Effect of P_2O_5 and $AlPO_4$ Coating on $LiCoO_2$ Cathode Material

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The thermal stability and electrochemical properties of P_2O_5-coated and $AlPO_4$-coated $LiCoO_2$ powders were compared with those of bare $LiCoO_2$. Even though all samples had a similar initial capacity at a low current rate, the capacity retention after 20 cycles at 1 C (= 140 mA/g) was in the order of $AlPO_4$-coated, bare, and P_2O_5-coated $LiCoO_2$. Differential scanning calorimetry (DSC) results of both the P_2O_5-coated and $AlPO_4$-coated samples (charged up to 4.3 V) showed that the initial exothermic-reaction temperatures with the flammable electrolytes increased to ∼230 °C (from ∼180 °C in bare $LiCoO_2$), and the coating greatly reduced the amount of exothermic heat generation by approximately 1 order of magnitude, compared to that of the bare $LiCoO_2$. This is consistent with the result of the 12-V overcharge tests in the Li-ion cells with the bare and coated $LiCoO_2$. Upon charging up to 12 V at the rate of 2 C, the coated samples did not exhibit thermal runaway, and the cell-surface temperature remained below 120 °C. On the other hand, bare $LiCoO_2$ under the same conditions caught fire and exploded, with the cell-surface temperature reaching 450 °C.

Introduction

Since Li-ion cells were first commercialized in 1995, their capacity has increased by ∼8% every year. This increase is due to the development of a high-density electrode manufacturing technology, and the use of lighter cell components and cases. However, the boost in the cell capacity leads to an increase in safety concerns. Consequently, a protection device (consisting of PTC material that blocks the rapid increase in the cell temperature, and the protective circuits that block overcharging, overdischarging, and overcurrent) needs to be installed in the Li-ion pack of mobile electronics to prevent any safety hazards during the cell operation. Nevertheless, many safety accidents involving overheating, fire, and explosion have been reported in the press, and the safety of Li-ion cells remains an unsolved problem.[1]

The safety of Li-ion cells is mainly related to the exothermic thermal decomposition of the electrolyte, cathode, and anode.[2−14] Among these, the exothermic reaction of the flammable electrolyte with the cathode material is known to be a trigger point for the thermal runaway.[4−7] As a way of minimizing such a reaction, many efforts have been focused on developing a nonflammable electrolyte using phosphorus-based additives and cosolvents in the electrolytes.[15−17] Some other additives, for example, γ-butyrolactone, have been used to reduce the direct reaction of the cathode with the electrolyte at the charged state, but this solvent was reported to decompose into the organic products, thereby encapsulating the cathode.[18] These additives caused problems related to their compatibility with the electrode, cycle-life performance, and rate capability. Therefore, other techniques to advance the safety aspects are needed.

Among the abuse tests of Li-ion cells, the 12-V overcharge test is the most crucial because the cell may be directly charged to 12 V (the limit of the power supply) at a higher current over the nominal capacity.

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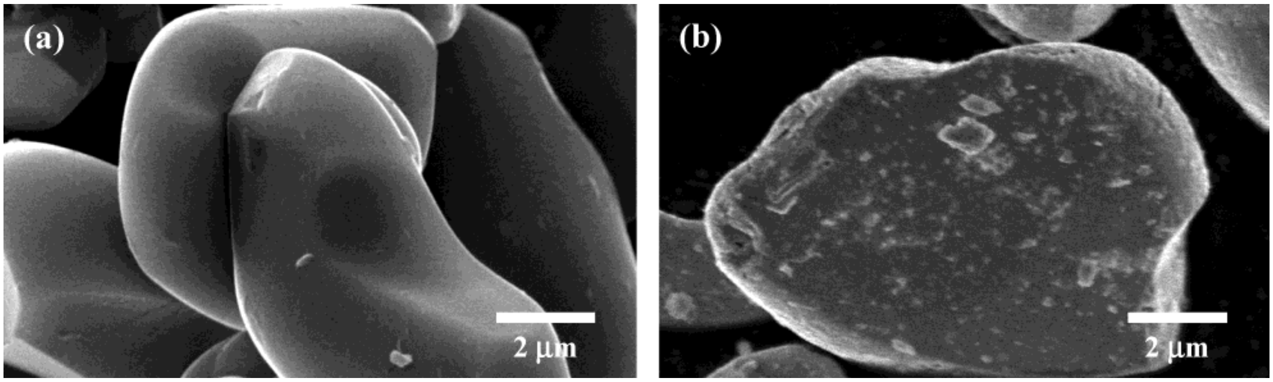

Figure 1. SEM images of the (a) P_2O_5-coated and (b) $AlPO_4$-coated $LiCoO_2$ powders. The surface morphology of the bare $LiCoO_2$ was similar to that of the P_2O_5-coated $LiCoO_2$.

This limiting condition can occur when the protection device malfunctions or an internal short-circuit occurs during charging, which can result in heat generation, causing an exponential temperature increase against the slow heat dissipation.[9] This leads to fire and explosion of the cell with the ignition of components.

As a way of preventing the thermal-runaway problem in a cathode, by minimizing the exothermic reaction of the cathode material with the electrolyte during the 12-V overcharge tests, without sacrificing the electrochemical properties, this paper investigated the effects of P_2O_5 and $AlPO_4$ coating on a $LiCoO_2$ cathode material.

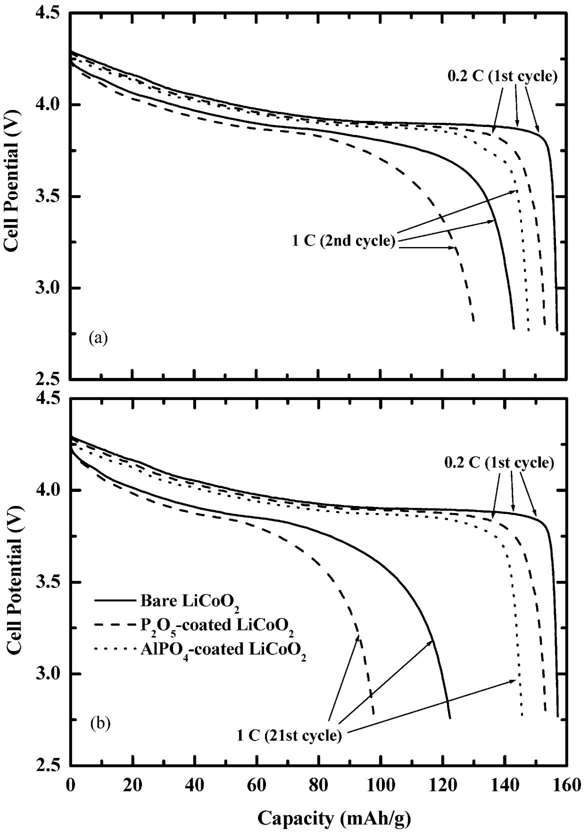

Figure 2. Discharge curves of the first cycle at 0.2 C rate in the bare, the P_2O_5-coated, and the $AlPO_4$-coated $LiCoO_2$, with (a) the second cycle at 1 C rate (= 140 mA/g) and (b) the 21st cycle at 1 C rate (for 20 cycles).

Experimental Section

To coat P_2O_5 on the $LiCoO_2$ powders, 4 g of $(NH_4)_2HPO_4$ was dissolved in distilled water (30 g) and mixed with the $LiCoO_2$ powders (with average particle size of 10 μm and BET surface area of 0.2 m^2/g). After being dried at 100 °C for 5 h, the mixed slurry was fired at 600 °C for 5 h, and cooled to room temperature for 2 h. The $AlPO_4$ coating was accomplished by mixing $Al(NO_3)_3{\cdot}9H_2O$ and $(NH_4)_2HPO_4$ (3 and 1 g, respectively) in ethanol (30 g) using a magnetic bar for 12 h. When a white suspension of nanosized $AlPO_4$ particles was formed, it was mixed with the cathode powder (50 g), dried at 120 °C for 6 h, and followed by firing at 600 °C for 5 h. X-ray diffraction (XRD) of both coated samples did not show the presence of any crystalline phase in the coating layer. The assembly of the coin-type half-cells and sample preparation were previously described in ref 19. The cells were then disassembled in a glovebox to get the charged cathode which typically contained ~35 wt. % electrolyte, ~30 wt. % Al foil, ~2 wt. % carbon black/binder, and ~33 wt. % cathode material. Approximately 10 mg of the cathode was hermetically sealed in a sample pan for the differential scanning calorimetry (DSC) measurements. Only the cathode material was used to calculate the specific-heat flow. The heating rate of the DSC measurements was 3 °C/min. The cathode electrode consisted of a $LiCoO_2$ cathode material, a PVDF binder, and Super P carbon black (94:3:3 wt. %). The electrolyte used was 1 M $LiPF_6$ with EC/DEC/EMC (30:30:40 vol. %).

Li diffusivities of the cathodes were measured using the galvanostatic intermittent titration technique (GITT) after precycles (with a Li-metal anode) at the rate of 0.1, 0.2, 0.5, and 1 C for each cycle between 4.4 and 3 V.[20−21] For the 12-V overcharge tests, pouch-type Li-ion cells were assembled using synthetic graphite (PHS) as the anode material. The anode/cathode dimensional ratio was fixed at 1.15. The cell standard capacity was set at 800 mAh [cell size: 6.5 × 48 × 34 mm^3]. The 12-V overcharge tests were performed following the safety test guidelines,[22,23] and the currents corresponding to 1 and 2 C were applied to the cell until the voltage reached 12 V, and kept at that voltage until the cell-surface temperature dropped to below ~50 °C. Before the overcharge tests for any potential overheating, fire, or explosion, all the fresh cells were first charged to 4.2 V at a rate of 1 C (= 800 mA).

Results and Discussion

Figure 1 compares the scanning electron microscopy (SEM) images of the P_2O_5-coated and $AlPO_4$-coated

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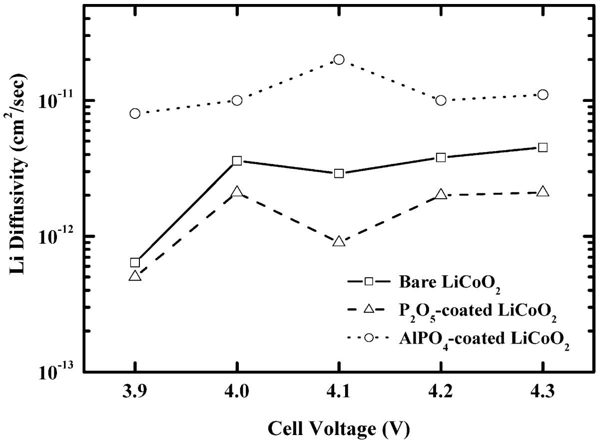

Figure 3. Li diffusivities as a function of the charge voltage of the bare, the P_2O_5-coated, and the $AlPO_4$-coated $LiCoO_2$. Test cells were pre-cycled at the rate of 0.1, 0.2, 0.5, and 1 C (= 140 mA/g) for each cycle between 4.4 and 3 V.

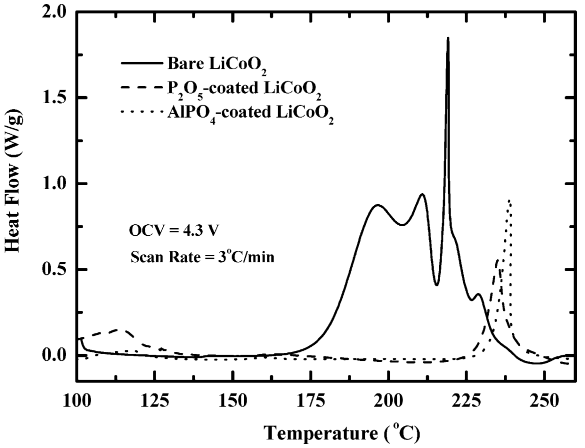

Figure 4. DSC scans of the bare, the P_2O_5-coated, and the $AlPO_4$-coated $LiCoO_2$, after the first charge to 4.3 V.

$LiCoO_2$, showing distinct surface morphologies. The surface morphology of the bare cathode particle is similar to that of the P_2O_5-coated one. Recent transmission electron microscopy (TEM) results confirmed the formation of an $AlPO_4$-nanoparticle coating layer with a thickness of ~10 nm.[24] Using these powders, the initial discharge curves at 0.2 C (= 28 mA/g) and the capacity retention after 20 cycles at 1 C were measured, as shown in Figure 2. The voltage profile of the bare and $AlPO_4$-coated $LiCoO_2$ at the 0.2 C rate appears similar, while that of the P_2O_5-coated $LiCoO_2$ is slightly inferior. After 20 cycles at 1 C, the capacity of the P_2O_5-coated $LiCoO_2$ decreases by ~24% (from 130 mAh/g). In contrast, the $AlPO_4$-coated $LiCoO_2$ sample has superior capacity retention, showing only an approximately 1% decrease after 20 cycles at 1 C. This capacity retention is well correlated with the trend of Li diffusivity, as shown in Figure 3. The $AlPO_4$-coated $LiCoO_2$ shows the least decrease of Li diffusivity after pre-cycles, and the P_2O_5-coated $LiCoO_2$ has worse diffusivity than the bare $LiCoO_2$.

To evaluate the reaction between the cathode electrodes and the electrolyte, DSC measurements of the charged electrodes at 4.3 V were carried out (Figure 4).

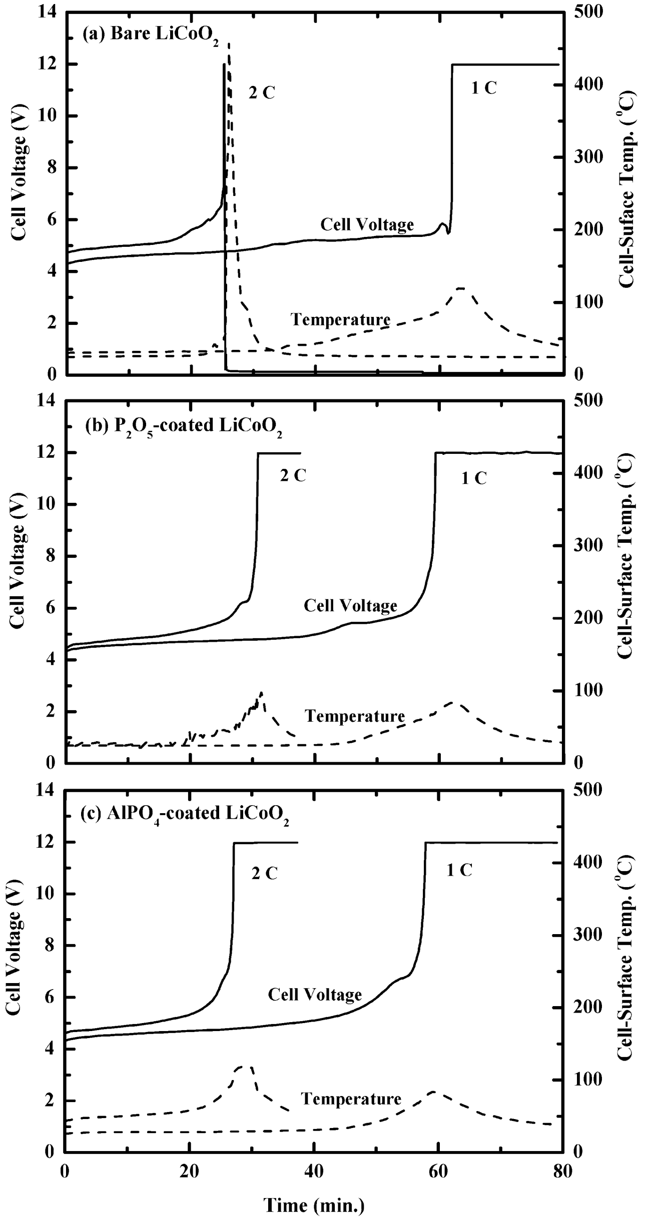

Figure 5. Cell voltage and cell-surface temperature vs time during the overcharge tests at 1 and 2 C (1 C = 800 mA) for the (a) bare, (b) P_2O_5-coated, and (c) $AlPO_4$-coated $LiCoO_2$. The currents were applied to the cell until the voltage reached 12 V. The cells were then kept at that voltage until the cell-surface temperature had dropped to below ~50 °C.

The extent of the exothermic reaction is related to the generation of oxygen from the cathode.[4,13,14] The exothermic reaction of the bare sample begins at ~180 °C. However, both the P_2O_5-coated and $AlPO_4$-coated $LiCoO_2$ powders show remarkably reduced heat generation by an order of magnitude compared to that of the bare sample, and the initial exothermic-reaction temperature is raised to ~230 °C. This result suggests that coating Li_xCoO_2 with phosphorus-containing compounds retards the reaction with the electrolytes.

To further examine the thermal stability of the bare, the P_2O_5-coated, and the $AlPO_4$-coated $LiCoO_2$, the 12-V overcharge tests were performed using Li-ion cells with a nominal capacity of 800 mAh (Figure 5). One main feature during the 12-V overcharge test is the steep voltage uprise above ~6 V. In this voltage region, depending on the cathode and applied current, the cell-

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surface temperature rises rapidly. The internal temperature can increase above the melting temperature of the Li metal ($T_m = 180$ °C) deposited on the anode, accompanying a separator shutdown and a rapid increase in the cell resistance. Furthermore, $LiCoO_2$ converts into Co_3O_4 with the evolution of oxygen and changes to thermally unstable states.[4−8] Therefore, any internal short circuit directly leads to the thermal runaway of the Li-ion cell, with an accompanying fire and explosion. In addition, melting of the deposited lithium metal significantly accelerates the thermal runaway of the cell.

Figure 5 shows the voltage and temperature profiles of the bare, P_2O_5-coated, and $AlPO_4$-coated $LiCoO_2$ cathodes during the 12-V overcharge test. The temperature profile of both the P_2O_5-coated and $AlPO_4$-coated samples is lower than that of the bare sample at 1 C. This means that the phosphorus-containing coating layer minimizes the reaction with the electrolyte that produces oxygen from the Li_xCoO_2, leading to less heat generation. These results correlate well with the DSC experiments shown in Figure 4. Note that bare $LiCoO_2$ shows the cell-voltage drop at approximately 5 V before the spike to 12 V, but not the coated samples. It has been reported that such a short-time voltage drop is associated with a decrease in the internal resistance of the cell due to the increasing temperature.[11]

Upon charging at a rate of 2 C, the voltage profile of the bare $LiCoO_2$ is totally different from that of the coated samples, showing a sharp voltage drop to 0 V from 12 V, with the cell-surface temperature of approximately 450 °C. This study found that the five tested cells were destroyed and soot-covered as a result of the fire and explosion. This is due to an instant internal short-circuit of the cell at 12 V. Surprisingly, the P_2O_5-coated and $AlPO_4$-coated samples did not burn or explode at the charge rate of 2 C, except that these cells began to swell due to the decomposition of the electrolyte itself. (Five tested full cells, of each type, showed similar results.) These results suggest that the $LiCoO_2$ powders encapsulated with the phosphorus-containing oxides have a significantly lower exothermic-reaction rate with the electrolyte. Note that the cell-surface temperature at 2 C rate is higher than that at 1 C, indicating accelerated heat generation. Generally, it is known that the cell-internal temperature can be ∼100 °C higher than the cell-surface temperature[11]. However, these results show that the cathode encapsulated with an inert P_2O_5 or $AlPO_4$ coating layer prevents such a thermal runaway.

Conclusions

The electrochemical properties and thermal stability of the P_2O_5-coated and $AlPO_4$-coated $LiCoO_2$ were compared with those of the bare $LiCoO_2$. The $AlPO_4$-coated $LiCoO_2$ showed excellent capacity retention, compared to those of the bare and P_2O_5-coated samples. Moreover, the phosphorus-containing oxide coating raised the initial exothermic-reaction temperatures with the flammable electrolytes by ∼50 °C, and reduced the exothermic heat generation by approximately 1 order of magnitude. In addition, in the overcharge tests at the rate of 2 C, the P_2O_5- and $AlPO_4$-coated samples did not exhibit thermal runaway, while the bare samples caught fire and exploded, with the cell-surface temperatures reaching ∼450 °C.

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