

## A Breakthrough in the Safety of Lithium Secondary Batteries by Coating the Cathode Material with $\text{AlPO}_4$ Nanoparticles \*\*

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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  $\text{LiCoO}_2$  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.<sup>[1,2]</sup> 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<sup>[†]</sup> of the cell, has not been prevented. Moreover, numerous battery accidents with accompanying fires and explosions have been reported.<sup>[3]</sup> The main cause of such disasters is that  $\text{LiCoO}_2$  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.<sup>[4–6]</sup> Furthermore, this process converts  $\text{LiCoO}_2$  into the strong oxidizing agent  $\text{Co}_2\text{O}_3$ , 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

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[†] 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.

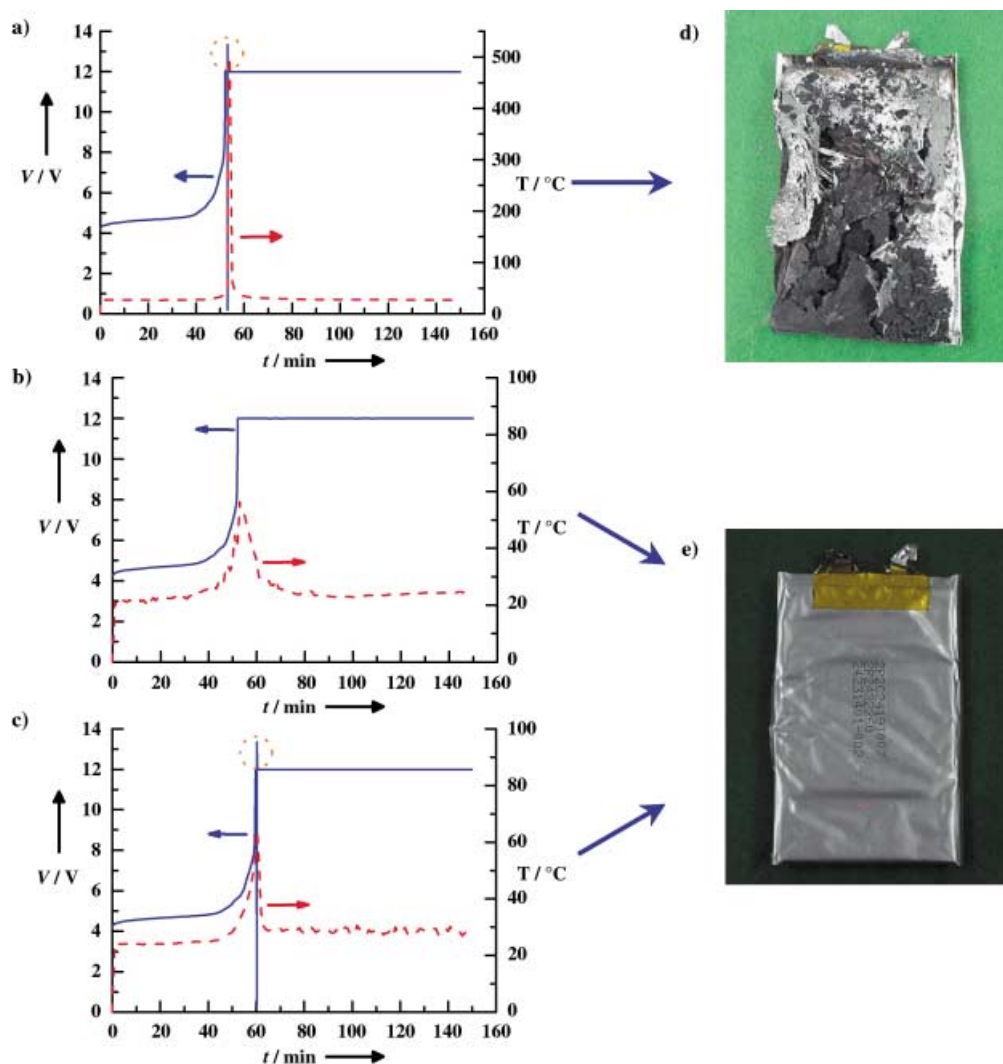
aluminum case, because the former is not able to withstand the severe deformation of the electrodes.

There have been many reports of the surface modification of nanoparticles with a functional monolayer or a polymer shell that tailors their surface properties.<sup>[7–12]</sup> 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<sub>2</sub> cathodes by applying a direct coating of AlPO<sub>4</sub> nanoparticles from an aqueous solution.

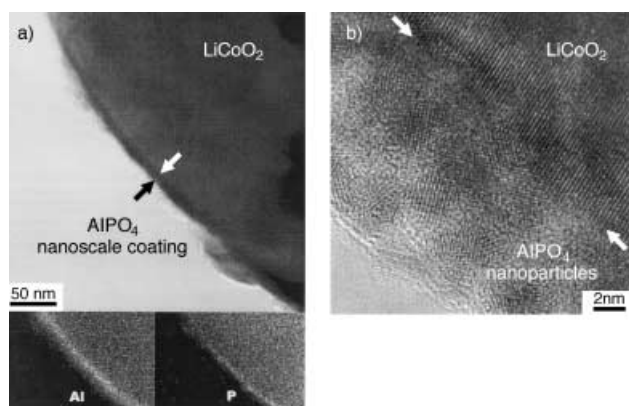
The overcharge safety tests were conducted following guidelines set out for the safety evaluation of secondary lithium cells. The guidelines require that although the casing of the cells may become swollen, the cells should not explode or catch fire.<sup>[13,14]</sup> Figure 1 shows the voltage and temperature

profiles of the cell with both bare LiCoO<sub>2</sub> cathodes and cathodes coated with AlPO<sub>4</sub> 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<sup>-1</sup> = 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<sub>4</sub> nanoparticle-coated LiCoO<sub>2</sub>. As shown in Figure 2a, a nanoscalar AlPO<sub>4</sub> layer (approximately 15 nm) was coated homogeneously over the LiCoO<sub>2</sub> 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<sub>4</sub> nanoparticles embedded in the nanoscalar coating layer. The layer consisted of randomly oriented AlPO<sub>4</sub> nanoparticles with an average



**Figure 1.** a) Voltage and temperature profiles of a cell with a bare LiCoO<sub>2</sub> 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<sup>-1</sup> = 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<sub>4</sub> nanoparticle-coated LiCoO<sub>2</sub> 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<sub>2</sub> cathode after the 12 V overcharge test; the cell burned and exploded at that voltage. e) a picture of a cell containing the AlPO<sub>4</sub> nanoparticle-coated LiCoO<sub>2</sub> after the 12 V overcharge test.



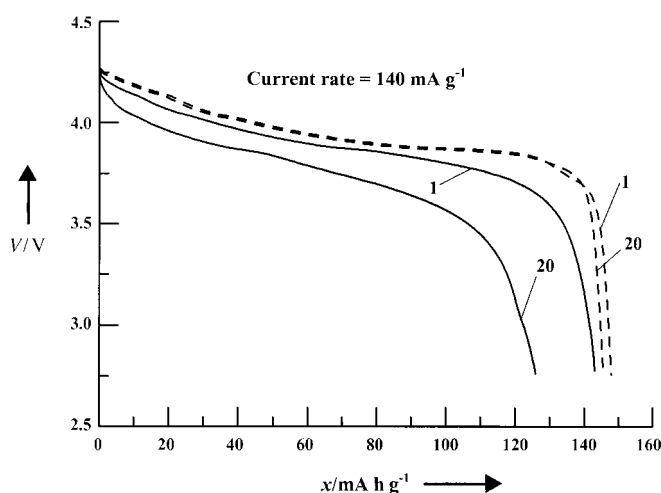
**Figure 2.** a) TEM bright-field image of the  $\text{AlPO}_4$  nanoparticle-coated  $\text{LiCoO}_2$ ; EDS confirms the Al and P components in the coating layer. b) High-resolution TEM image showing the  $\text{AlPO}_4$  nanoparticles ( $\approx 3$  nm in diameter) in the nanoscale coating layer; the arrows indicate the interface between the  $\text{AlPO}_4$  layer and  $\text{LiCoO}_2$ .

diameter of approximately 3 nm, with a regular distribution of Al and P components throughout the layer. X-ray diffraction patterns of the  $\text{LiCoO}_2$  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  $\text{AlPO}_4$  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  $\text{LiCoO}_2$  and the  $\text{AlPO}_4$  nanoparticle layer at  $700^\circ\text{C}$ .

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  $120^\circ\text{C}$ . Therefore, any direct contact of the anode and cathode electrodes induces a short circuit. This has been the problem in cells with a bare  $\text{LiCoO}_2$  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  $500^\circ\text{C}$ , 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. Nanoscale metal oxides ( $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$ ) as a coating layer on  $\text{LiCoO}_2$  powders have been tried as they are less reactive against the electrolyte.<sup>[15,16]</sup> 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.<sup>[17–19]</sup> When the  $\text{AlPO}_4$  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  $60^\circ\text{C}$ , 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  $60^\circ\text{C}$  (Figure 1c), with the result that no explosion was observed (Figure 1e). These findings show that the nanosized  $\text{AlPO}_4$  coating layer remains stable, with a double layer (Helmholtz and diffuse layers) exhibiting a steep voltage drop within a few nm.<sup>[20]</sup> The reason that the  $\text{AlPO}_4$  nanoparticle-coated  $\text{LiCoO}_2$  is superior to bare  $\text{LiCoO}_2$  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.<sup>[17–19]</sup> High thermal stability of the  $\text{AlPO}_4$  nanoparticle layer can be attributed to the strong covalency of the  $\text{PO}_4$  polyanions with the  $\text{Al}^{3+}$  ions in  $\text{AlPO}_4$ .<sup>[19]</sup> Differential scanning calorimetry (DSC) analysis of the  $\text{AlPO}_4$ -coated  $\text{LiCoO}_2$  (charged to 4.3 V) exhibited an increased onset temperature of exothermic reaction by approximately  $50^\circ\text{C}$ , with a drastic decrease of heat generation by approximately one order of magnitude, when compared to bare  $\text{LiCoO}_2$ . The effect of  $\text{AlPO}_4$  concentration on the thermal stability is currently being evaluated.

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



**Figure 3.** Voltage profiles of coin-type half cells with bare (—) and  $\text{AlPO}_4$  nanoparticle-coated  $\text{LiCoO}_2$  (----) 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  $140 \text{ mA g}^{-1}$ ).

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 nanoscale coating on the cathode material can be easily extended to mass production.

### Experimental Section

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (3 g) and  $(\text{NH}_4)_2\text{HPO}_4$  (1 g) were dissolved in distilled water until a white suspension (of  $\text{AlPO}_4$  nanoparticles) was obtained.  $\text{LiCoO}_2$  powders (with an average particle size of  $\approx 10 \mu\text{m}$ ) 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  $\text{AlPO}_4$  and  $\text{LiCoO}_2$  was 3:97. The  $\text{LiCoO}_2$  powders were obtained from Nippon Chemicals, and inductively coupled plasma (ICP) analysis showed that the Li content in  $\text{Li}_x\text{CoO}_2$  was 1.0. Subsequently, the slurry was poured into a tray, dried in an oven for 6 h at  $130^\circ\text{C}$ , and annealed at  $700^\circ\text{C}$  for 5 h in a furnace. Several hundred Li-ion batteries with bare and  $\text{AlPO}_4$  nanoparticle-coated  $\text{LiCoO}_2$  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:  $3.2 \times 85 \times 53 \text{ mm}^3$ ).  $\text{AlPO}_4$  nanoparticle-coated  $\text{LiCoO}_2$  or bare  $\text{LiCoO}_2$  was used as the cathode, and the anode material was synthetic graphite. The electrolyte used was 1.03 M  $\text{LiPF}_6$  in ethylene carbonate/diethylene carbonate/ethyl methyl carbonate (EC/DEC/EMC; 3:3:4 v/v/v).

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