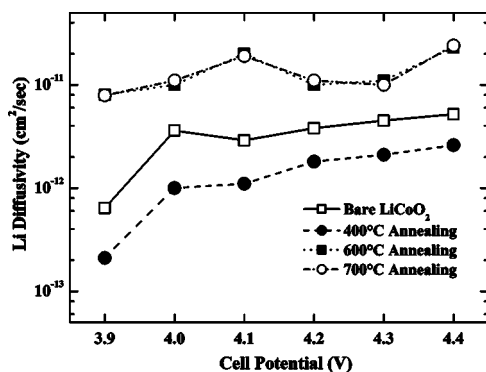


Figure 5. Li diffusivities of the bare and AlPO₄-coated LiCoO₂ cathodes, using GITT. The test cells (with a Li-metal anode) were pre-cycled at a rate of 0.1, 0.2, 0.5, and 1 C (=140 mA/g) for each cycle.

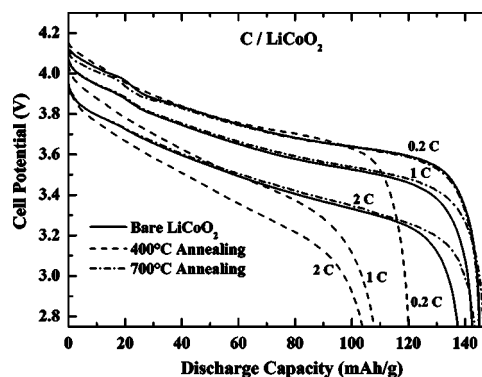


Figure 6. Rate capabilities of the coin-type Li-ion cells (with a graphite anode) using the bare and AlPO₄-coated LiCoO₂ cathodes. The discharge rate was 0.2, 1, or 2 C, while the charging rate was fixed at 1 C between 4.2 and 2.75 V.

As shown in Fig. 4, the coated cathodes have excellent capacity retention compared to the bare ones at a high charge-cutoff voltage. The capacity retention after 46 cycles at a rate of 1 C is shown in Fig. 7. All the cathodes show relatively good capacity retention with a 4.3 V charge-cutoff voltage. As the cutoff voltage increases, the coated cathodes exhibit excellent capacity retention, but the bare cathode degrades rapidly. To understand the electrochemical-performance enhancement by the AlPO₄ coating, the dissolution of cobalt from the cathodes was measured by ICP-AES, and a nonuniform distribution of local strain was obtained by XRD peak broadening.

Figure 8 shows the dissolution of cobalt from the cathodes at the initial charging and after 50 cycles, respectively. Initially, the bare and coated cathodes were charged to 4.3, 4.6, and 4.8 V, respectively, maintained at each voltage for 30 min, and disassembled in an Ar-filled glove box. As the charge voltage increases, the amount of Co dissolution from the bare cathode rapidly increases at the initial charging (Fig. 8a). The bare cathode charged to 4.8 V has a larger Co dissolution (by approximately two orders of magnitude) than that charged to 4.3 V. The AlPO₄-coated cathodes show suppressed Co dissolution. Furthermore, Co dissolution from the coated cathodes after 50 cycles, as shown in Fig. 8b, has very similar behavior to that at the initial charging. The cobalt dissolution from the coated cathodes is effectively suppressed by the AlPO₄-nanoparticle coating, and correlates with the enhanced electrochemical performance of cathodes with the high charge-cutoff voltages (≥ 4.6 V).

Amatucci *et al.* proposed that the capacity decay in LiCoO₂ is coupled with cobalt and oxygen decomposition from LiCoO₂, thus inducing structural degradation.^{26,27} Therefore, variations in the lat-

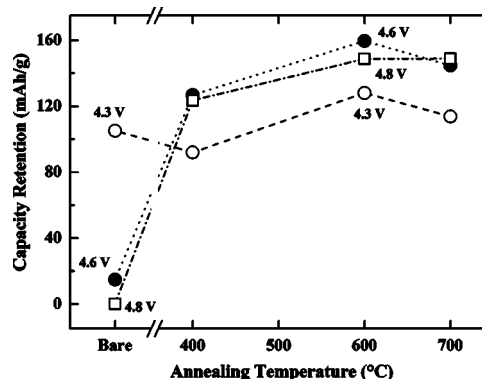


Figure 7. Capacity retention of the bare and AlPO₄-coated LiCoO₂ cathodes after 50 cycles.

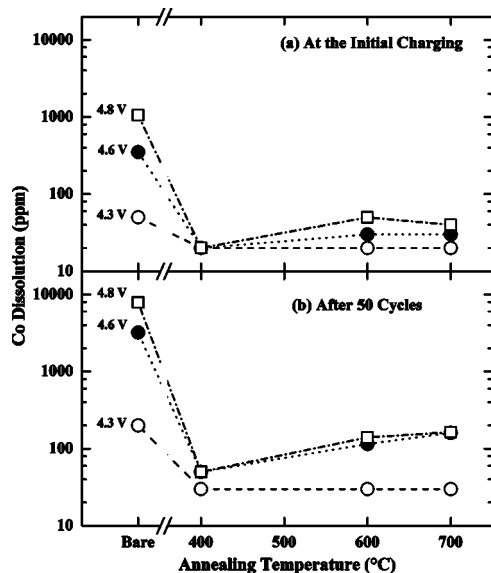


Figure 8. Plots of the Co concentration as a result of Co dissolution from the bare and AlPO_4 -coated LiCoO_2 cathodes (a) at the initial charging and (b) after 50 cycles. For the Co dissolution measurements before cycling, each cell was initially charged to 4.3, 4.6, or 4.8 V at the rate of 0.1 C (=14 mA/g).

tice constant c and the c/a ratio (at 3 V) are measured after 50 cycles with different charge-cutoff voltages (Fig. 9). The c -axis in the bare LiCoO_2 after cycling expands as the charge-cutoff voltage increases, which is unlike the coated cathodes. A similar behavior is observed from the change in the c/a ratio (indicating structural degradation) on the bare and AlPO_4 -coated LiCoO_2 cathodes: the coated cathodes show much smaller changes in the c/a ratio than the bare ones. An AlPO_4 nanoparticle coating may inhibit LiCoO_2 from structural degradation during cycling, and can therefore improve the capacity retention over the bare cathodes.

To quantitatively estimate the structural degradation after cycling, the nonuniform distribution of local strain was obtained from the broadening of diffraction peaks, before and after cycling. Figure 10 shows the XRD patterns of the bare and AlPO_4 coated (600°C

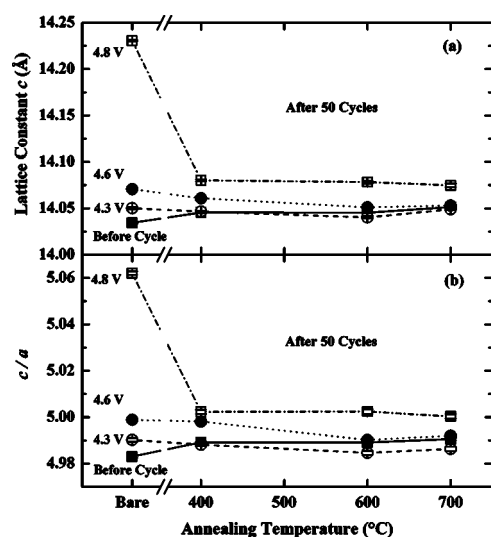


Figure 9. Plots of (a) the lattice constants c , and (b) c/a ratio (at the discharged state) in the bare and AlPO_4 -coated LiCoO_2 cathodes, after 50 cycles with different charge-cutoff voltages of 4.3, 4.6, and 4.8 V.

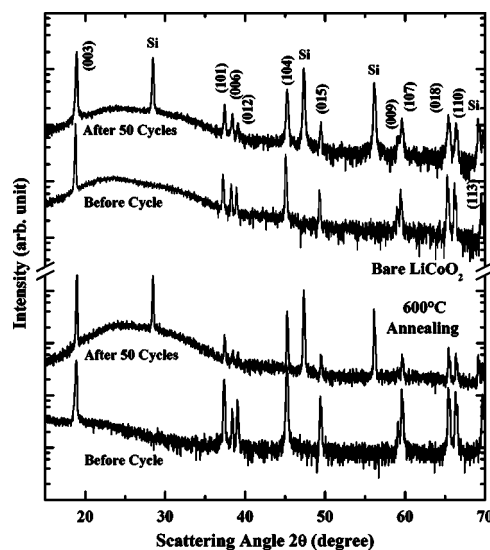


Figure 10. XRD patterns of the bare and AlPO_4 -coated (annealed at 600°C) LiCoO_2 cathodes, before and after 50 cycles with 4.6 V charge-cutoff voltage (all measured at 3 V).

annealing) cathodes with a 4.6 V cutoff voltage. The peak widths Δk (full width at half-maximum, fwhm) were fitted for five selective peaks ((003), (101), (104), (015), and (018)) with a scattering vector $k = (4\pi/\lambda)\sin\theta$ using a double-peak Lorentzian function for $\text{K}\alpha_1$ and $\text{K}\alpha_2$. Peak broadening may be associated with microstructural defects or a nonuniform distribution of local strain.^{28,29} To remove the instrumental broadening effect, a resolution function ($\Delta k_{\text{res}} = 0.0076 - 0.00003 k$ (\AA^{-1}) obtained from Si crystals) was subtracted after fitting each peak. The nonuniform distribution of local strain in the cathode is estimated from the slope of Δk vs. k plots (Fig. 11). The local strains of both the bare and coated cathodes prior to cycling have similar values of $\sim 0.04\%$. With the 4.6 V charge-cutoff, the local strain in the cycled-bare cathode increased by a factor of three, compared to the uncycled bare one. Local-strain analysis clearly demonstrates that the AlPO_4 -nanoparticle coating successfully suppresses the structural degradation caused by Co dissolution, thereby preventing the capacity fading during cycling with high charge-cutoff voltages.

Conclusions

The annealing temperature significantly affected the electrochemical properties of the AlPO_4 coated LiCoO_2 cathodes. After

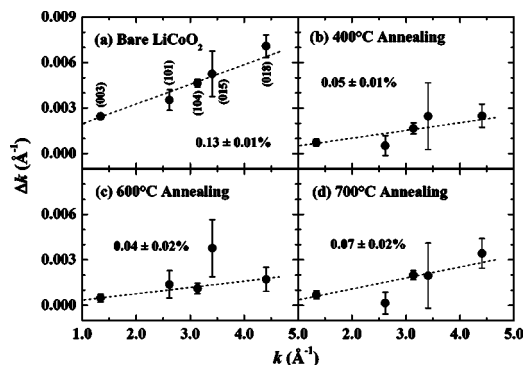


Figure 11. Plots of Δk vs. k in the bare and AlPO_4 -coated LiCoO_2 cathodes after 50 cycles with a 4.6 V charge-cutoff voltage. The slope of the linear-fitted function (dotted line) describes the nonuniform distribution of local strain in the sample.

600 and 700°C annealing, the coated cathodes showed excellent electrochemical performance with high cutoff voltages (≥ 4.6 V). While 400°C annealed cathodes had a relatively low initial discharge capacity and a poor rate capability, they also exhibited good capacity retention after 50 cycles. Cobalt dissolution from the cathode and a nonuniform distribution of local strain were attributed to the suppressed structural degradation during cycling. More studies aimed at identifying the detailed mechanisms of enhanced electrochemical performance in the AlPO_4 -coated LiCoO_2 are underway.

Acknowledgment

This work is supported by Kumoh National Institute of Technology, by the Basic Research Program (R01-2004-000-10173-0) of KOSEF, by the National R&D Program of the Ministry of Science and Technology, and by KOSEF through the Research Center for Energy Conversion and Storage at Seoul National University.

Seoul National University assisted in meeting the publication costs of this article.

References

- H. Wang, Y.-I. Jang, B. Huang, D. R. Sadoway, and Y.-M. Chiang, *J. Electrochem. Soc.*, **146**, 473 (1999).
- E. Plichta, S. Slane, M. Uchiyama, M. Salomon, D. Chua, W. B. Ebner, and H. W. Lin, *J. Electrochem. Soc.*, **136**, 1865 (1989).
- H. Tukamoto and A. R. West, *J. Electrochem. Soc.*, **144**, 3164 (1997).
- Y.-I. Jang, B. Huang, H. Wang, D. R. Sadoway, G. Ceder, Y.-M. Chiang, H. Liu, and H. Tamura, *J. Electrochem. Soc.*, **146**, 862 (1999).
- J. Cho, Y. J. Kim, T.-J. Kim, and B. Park, *Angew. Chem., Int. Ed. Engl.*, **40**, 3367 (2001).
- J. Cho, Y. J. Kim, and B. Park, *Chem. Mater.*, **12**, 3788 (2000).
- J. Cho, Y. J. Kim, and B. Park, *J. Electrochem. Soc.*, **148**, A1110 (2001).
- J. Cho, T.-J. Kim, Y. J. Kim, and B. Park, *Electrochem. Solid-State Lett.*, **4**, A159 (2001).
- Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.-G. Lee, T.-J. Kim, D. Son, J. Cho, Y.-W. Kim, and B. Park, *Chem. Mater.*, **15**, 1505 (2003).
- A. M. Kannan, L. Rabenberg, and A. Manthiram, *Electrochem. Solid-State Lett.*, **6**, A16 (2003).
- Z. Chen and J. R. Dahn, *Electrochem. Solid-State Lett.*, **5**, A213 (2002).
- Z. Chen and J. R. Dahn, *Electrochem. Solid-State Lett.*, **7**, A11 (2004).
- Z. Chen and J. R. Dahn, *Electrochim. Acta*, **49**, 1079 (2004).
- J. R. Dahn, E. W. Fuller, M. Obrovac, and U. von Sacken, *Solid State Ionics*, **69**, 265 (1994).
- D. D. MacNeil, L. Christensen, J. Landucci, J. M. Paulsen, and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 970 (2000).
- C. W. Lee, R. Venkatchalapathy, and J. Prakash, *Electrochem. Solid-State Lett.*, **3**, 63 (2000).
- J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, and B. Park, *Angew. Chem., Int. Ed. Engl.*, **42**, 1618 (2003).
- J. Cho, J.-G. Lee, B. Kim, and B. Park, *Chem. Mater.*, **15**, 3190 (2003).
- J. Cho, *Electrochem. Commun.*, **5**, 146 (2003).
- P. Birke, W. F. Chu, and W. Weppner, *Solid State Ionics*, **93**, 1 (1997).
- Y.-M. Choi, S.-I. Pyun, J.-S. Bae, and S.-I. Moon, *J. Power Sources*, **56**, 25 (1995).
- A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse, and J. Hafner, *Phys. Rev. B*, **58**, 2975 (1998).
- A. Van der Ven, M. K. Aydinol, and G. Ceder, *J. Electrochem. Soc.*, **145**, 2149 (1998).
- Z. Chen, Z. Lu, and J. R. Dahn, *J. Electrochem. Soc.*, **149**, A1604 (2002).
- J. Cho, J.-G. Lee, B. Kim, J. Kim, and B. Park, *Electrochim. Acta*, Submitted.
- G. G. Amatucci, J.-M. Tarascon, and L. C. Klein, *J. Electrochem. Soc.*, **143**, 1114 (1996).
- G. G. Amatucci, J.-M. Tarascon, and L. C. Klein, *Solid State Ionics*, **83**, 167 (1996).
- Y. Kim, J. Oh, T.-G. Kim, and B. Park, *Appl. Phys. Lett.*, **78**, 2363 (2001).
- B. Kim, J.-G. Lee, M. Choi, J. Cho, and B. Park, *J. Power Sources*, **126**, 190 (2004).