A Breakthrough in the Safety of Lithium Secondary Batteries by Coating the Cathode Material with AlPO₄ 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 LiCoO₂ 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 LiCoO₂ 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 LiCoO₂ into the strong oxidizing agent Co₂O₃, 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

[+] 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 LiCoO₂ cathodes by applying a direct coating of AlPO₄ 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 LiCoO₂ cathodes and cathodes coated with AlPO₄ 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 AlPO₄ nanoparticle-coated LiCoO₂. As shown in Figure 2a, a nanoscalar AlPO₄ layer (approximately 15 nm) was coated homogeneously over the LiCoO₂ 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 AlPO₄ nanoparticles embedded in the nanoscalar coating layer. The layer consisted of randomly oriented AlPO₄ nanoparticles with an average
The metal-oxide coatings are able to have been tried as they are less reactive against the electrolyte. Even though the AlPO4 nanoparticles were coated 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. When the AlPO4 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 AlPO4 coating layer remains stable, with a double layer (Helmholtz and diffuse layers) exhibiting a steep voltage drop within a few nm. Differential scanning calorimetry (DSC) analysis of the AlPO4-coated LiCoO2 (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 LiCoO2. The effect of AlPO4 concentration on the thermal stability is currently being evaluated. Furthermore, the electrochemical properties of the AlPO4 nanoparticle-coated LiCoO2 are superior to bare LiCoO2 or to Al2O3-coated cathodes, prepared using sol–gel techniques. As shown in Figure 3, the AlPO4 nanoparticle-coated LiCoO2 shows approximately 99% retention of capacity at 1 C (equivalent to 140 mA g⁻¹), even after 20 cycles, whereas the bare LiCoO2 gives only 88% retention. This result is also better than that reported for Al2O3-coated LiCoO2 at a charging rate of 0.5 C (~94%). In contrast to Al2O3- and ZrO2-coated LiCoO2, the AlPO4 nanoparticle coating did not suppress c-axis expansion (approximately

Figure 2. a) TEM bright-field image of the AlPO4 nanoparticle-coated LiCoO2; EDS confirms the Al and P components in the coating layer. b) High-resolution TEM image showing the AlPO4 nanoparticles (~3 nm in diameter) in the nanoscale coating layer; the arrows indicate the interface between the AlPO4 and LiCoO2.

Figure 3. Voltage profiles of coin-type half cells with bare (---) and AlPO4 nanoparticle-coated LiCoO2 (-----) 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 mA g⁻¹).
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(NO₃)₃·9H₂O (3 g) and (NH₄)₂HPO₄ (1 g) were dissolved in distilled water until a white suspension (of AlPO₄ nanoparticles) was obtained. LiCoO₂ powders (with an average particle size of approximately 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 AlPO₄ and LiCoO₂ was 3:97. The LiCoO₂ powders were obtained from Nippon Chemicals, and inductively coupled plasma (ICP) analysis showed that the Li content in LiₓCoO₂ 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 AlPO₄ nanoparticle-coated LiCoO₂ cathodes were assembled using an automated pilot production line in a clean room. The cell standard capacity was set at 1600 mAh (cell size: 3.2 V × 53 mm × 53 mm). AlPO₄ nanoparticle-coated LiCoO₂ or bare LiCoO₂ was used as the cathode, and the anode material was synthetic graphite. The electrolyte used was 1.03 M LiPF₆ in ethylene carbonate/diethylene carbonate/ethyl methyl carbonate (EC/DEC/EMC; 3:3:4 v/v/v).

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**Mixed-Valent Spin-Crossover System**

An Unprecedented Homochiral Mixed-Valence Spin-Crossover Compound

Spin doctoring: \([\text{Fe}^{II}H_3L][\text{Fe}^{III}L](\text{NO}_3)_2\), where \(H_3L\) is a hexadentate tripod ligand bearing three imidazole groups, is formed in a one-pot assembly reaction, and is shown to be a homochiral mixed-valence spin-crossover compound. The structure consists of a 2D assembled sheet that is held together by imidazole–imidazolate hydrogen bonds between \([\text{Fe}^{II}H_3L]^+\) and \([\text{Fe}^{III}L]\) units (see picture). At least three electronic states can be accessed by temperature effects and photoirradiation.

**Nanoparticle-Coated Electrodes**

J. Cho,* Y.-W. Kim, B. Kim, J.-G. Lee, B. Park*  
A Breakthrough in the Safety of Lithium Secondary Batteries by Coating the Cathode Material with AlPO\(_4\) Nanoparticles

The hard cell! There have been numerous reports highlighting the questionable safety of lithium secondary batteries, an example of which is shown here, where exothermic reactions of LiCoO\(_2\) electrodes have considerable fire and explosion potential. The coating of such electrodes with a layer of AlPO\(_4\) nanoparticles is shown to reduce these risks significantly, even where a short circuit of the cell was observed.

**Carbon Nanorings**

T. Kawase,* Y. Seirai, H. R. Darabi, M. Oda,* Y. Sarakai, K. Tashiro*  
All-Hydrocarbon Inclusion Complexes of Carbon Nanorings: Cyclic [6]- and [8]Paraphenyleneacetylenes

Ringing the changes: The belt-shaped \(\pi\)-conjugated [6]- and [8]paraphenyleneacetylenes exhibit nanosized cavities (see picture), and act as host molecules in crystalline inclusion complexes with hexamethylbenzene and toluene, respectively. The concave side of the cavities appears to possess a negative electronic potential.

**Nanoring–Fullerene Complexes**

T. Kawase,* K. Tanaka, N. Fujiwara, H. R. Darabi, M. Oda*  
Complexation of a Carbon Nanoring with Fullerenes

Unusually stable complexes are formed between [6]paraphenyleneacetylene ([6]CPPA, see picture) and fullerenes (either C\(_{60}\) or bis(ethoxy carbonyl)methanofullerene). Crystallographic analysis reveals that a major driving force for the formation of such complexes is the existence of a novel concave–convex \(\pi\)-\(\pi\) interaction (see structure).