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Comparison of Overcharge Behavior of $AlPO_4$-Coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ Cathode Materials in Li-Ion Cells

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The overcharge behavior of $AlPO_4$-coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes was compared to that of $AlPO_4$-coated Li_xCoO_2 cathodes in Li-ion cells. The former exhibited less heat generation than the latter as the charge voltage increased. Moreover, the coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode showed two distinct sets of exothermic peaks beginning at ~75 and ~200°C, respectively, while the coated Li_xCoO_2 exhibited relatively continuously increasing exothermic peak beginning at ~150°C. The results were consistent with the 12 V overcharge tests using Li-ion full cells. As the C rate increased from 1 to 3 C, the cell-surface temperature with the $AlPO_4$-coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode did not exceed ~125°C, and that of the coated Li_xCoO_2 exceeded ~170°C. However, the Li-ion cells containing either cathode with the $AlPO_4$-nanoparticle coating did not exhibit thermal runaway, although short-circuits occurred at 12 V during a 3 C overcharging rate. It is evident that the $AlPO_4$-coating layer on the powder drastically reduced the violent exothermic reaction between the electrolyte and cathode, controlling the overall safety of the Li-ion cells.
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Along with the improvement in the electrochemical properties of Ni-based cathode materials ($LiNi_{1-x}M_xO_2$ where M = metals), thermal instability with respect to Li_xCoO_2 is a great concern for use in Li-ion cells.[1-12] Ni-based cathode materials have not met the safety guidelines that require no explosions, fire, or smoke during the nail penetration test at a 4.35 V overcharged state in Li-ion cells.[13] In terms of thermal stability, the violent exothermic reaction of the cathode with the electrolyte accompanying substantial heat generation should be avoided. Otherwise, it causes thermal runaway, exhibiting fire, sparks, and explosions.

To minimize oxygen evolution (heat generation), addition of Mg, Ti, or Al in $LiNiO_2$ was reported to be effective in reducing the exothermic reaction, but greatly sacrificed the discharge capacity.[14,15] For example, a $LiNi_{0.7}Ti_{0.15}Mg_{0.15}O_2$ cathode showed 190 mAh/g even at the charged voltage of 5 V, and its specific capacity at a 4.3 V cutoff is smaller than $LiCoO_2$.[14] To overcome the thermal instability of Ni-based cathode materials, some additives (for example, γ-butyrolactone) were used to reduce the direct reaction of the cathode with the electrolyte at the charged states. This solvent was reported to decompose into the organic products, thereby encapsulating the cathode, blocking any direct reaction with the electrolyte.[13] As a consequence, Li-ion cells containing this solvent did not explode during the nail penetration (at 4.35 V) and overcharge tests to 12 V. However, such an additive has raised concerns about its compatibility with the anode and cathode, which therefore still needs to tailor its electrochemical properties.

Recently, a more fundamental approach was used to improve the thermal stability of the cathode materials.[16] Cho *et al.* demonstrated that a nanoparticle-$AlPO_4$ coating on the $LiCoO_2$ cathodes blocked the thermal runaway of the Li-ion cell, and significantly reduced the electrolyte oxidation as well as Co dissolution into the electrolyte. In this paper, we report the 12 V overcharge behavior of the $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in terms of their exothermic behavior.

Experimental

Synthesis of $AlPO_4$*-coated* $LiCoO_2$ *and* $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.—$LiCoO_2$ was prepared from stoichiometric amounts of Li_2CO_3 and Co_3O_4 (average particle size of 2-3 μm). After mixing these starting materials using an automatic mixer for 2 h, the mixture was preheated at 600°C for 6 h, and thoroughly remixed again, followed by firing at 900°C for 24 h. To coat the $AlPO_4$ nanoparticles on the $LiCoO_2$ cathode, 3 g of $Al(NO_3)_3 \cdot 9H_2O$ and 1.04 g of $(NH_4)_2HPO_4$ were dissolved and stirred in 20 g of water until a white $AlPO_4$ nanoparticle suspension was observed. $LiCoO_2$ (100 g) with an average particle size of ~10 μm was added to the coating solution and thoroughly mixed for 5 min. The slurry was then dried in an oven at 120°C for 6 h and heat-treated in a furnace at 700°C for 5 h. Transmission electron microscopy (TEM) confirmed that the Al and P elements were confined within ~10 nm from the surface.[16]

The $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ starting material consisting of spherical particles (~13 μm diam) was prepared by co-precipitation from a solution containing stoichiometric amounts of nickel and cobalt nitrates, and manganese nitrate by the addition of NaOH and NH_4OH solutions in the reactor.[2] The $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was prepared by mixing stoichiometric amounts of LiOH and $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$, followed by heat-treatment at 800°C for 20 h in a stream of dried air. An excess amount of Li (1.02 mole) was used to compensate for the loss of Li during firing. The resultant powders showed a Brunauer, Emmett, and Teller (BET) surface area of 1 m^2/g. The process for $AlPO_4$ coating on the cathode is identical to the $LiCoO_2$ described above.

Preparation of test cells.—The cathodes for the battery test cells were made from the cathode material, Super P carbon black, and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 96:2:2. The electrodes were prepared by coating a cathode-slurry onto an Al foil followed by drying at 130°C for 20 min. The slurry was prepared by thoroughly mixing a N-methyl-2-pyrrolidone (NMP) solution of PVdF, carbon black, and the powdery cathode material. The coin-type battery test cells (size 2016) prepared in helium-filled glove box contained a cathode, a Li metal anode, and a microporous polyethylene separator. The electrolyte was 1 M $LiPF_6$ with ethylene carbonate/diethylene carbonate/ethylmethyl carbonate (EC/DEC/EMC) (30:30:40 vol %, Cheil Ind. Korea). We used standardized coin-cell parts (2016R-type), and normally the amount of the electrolyte was ~0.1 g in each cell. Each test cathode contained ~25 mg of either $LiCoO_2$ or $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The test cells were aged at room temperature for 24 h prior to the electrochemical test. Cells with a dimension 3.4 × 40 × 62 mm were used for the 12 V overcharging experiments, and the anode material was synthetic graphite. The dimensional ratio of anode to cathode (matching ratio) was 1.08:1 for the Li-ion cells. The overcharge test used the guidelines reported elsewhere.[17] The cell-surface temperature was monitored using a

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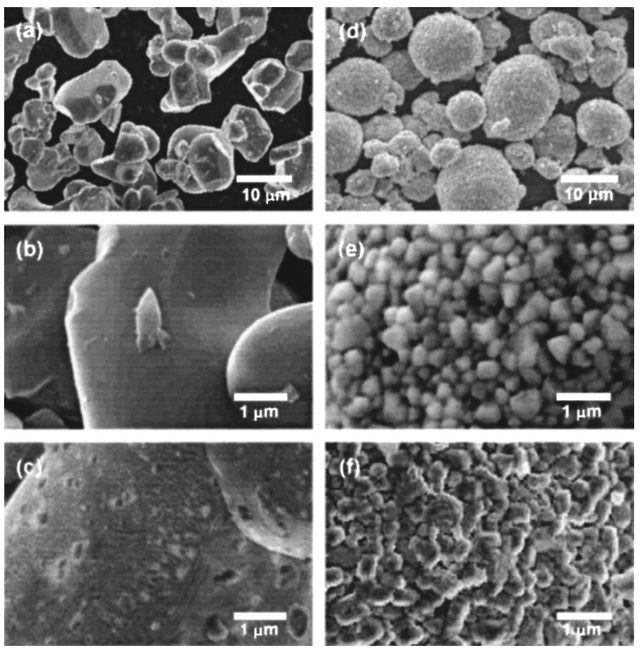

Figure 1. (a) and (b) SEM micrographs for bare $LiCoO_2$, and (c) for $AlPO_4$-coated $LiCoO_2$. (d) and (e) Micrographs of bare $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. (f) Micrograph from $AlPO_4$-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

K-type thermocouple placed on the center of the largest face in the cell can, and the thermocouple was tightly glued with insulating tape.

Electrochemical and DSC testing.—To compare the capacity of the $AlPO_4$-coated $LiCoO_2$ with $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode, coin-type half-cells were used with a charge cutoff voltage of 4.3 V at the charge and discharge rates with a constant current of 0.1 C (14 and 18 mA/g, respectively). The cycling tests of the Li-ion cells containing $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ were carried out by charging and discharging the cells at a 1 C rate for 200 cycles at 21°C. The rate-capability tests of the Li-ion cells containing

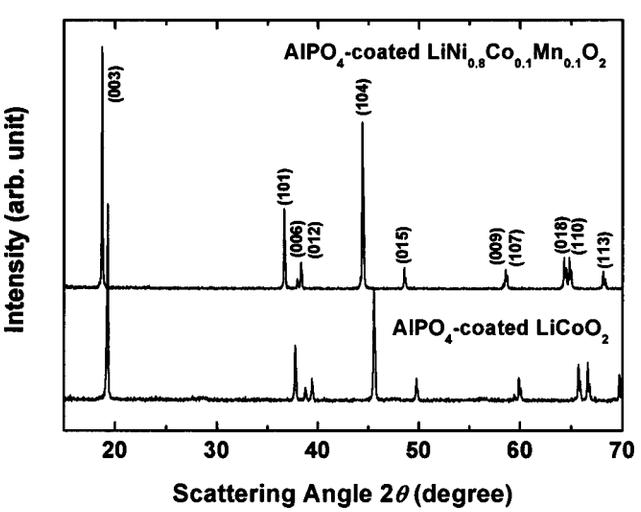

Figure 2. XRD patterns of the $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes.

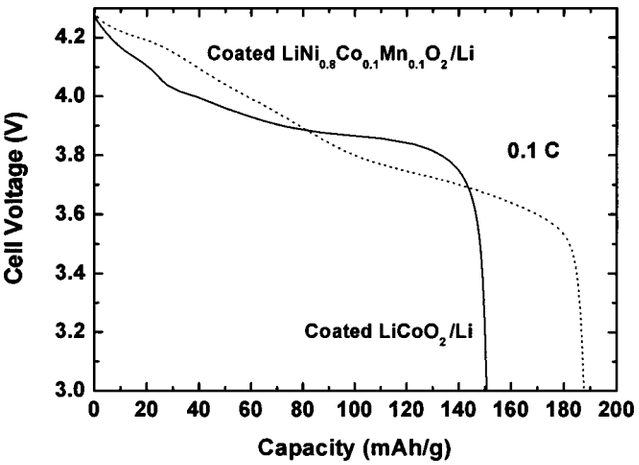

Figure 3. Plots of the first discharge curves from the $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes in the coin-type half-cells between 4.3 and 3 V at 0.1 C rate (Li as an anode), while the 1 C rate corresponds to 140 and 180 mA/g, respectively.

$AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ were carried with a discharge rate of 0.5, 1, and 2 C (while the charge rate was fixed at 1 C).

The Li-ion cells for the differential scanning calorimetry (DSC) tests were charged to the pre-determined cell voltages, 4.2 and 4.6 V for bare cathodes, and 4.2, 4.4, 4.6, and 4.8 V for the coated cathodes at the constant-current mode of 1 C (710 and 820 mA for Li_xCoO_2 and $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, respectively), which was followed by holding these voltages until the currents decreased to 30 mA. The charged cathodes were then disassembled from the cells in a dry room. The cathode electrode typically contained ~20 wt % electrolyte, ~25 wt % Al foil, a ~5 wt % combined binder and carbon black, and a ~50 wt % cathode material. Approximately 10 mg of the cathode was cut and hermetically sealed in an aluminum DSC sample pan. Only the cathode material was used to calculate the specific heat flow. The heating rate of the DSC tests was 3°C/min. Due to the high reactivity of the electrolyte with moisture, its content in the dry room was maintained below 50 ppm. Because the dry room was used for dissembling the cells for the DSC experiments, compressed DSC pans may contain oxygen. However, our DSC experiments up to 300°C showed negligible effects: pans assembled in the dry room were identical to those assembled in a glove box.

Results and Discussion

Scanning electron microscopy (SEM) images of the bare, $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode particles are shown in Fig. 1. The surface morphologies of both coated particles are distinctly different from those of the bare ones, and that of the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ changed from a rough to smooth shape after the coating. This suggests that the $AlPO_4$ nanoparticles at least reacted at the surface of powders. A high-resolution TEM image of the coated $LiCoO_2$ showed the $AlPO_4$ nanoparticles embedded in a nanoscale-coating layer of ~10 nm. The nanoscale-coating layer consisted of random-oriented $AlPO_4$ nanoparticles with an average diameter of ~3 nm, and the Al and P components were distributed uniformly in the nanoscale-coating layer.[16]

Figure 2 shows the X-ray diffraction (XRD) patterns of $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powders. Both materials are indexed to the hexagonal-type space group R3m. The lattice constants, a and c, for the $AlPO_4$-coated $LiCoO_2$ material are $a = 2.815 \pm 0.004$ Å and $c = 14.051 \pm 0.043$ Å (with 2.816 ± 0.004 Å and 14.034 ± 0.043 Å, respectively, for bare

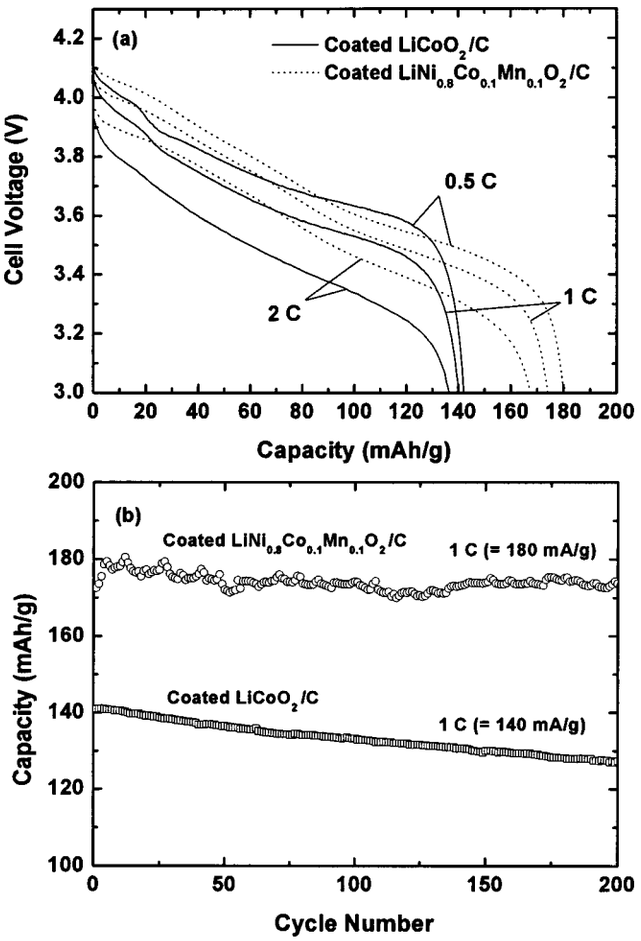

Figure 4. Plots of (a) the rate capabilities of the $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes in the Li-ion cells at 0.5, 1, and 2 C rates between 4.2 and 3 V, and (b) the discharge capacity as a function of the cycle number at 1 C rate.

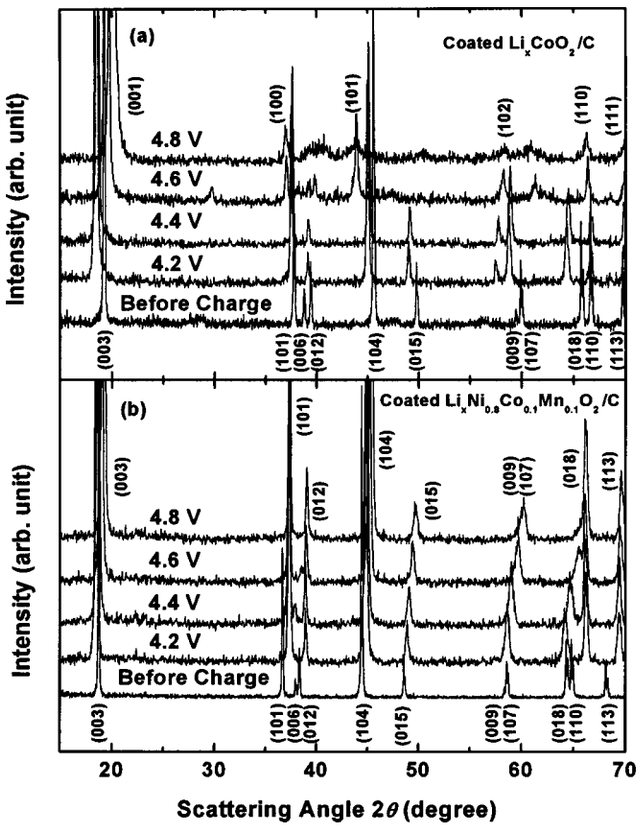

Figure 5. XRD patterns of (a) coated Li_xCoO_2, and (b) coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode electrodes as a function of the charge voltage during the first charge.

samples), and those for the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ material are $a = 2.874 \pm 0.001$ Å and $c = 14.217 \pm 0.008$ Å (with 2.877 ± 0.001 Å and 14.219 ± 0.003 Å, respectively, for bare samples). The XRD patterns of the coated $LiCoO_2$ or $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powders are identical to those of the bare samples, even though the possible formation of nanophases or interdiffusion could not be ruled out.

To examine the electrochemical properties, coin-type half-cells with the coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ were charged between 4.3 and 3 V at a rate of 0.1 C (14 mA/g and 18 mA/g, respectively). The first discharge curves in Fig. 3 show that the initial voltage profiles of the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes above 4 V are higher than that of the coated $LiCoO_2$. The discharge capacity of the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ is 188 mAh/g while that of the coated $LiCoO_2$ is 150 mAh/g. These values are identical to those of the bare cathodes. The larger discharge capacity of the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode than the coated $LiCoO_2$ is expected to increase the nominal capacity of the Li-ion cell.

The rate capabilities of the coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in the Li-ion full cells (between 4.2 and 3 V) are shown in Fig. 4a at a discharge rate of 0.5, 1, and 2 C (with the charge rate of 1 C). With relatively good capacity retention, the overall voltage profiles of the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ appear enhanced as the C rate increased from 0.5 to 2 C, compared to the coated $LiCoO_2$. For the cycle-life performance, the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ exhibits better capacity retention than the $LiCoO_2$ cathodes after 200 cycles, as shown in Fig. 4b.

Figure 5 compares the XRD patterns of the charged $AlPO_4$-coated Li_xCoO_2 and $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode electrodes at 4.2, 4.4, 4.6, and 4.8 V in Li-ion cells (with carbon anode). In both cases, the (003) lines shift toward lower diffraction angles during the charge up to 4.2 V, and then shift back to the higher diffraction angles as the Li ions are further removed. At 4.8 V, the XRD pattern of the coated Li_xCoO_2 is indexed to the hexagonal unit cell in the space group of P3m1 (CdI_2 or O1 type). Because 4.8 V in the Li-ion cell corresponds to ~4.9 V *vs.* Li metal, the Li content in the Li_xCoO_2 is zero at 4.8 V. These results agree well with Ohzuku *et al.*[18] and Amatucci *et al.*[19] On the other hand, the XRD patterns of the coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ are indexed to the R3m ($CdCl_2$ or O3 type) space group even at a low Li content. Usually, the (101) and (104) peaks for a hexagonal lattice observed for $LiNiO_2$ were split into two peaks in the monoclinic lattice (C2/m).[20] However, these are not observed in the XRD patterns of the $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, which is similar to those of $Li_xNi_{0.5}Co_{0.5}O_2$ having a homogenous hexagonal phase transition.[20] Ohzuku *et al.* and Amatucci *et al.* reported that delithiated Li_xNiO_2 to $x \sim 0$ maintained the R3m structure without a monoclinic distortion at a low lithium content, which is unlike $LiCoO_2$.[18,19] Similarly, the XRD patterns of $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ show that its structure at $x \sim 0$ (at 4.8 V) remains as R3m.

A comparison of the $AlPO_4$-coating effect on the cathode materials was investigated using DSC. Figure 6 shows the DSC scans of the $AlPO_4$-coated and the bare Li_xCoO_2 cathodes in the Li-ion cells at different charge voltages. It shows continuous heat generation of

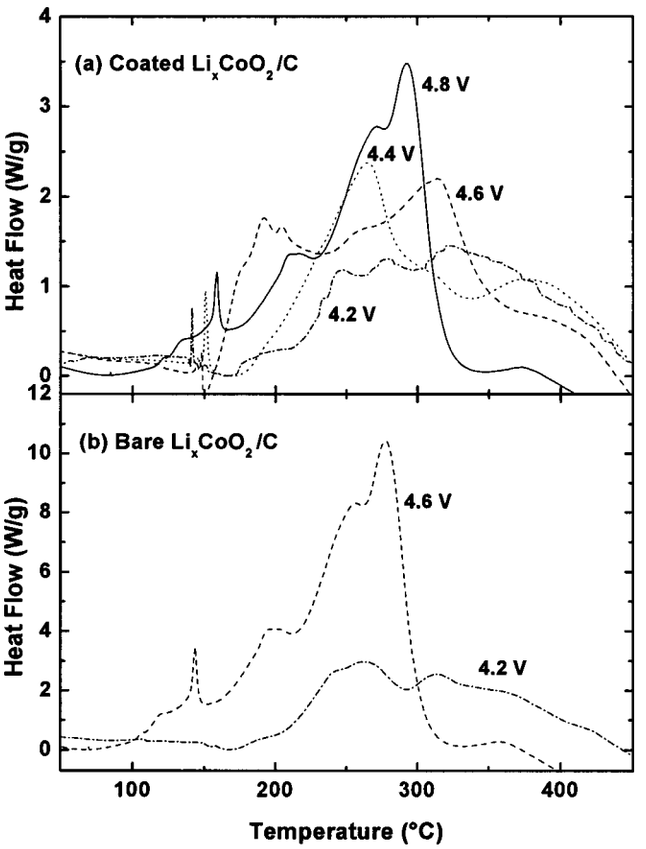

Figure 6. DSC scans of the coated and bare Li_xCoO_2 cathodes at different charge voltages. The cathodes were extracted from the Li-ion cells, and the scan rate was 3°C/min.

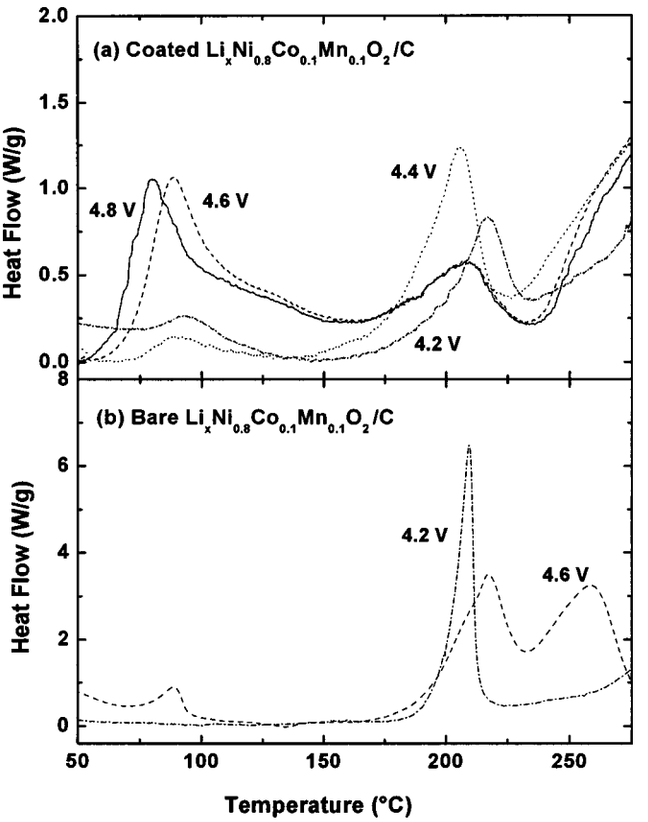

Figure 7. DSC scans of the coated and bare $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes at different charge voltages. The cathodes were extracted from the Li-ion cells, and the scan rate was 3°C/min.

cathodes beginning at ~150°C. As the charge voltage increases, the exothermic peak above 150°C, which is indicative of oxygen evolution from cathode decomposition, increases in both cathodes. The peak area of the coated $LiCoO_2$ cathode is approximately 2 to 3 times lower than that of the bare $LiCoO_2$.

Figure 7 compares the DSC scans of the $AlPO_4$-coated and the bare $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes in the Li-ion cells at the different charge voltages. The coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ shows two sets of exothermic peaks at ~75 and ~200°C, which is similar to the bare ones. The peak at ~75°C may be related to the decomposition of organic compounds residing at the particle surface.[21,22] Andersson *et al.*[21] reported that the delithiated $LiNi_{0.8}Co_{0.2}O_2$ cathode surface contained a mixture of organic polycarbonates species, LiF or $Li_xPF_yO_z$-type compounds, and electrolyte species due to high surface reactivity of the cathode powder.[23] A solid-electrolyte interphase (SEI) layer on delithiated electrodes containing various organic and inorganic electrolyte-decomposition products showed a mild heat generation below 100°C.[21-23]

The DSC results suggest that the $AlPO_4$-nanoparticle coating reduces heat generation during the electrochemical reactions. It should be noted that the peak size of the bare cathodes is significantly diminished after the $AlPO_4$ coating (Fig. 6 and 7). The BET surface area of all the samples were measured, and values from the $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powders were 0.6 and 1 m^2/g, respectively, whether the samples were coated or not. However, the DSC results showed significant heat reduction after the $AlPO_4$ coating, indicating that the crucial factor governing the exothermic reaction is the interfacial reaction with the electrolyte and cathode. With the surface reaction minimized by the coating, the oxygen generation inside the powders can be reduced. It is also believed that the covalent-bond nature of $(PO_4)^{3-}$ with the Al cation contributes to a strong resistance to the reaction with the electrolyte. Oxides with $(PO_4)^{3-}$ bonding were reported to be thermally stable even at the fully delithiated state, and the MPO_4 (M = Fe and Co) compounds exhibited a minimal weight loss from oxygen evolution when heated to 500°C.[24,25]

The coated $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode exhibits more diffuse peaks than the coated Li_xCoO_2 with increasing cell voltage, suggest-

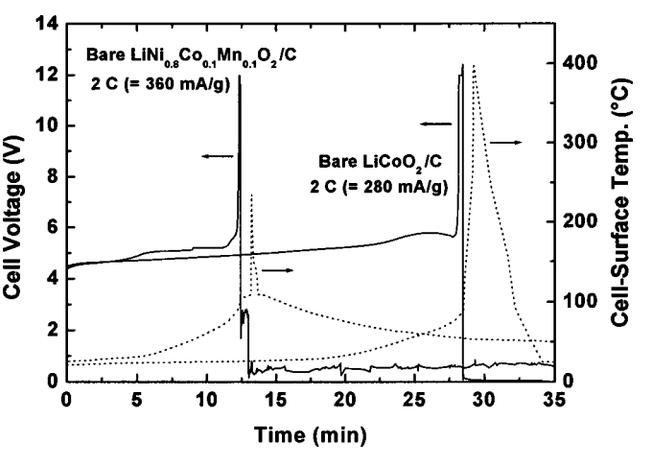

Figure 8. Plots of the cell voltage and cell-surface temperature in Li-ion cells containing the bare $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes as a function of time at 2 C rate during the 12 V overcharge test.

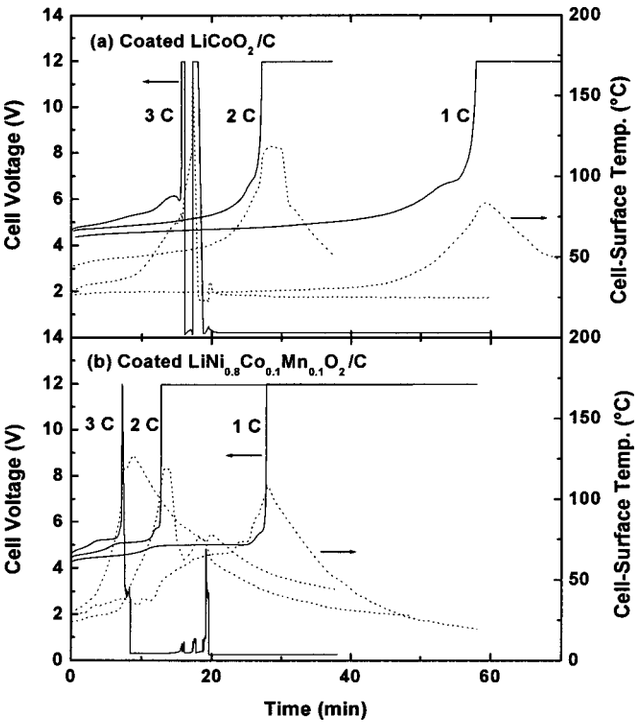

Figure 9. Plots of the cell voltage and cell-surface temperature in Li-ion cells containing $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes at 1, 2, and 3 C rates during the 12 V overcharge test.

ing possibly slower reaction kinetics. This indicates that Li_xCoO_2 has a higher chance of undergoing thermal runaway compared to the $Li_xNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, with the competing heat-generation *vs.* heat-dissipation rates in Li-ion cells.[21] To evaluate the effect of heat generation on the bare and $AlPO_4$-coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ in the Li-ion cells during the overcharge to 12 V, the cells were charged at three different current rates of 1, 2, and 3 C to 12 V (Fig. 8 and 9). At higher C rates, the cell-surface temperature increases rapidly due to the rapid increase in the joule heat, electrolyte oxidation, cathode decomposition, and other cell-component reactions. Among these, a violent exothermic reaction of the cathode with the electrolyte was reported to trigger thermal runaway of the cell.[26,27] The Li-ion cell containing $AlPO_4$-coated $LiCoO_2$ exhibits increasing cell-surface temperature with an increasing C rate: the cell-surface temperature reaches ~170°C at a 3 C overcharging rate. Because the difference between the internal and external temperature is ~100°C above 6 V,[26] the cell-internal temperature is estimated to be ~270°C.

The $AlPO_4$-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ exhibits lower maximum cell-surface temperatures than the coated $LiCoO_2$. This is due to faster heat dissipation than heat accumulation, which is consistent with the DSC results. A common feature of the coated $LiCoO_2$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ is that a short-circuit occurred after shooting to 12 V at a 3 C rate charging. With the exothermic reactions of the cell components occurring within ~10 min, any direct contact between the cathode and the anode electrode can cause a short-circuit, which usually results in the thermal runway of the cell containing a bare cathode.[16] However, the surface temperature of the cell containing the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ is limited to ~125°C, lower than that containing the coated $LiCoO_2$. Also, the $AlPO_4$-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode reaches 12 V ~10-30 min earlier than $LiCoO_2$. This may be related to the different decomposition behaviors of the cathodes. When the first heat generation from the cathode particle induces a separator shutdown before the second heat generation begins at higher temperatures, the internal resistance of the cell increases greatly. Eventually, this causes a decrease of current, resulting in a decrease in temperature. However, the coated $LiCoO_2$ cathode exhibits continuous heat generation beginning at ~150°C with a slimmer peak shape. Because this behavior causes faster heat accumulation than heat dissipation, the maximum cell-surface temperature at 12 V increases. This is well supported by the fact that the cell temperature of the bare $LiCoO_2$ cathode increases abruptly to ~400°C at 12 V upon short-circuiting, as shown in Fig. 8. However, a Li-ion cell containing bare $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ exhibits a maximum temperature of ~225°C, accompanying only smoke from the bottom rupture of the can.

Conclusions

The DSC and 12 V overcharge tests demonstrated the enhanced thermal stability of the $AlPO_4$-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes compared to the $AlPO_4$-coated $LiCoO_2$. Although the reduced heat generation by the nanoparticle coating resulted in an improved thermal stability at high charge voltages, the distinctly separate heat generation with a wide temperature gap in the coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ plays a key role in decreasing the cell-surface temperature, unlike $LiCoO_2$.

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