Communications

A Breakthrough in the Safety of Lithium Secondary Batteries by Coating the Cathode Material with AlPO$_4$ Nanoparticles **

Jaephil Cho,* Young-Woon Kim, Byoungsoo Kim, Joon-Gon Lee, and Byungwoo Park*

The production of lithium secondary batteries (Li-ion and Li-polymer cells) has rapidly expanded because of their applicability to mobile electronics, such as cellular phones, camcorders, personal digital assistants (PDAs), and notebook personal computers. Sales of Li secondary batteries were expected to increase to more than 1 billion cells in 2002. Even though most Li secondary batteries use LiCoO$_2$ as a cathode material, because of its high volumetric energy density and excellent high-temperature performance (such as the cycle life at 60 °C and swelling characteristics at 90 °C), their safety is still a major concern, and are less safe as the capacity of the battery increases.[1,2] In particular, one of the unsolved problems that can occur during operation, abrupt overcharge to the voltage-supply limit (12 V) owing to a defect or a malfunction in the protective devices[+] of the cell, has not been prevented. Moreover, numerous battery accidents with accompanying fires and explosions have been reported.[3] The main cause of such disasters is that LiCoO$_2$ cathodes can undergo a violent exothermic reaction with the electrolyte during overcharge, which may result in the cell short-circuiting. In addition, lithium deposited on the graphite anode accelerates the reaction, and results in a sharp rise in temperature.[4–6] Furthermore, this process converts LiCoO$_2$ into the strong oxidizing agent Co$_2$O$_3$, which releases oxygen during overcharging. A combination of the temperature increase and the internal short circuit of the cell eventually results in an explosion of the cell. In spite of this, no fundamental solution has been found. In particular, Li-ion batteries using a laminated film case are more susceptible to these hazards during an overcharge than those using an

[*] Prof. Dr. J. Cho
Department of Applied Chemistry
Kumoh National Institute of Technology
Gumi 730-701 (Korea)
Fax: (+82) 54-467-4477
E-mail: jpcho@kumoh.ac.kr

Prof. Dr. B. Park, Prof. Dr. Y.-W. Kim, B. Kim, J.-G. Lee
School of Materials Science and Engineering
Research Center for Energy Conversion and Storage
Seoul National University, Seoul 151-744 (Korea)
Fax: (+82) 2-885-9671
E-mail: byungwoo@snu.ac.kr

[+] Protective devices consist of a positive temperature coefficient (PTC) material and protective circuits that block the overcharging above 4.2 V, the overdischarging below 3 V, and the overcurrent above 1 C.

aluminum case, because the former is not able to withstand the severe deformation of the electrodes.

There have been many reports of the surface modification of nanoparticles with a functional monolayer or a polymer shell that tailors their surface properties.[7–12] In contrast, a nanoparticle coating on oxides or other inorganic compounds has remained a technical challenge, and has not been reported in the literature. In this communication, we report a drastic improvement in both the safety and the electrochemical properties of $LiCoO_2$ cathodes by applying a direct coating of $AlPO_4$ nanoparticles from an aqueous solution.

The overcharge safety tests were conducted following guidelines set out for the safety evaluation of secondary lithium cells. The guidelines require that although the casing of the cells may become swollen, the cells should not explode or catch fire.[13,14] Figure 1 shows the voltage and temperature

profiles of the cell with both bare $LiCoO_2$ cathodes and cathodes coated with $AlPO_4$ nanoparticles, in addition to the cell morphologies after the overcharge test. The cells used for the 12 V overcharge safety test were initially charged to 4.2 V, and subsequently charged to 12 V at a rate of 1 C (equivalent to 140 mA g^{-1} = 1.6 A). The cells were then maintained at that voltage for 2 h.

Figure 2 shows transmission electron microscopy (TEM) images of the $AlPO_4$ nanoparticle-coated $LiCoO_2$. As shown in Figure 2a, a nanoscalar $AlPO_4$ layer (approximately 15 nm) was coated homogeneously over the $LiCoO_2$ surface, and energy-dispersive spectroscopy (EDS) confirms the Al and P components of the coating layer. Figure 2b displays a high-resolution TEM image showing $AlPO_4$ nanoparticles embedded in the nanoscalar coating layer. The layer consisted of randomly oriented $AlPO_4$ nanoparticles with an average
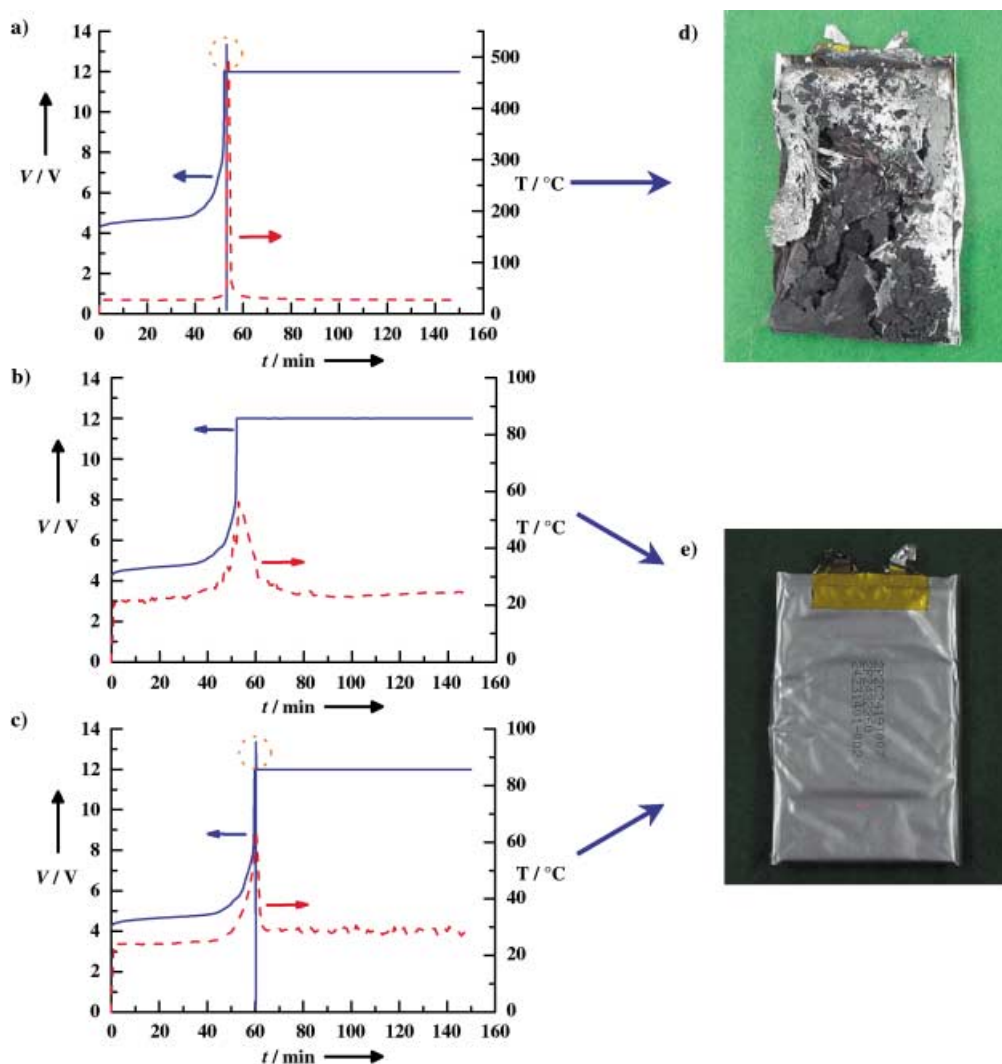

Figure 1. a) Voltage and temperature profiles of a cell with a bare $LiCoO_2$ cathode, as a function of time. All the cells were initially charged to 4.2 V, then charged to 12 V at a rate of 1 C (equivalent to 140 mA g^{-1} = 1.6 A), and then maintained at that voltage for 2 h. Cells with bare cathodes exhibit an abrupt voltage drop to 0 V resulting from a short circuit and a rapid temperature increase to approximately 500 °C; b, c) temperature and voltage profiles of a cell with an $AlPO_4$ nanoparticle-coated $LiCoO_2$ cathode. Even though the cell had a short circuit (Figure 1c), the temperature only increased to approximately 60 °C without burning; d) a picture of a cell containing a bare $LiCoO_2$ cathode after the 12 V overcharge test; the cell burned and exploded at that voltage. e) a picture of a cell containing the $AlPO_4$ nanoparticle-coated $LiCoO_2$ after the 12 V overcharge test.
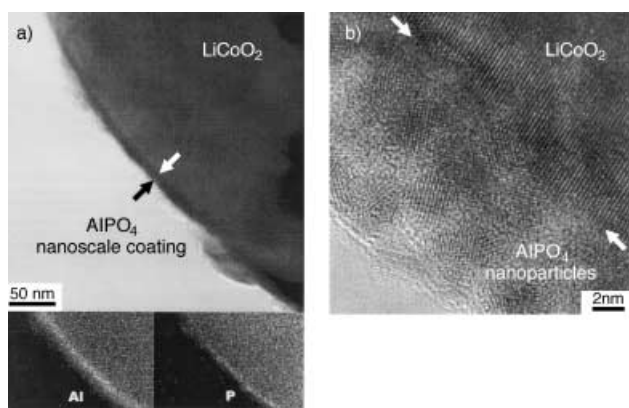
Figure 2. a) TEM bright-field image of the AlPO$_4$ nanoparticle-coated LiCoO$_2$; EDS confirms the Al and P components in the coating layer. b) High-resolution TEM image showing the AlPO$_4$ nanoparticles ($\approx$3 nm in diameter) in the nanoscale coating layer; the arrows indicate the interface between the AlPO$_4$ layer and LiCoO$_2$.

diameter of approximately 3 nm, with a regular distribution of Al and P components throughout the layer. X-ray diffraction patterns of the LiCoO$_2$ powders, before and after coating, and after annealing, were identical even though it was not possible to rule out the formation of other phases or interdiffusion. While Figure 2b shows AlPO$_4$ nanoparticles embedded in the amorphous phase, the exact stoichiometry and phases of both the nanoparticle and the matrix need to be identified, which will aid the understanding of any reaction between LiCoO$_2$ and the AlPO$_4$ nanoparticle layer at 700°C.

Figure 1 shows the voltage and cell-surface temperature profiles during the 12 V overcharge test. Overcharging to this voltage increases the electrolyte decomposition rate, and the internal cell resistance (joule heat) increases because of electrolyte decomposition. At 12 V, a separator melts down and shrinks when the temperature inside the cell increases to approximately 120°C. Therefore, any direct contact of the anode and cathode electrodes induces a short circuit. This has been the problem in cells with a bare LiCoO$_2$ cathode, as shown in Figure 1a. Electrolyte decomposition occurs at a plateau of approximately 5 V, followed by a rapid increase in the cell voltage to 12 V. Immediately after the cell voltage reaches 12 V, an internal short circuit occurs (note the abrupt voltage drop to 0 V), and the surface temperature increases to almost 500°C, which results in a fire and an explosion of the cell (Figure 1d). All 15 cells without a nanoparticle coating exhibited the same failure pattern. This result shows that thermal runaway from cathode decomposition during accidental overcharging must be avoided. Nanoscalar metal oxides (Al$_2$O$_3$ or ZrO$_2$) as a coating layer on LiCoO$_2$ powders have been tried as they are less reactive against the electrolyte.[15,16] Even though the metal-oxide coatings are able to enhance the electrochemical properties, they failed to improve the thermal stability during overcharging. Aluminum phosphates have been reported to have a good chemical stability. Therefore, a surface coating of such materials is a potential candidate for improving the corrosion resistance.[17–19] When the AlPO$_4$ nanoparticles were coated uniformly on the cathode, the cells did not exhibit any

short-circuiting problems after being maintained at 12 V for up to 2 h (Figure 1b). However, the cell case, with a surface temperature of approximately 60°C, was swollen because of electrolyte decomposition. Furthermore, even with an instant short circuit, the voltage recovered to 12 V instantly and the surface temperature did not exceed 60°C (Figure 1c), with the result that no explosion was observed (Figure 1e). These findings show that the nanosized AlPO$_4$ coating layer remains stable, with a double layer (Helmholtz and diffuse layers) exhibiting a steep voltage drop within a few nm.[20] The reason that the AlPO$_4$ nanoparticle-coated LiCoO$_2$ is superior to bare LiCoO$_2$ or other metal-oxide coated cathodes, may be attributed to the strong P=O bond (bond energy = 5.64 eV), which is very resistant to chemical attack.[17–19] High thermal stability of the AlPO$_4$ nanoparticle layer can be attributed to the strong covalency of the PO$_4$ polyanions with the Al^{3+} ions in AlPO$_4$.[19] Differential scanning calorimetry (DSC) analysis of the AlPO$_4$-coated LiCoO$_2$ (charged to 4.3 V) exhibited an increased onset temperature of exothermic reaction by approximately 50°C, with a drastic decrease of heat generation by approximately one order of magnitude, when compared to bare LiCoO$_2$. The effect of AlPO$_4$ concentration on the thermal stability is currently being evaluated.

Furthermore, the electrochemical properties of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ are superior to bare LiCoO$_2$ or to Al$_2$O$_3$-coated cathodes, prepared using sol–gel techniques.[15,16] As shown in Figure 3, the AlPO$_4$ nanoparticle-coated LiCoO$_2$ shows approximately 99% retention of capacity at 1 C (equivalent to 140 mA g^{-1}), even after 20 cycles, whereas the bare LiCoO$_2$ gives only 88% retention. This result is also better than that reported for Al$_2$O$_3$-coated LiCoO$_2$ at a charging rate of 0.5 C ($\sim$94%).[16] In contrast to Al$_2$O$_3$- and ZrO$_2$-coated LiCoO$_2$, the AlPO$_4$ nanoparticle coating did not suppress c-axis expansion (approximately
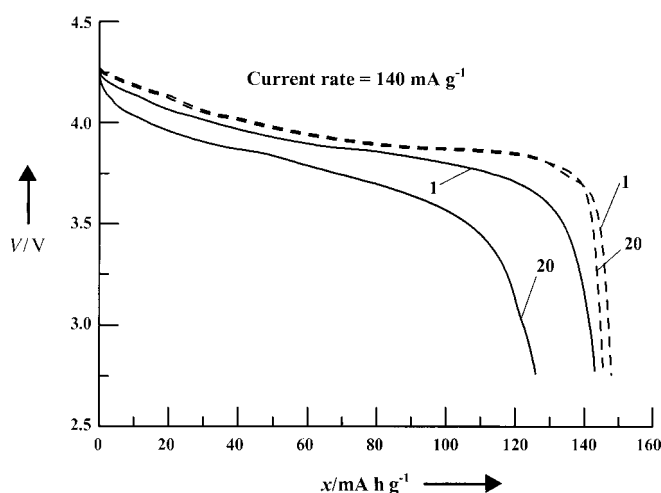

Figure 3. Voltage profiles of coin-type half cells with bare (——) and AlPO$_4$ nanoparticle-coated LiCoO$_2$ (-----) cathodes between 4.3 V and 2.75 V, after the first and twentieth charge cycles; the anode of the half cell was Li metal. After 0.1 C charging and discharging rates for the first two cycles, the charge and discharge current rates were 1 C (equivalent to 140 mAg^{-1}).

2.6 %). More detailed experiments regarding lattice constants are currently under way.

The remarkable improvements described herein can provide more tolerable cell design to battery manufacturers and hazard-free portable electronics to users. The simple process of using a water-based nanoparticle solution to prepare a nanoscalar coating on the cathode material can be easily extended to mass production.

Experimental Section

$Al(NO_3)_3 \cdot 9H_2O$ (3 g) and $(NH_4)_2HPO_4$ (1 g) were dissolved in distilled water until a white suspension (of $AlPO_4$ nanoparticles) was obtained. $LiCoO_2$ powders (with an average particle size of $\approx$ 10 μm) were then slowly added to the coating solution and were mixed until the final viscosity of the slurry reached approximately 100 poise. The weight ratio of $AlPO_4$ and $LiCoO_2$ was 3:97. The $LiCoO_2$ powders were obtained from Nippon Chemicals, and inductively coupled plasma (ICP) analysis showed that the Li content in Li_xCoO_2 was 1.0. Subsequently, the slurry was poured into a tray, dried in an oven for 6 h at 130°C, and annealed at 700°C for 5 h in a furnace. Several-hundred Li-ion batteries with bare and $AlPO_4$ nanoparticle-coated $LiCoO_2$ cathodes were assembled using an automated pilot production line in a clean room. The cell standard capacity was set at 1600 mA h (cell size: $3.2 \times 85 \times 53$ mm^3). $AlPO_4$ nanoparticle-coated $LiCoO_2$ or bare $LiCoO_2$ was used as the cathode, and the anode material was synthetic graphite. The electrolyte used was 1.03 M $LiPF_6$ in ethylene carbonate/diethylene carbonate/ethyl methyl carbonate (EC/DEC/EMC; 3:3:4 v/v/v).

[1] J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359–367.
[2] a) *Advanced Rechargeable Battery Industry 2001/02*, Nomura Research Institute Ltd., **2002**; b) *Annual Report on Sales of Li Secondary Battery in 2002*, Samsung SDI Co. Ltd., **2001**.
[3] a) "Laptop Batteries Are Linked to Fire Risk": New York Times, March 15, **2001**; b) US Consumer Product Safety Commission (http://www.cpsc.gov/cpscpub).
[4] R. A. Leising, M. J. Palazzo, E. S. Takeuchi, K. J. Takeuchi, *J. Electrochem. Soc.* **2001**, *148*, A838-A844.
[5] H. Maleki, S. A. Hallaj, J. R. Selman, R. B. Dinwiddie, H. Wang, *J. Electrochem. Soc.* **1999**, *146*, 947–954.
[6] Ph. Biensan, B. Simon, J. P. Pérès, A. de Guibert, M. Broussely, J. M. Bodet, F. Perton, *J. Power Sources* **1999**, *81–82*, 906–912.
[7] R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. I. Henderson, C. P. Kubiak, W. Mahoney, R. G. Osifchin, R. Reifenberger, *Science* **1996**, *272*, 1323–1325.
[8] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335–1338.
[9] L. N. Lewis, *Chem. Rev.* **1993**, *93*, 2693–2730.
[10] X. Peng, T. E. Wilson, A. P. Alivisatos, P. G. Schultz, *Angew. Chem.* **1997**, *109*, 113–115; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 145–147.
[11] A. P. Alivisatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, Jr., P. G. Schultz, *Nature* **1996**, *382*, 609–611.
[12] T. Cassagneau, F. Caruso, *Adv. Mater.* **2002**, *14*, 732–736.
[13] *Guideline for the Safety Evaluation of Secondary Lithium Cells*, Japan Battery Association, **1997**.
[14] *A Safety Standard for Lithium Batteries, UL1642*, 3rd ed., Underwriters Laboratories, **1995**.
[15] J. Cho, Y. J. Kim, T.-J. Kim, B. Park, *Angew. Chem.* **2001**, *113*, 3471–3473; *Angew. Chem. Int. Ed.* **2001**, *40*, 3367–3369.
[16] J. Cho, Y. J. Kim, B. Park, *Chem. Mater.* **2000**, *12*, 3788–3791.
[17] P. K. Rastogi, Y.-W. Kim, *J. Appl. Phys.* **1985**, *57*, 4223–4225.
[18] S. W. Martin, Ph.D. Thesis, Purdue University, **1986**.
[19] *Encyclopedia of Inorganic Chemistry, Vol. 1* (Ed.: R. B. King), Wiley, New York, **1994**, pp. 302–305.
[20] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, pp. 544–554.