Control of AlPO$_4$-nanoparticle coating on LiCoO$_2$ by using water or ethanol

Jaephil Cho [a, *], Joon-Gon Lee [b], Byoungsoo Kim [b], Tae-Gon Kim [b],
Jisuk Kim [a], Byungwoo Park [b]

[a] Department of Applied Chemistry, Kumoh National Institute of Technology, Gumi, South Korea
[b] School of Materials Science and Engineering, and Research Center for Energy, Conversion and Storage,
Seoul National University, Seoul, South Korea

Abstract

The electrochemical properties of AlPO$_4$-coated LiCoO$_2$ cathodes prepared in a water or ethanol solvent were characterized with the view of stabilizing LiCoO$_2$ at charge-cutoff voltages of 4.6 and 4.8 V. Under the influence of the AlPO$_4$ crystallinity, the coated LiCoO$_2$ prepared in ethanol had better capacity retention than those prepared in water. This enhancement also correlated with the improved suppression of Li-diffusivity decay in the coated cathode from the ethanol compared to that from water. In addition, the differential scanning calorimetry (DSC) results of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ with ethanol showed an enhanced thermal stability.
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1. Introduction

Nano-sized inorganic compounds have attracted a great deal of scientific and technical interest as a result of their unique physical and chemical properties that bulk materials may not possess [1–15]. Because nanoparticles have a large surface area to volume ratio, the state of the surface molecules plays a key role in determining their properties. In addition, many studies on nanoparticle coatings with oxides or monomer shells aimed at optimizing the properties of the nanoparticles have been reported [1–7]. While most of these studies have been focused on polymer-supported metal-nanoparticle coatings on metallodielectric spheres, there are few reports of the direct coating of oxide nanoparticles on macro-sized inorganic compounds [16–20].

The recent increase in mobile electronics has led to the rapid expansion in the demand for Li batteries. In Li-ion cells, the cathode material is the most important part deter-

mining the cell capacity and safety, and LiCoO$_2$ is the most widely used material. However, the thermal stability and electrochemical properties of the cathode materials, such as the cycle-life performance and rate capability, largely depend on their powder size, i.e., BET surface area [21–29]. A cathode material with a larger powder size has larger thermal stability upon charging, but the rate capability and cycle-life performance deteriorate at a higher current rate [29]. The former result is associated with a decreased exothermic reaction of the cathode/electrolyte interface, and the latter is related to the increased Li-diffusion length. Metal-oxide (Al$_2$O$_3$, ZrO$_2$, TiO$_2$, etc.) coatings have been reported to be effective in overcoming these electrochemical shortcomings [30–33]. Although this method improves the capacity retention and Li diffusivity during cycling, it does not show any noticeable enhancement in thermal stability at the overcharged state (12 V). Recently, a direct nanoparticle coating on the powders in a water-based solution with a uniform nanoscale (~20 nm) coating on the cathode surface was reported [34–38].

This paper reports that the AlPO$_4$-nanoparticle crystallinity can be controlled by varying the solvent, and ex-

* Corresponding author. Tel.: +82 54 478 7824; fax: +82 54 478 7710.
E-mail address: jpcho@kumoh.ac.kr (J. Cho).

amines its effects on the electrochemical and thermal properties while our previously work that solely dealt with the dependence of AlPO$_4$ coating concentration (1.2–3 wt.%) on electrochemical cycling above 4.6 V [39]. None of previous coating papers did not report any correlation between crystallinity of coating material and electrochemical properties.

2. Experimental

Aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, 1 g) and ammonium phosphate ((NH$_4$)$_2$HPO$_4$, 0.33 g) were dissolved in either distilled water or ethanol, and were mechanically mixed, until a white-colored AlPO$_4$-nanoparticle dispersed solution was observed. These were mixed with LiCoO$_2$ (with an average particle size of ∼10 μm and BET surface area of 0.2 m^2/g), which were followed by drying at 130 °C for 6 h and annealing at 700 °C for 5 h, respectively. The estimated AlPO$_4$ to LiCoO$_2$ ratio was 0.3 wt.%.

The cathodes for the test cells consisted of LiCoO$_2$, super P carbon black, and a polyvinylidene fluoride (PVDF) binder at a weight ratio of 94:3:3. The slurry was prepared by thoroughly mixing an *N*-methyl-2-pyrrolidone (NMP) solution of PVDF (below 0.01 wt.% water content), carbon black, and a cathode material. The coin-type half cells (2016 size) prepared in an argon-filled glove box contained a cathode, a Li-metal anode, a microporous polyethylene separator, and an electrolyte solution of 1*M*LiPF$_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (50:50 vol.%). Each cathode contained ∼30 mg of the LiCoO$_2$ materials. For the galvanostatic intermittent titration technique (GITT) [19,20], the test cells (cycled between 4.3 and 3 V) were allowed to reach equilibrium after each incremental charge step using a constant current of 0.1 C by allowing an open-circuit period of 10 h, and a spherical particle with 10 μm in diameter is assumed. The Li diffusivities obtained using GITT include values for Li diffusion through the solid-state LiCoO$_2$, coating layer, and resistive surface layer.

Differential scanning calorimetry (DSC) samples of the cathode were prepared by charging the coin-type half cells to 4.3 V at the rate of 0.1 C (=14 mA/g) and holding them at that potential for 10 h. These cells were then disassembled in a glove box to remove the charged cathode which typically contained ∼35 wt.% electrolyte, ∼30 wt.% Al foil, ∼5 wt.% carbon black/binder, and ∼30 wt.% cathode material (DSC samples were neither washed nor dried). Approximately 10 mg of the cathode was hermetically sealed in a DSC pan. Only the cathode material was used to calculate the specific-heat flow.

3. Results and discussion

Fig. 1 shows transmission electron microscopy (TEM) images of the AlPO$_4$ nanoparticles prepared in water and ethanol. The size distribution of the particles prepared in wa-
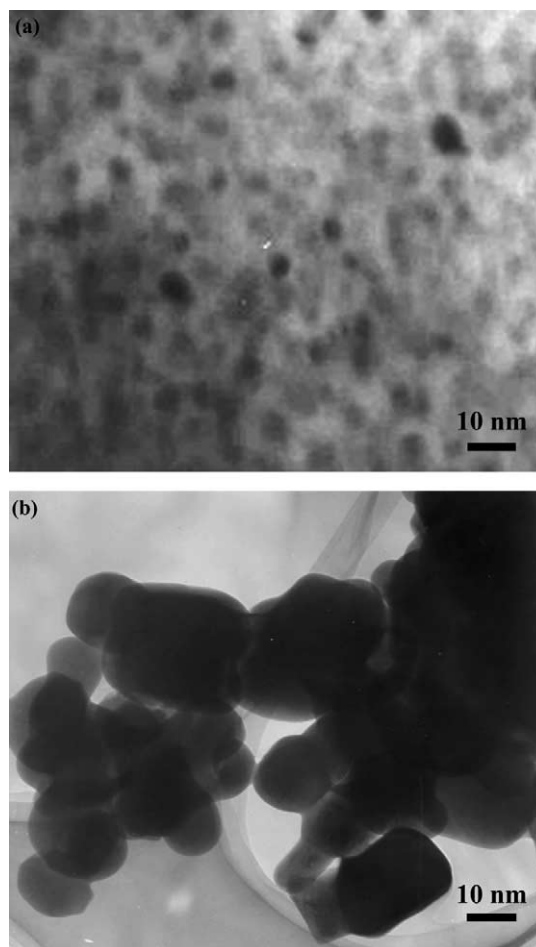

Fig. 1. TEM images of the AlPO$_4$ nanoparticles prepared in (a) water and (b) ethanol.

ter and ethanol is approximately 3–5 nm and 10–20 nm, respectively, indicating that the particle size is greatly affected by the solvent. The AlPO$_4$ nanoparticles in water instantly began to precipitate from the dissolved Al(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$HPO$_4$ according to the following reaction:

$$Al(NO_3)_3 \cdot 9H_2O + (NH_4)_2HPO_4 \rightarrow AlPO_4 (\downarrow) + HNO_3$$
$$+ 2NH_4NO_3 + 9H_2O.$$
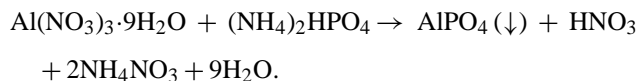
However, the AlPO$_4$ nanoparticles in ethanol began to precipitate very slowly, and the presence of AlPO$_4$ can be visually identified after 12 h. Hence, the AlPO$_4$ nanoparticles in ethanol grew with a lower *nucleation rate* than in water, leading to larger precipitates. X-ray diffraction (XRD) was performed to identify the crystallinity of the as-prepared AlPO$_4$ nanoparticles in water and ethanol (Fig. 2). The AlPO$_4$ nanoparticles prepared in water are somewhat amorphous after drying at 130 °C, while those prepared in ethanol show a crystallized phase. However, an additional phase, NH$_4$NO$_3$, which is a by-product from the Al(NO$_3$)$_3$·9H$_2$O and (NH$_4$)$_2$HPO$_4$ reaction after drying at 130 °C is observed. Even after annealing at 700 °C, the AlPO$_4$ nanoparticles prepared in water are not fully crystallized, which contrasts with
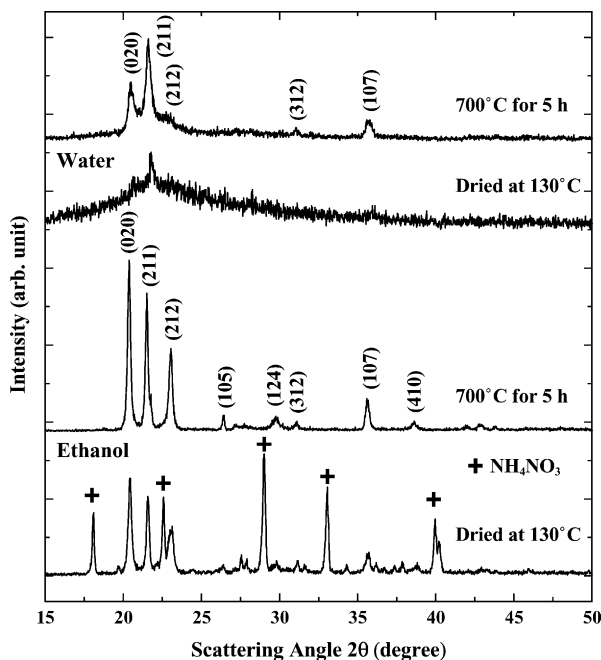
Fig. 2. X-ray diffraction patterns of the $AlPO_4$ nanoparticles prepared in water and ethanol: after drying at 130 °C for 6 h, and after annealing at 700 °C for 5 h. The peaks correspond to the orthorhombic phase (JCPDS 48-0652).

Fig. 4. Plots of the discharge capacity vs. cycle number of bare and coated $LiCoO_2$ prepared in water and ethanol (a) between 4.6 and 3 V, and (b) between 4.8 and 3 V. The C rate was increased stepwise from 0.1 (2 cycles), 0.2 (1 cycle), 0.5 (1 cycle), and 1 C rates (46 cycles) in the coin-type half cells (Li/$LiCoO_2$).

those prepared in ethanol. (The NH_4NO_3 phase disappears completely after annealing at 700 °C.) These results indicate that the coating layer prepared in ethanol could have better crystallinity on $LiCoO_2$. Fig. 3 shows TEM images of the coated $LiCoO_2$ prepared in water and ethanol and uniform coating layers with a thickness of 8–10 nm were formed in both cases. Note that coating concentration was 0.33 wt.% in both coated cathodes.

Coin-type half cells containing the coated cathodes were cycled with 4.6 V and 4.8 V charge cutoffs, respectively, in order to evaluate the effect of $AlPO_4$-nanoparticle coating derived from water and ethanol on the electrochemical properties. Figs. 4 and 5 show the cycle-life performance and voltage
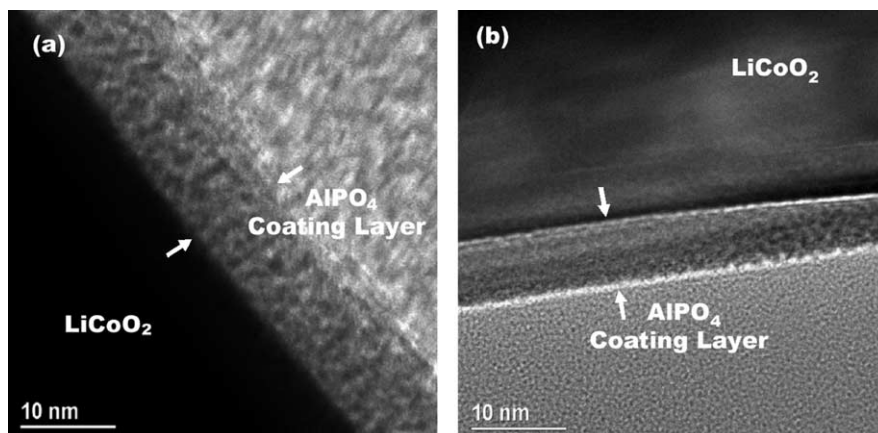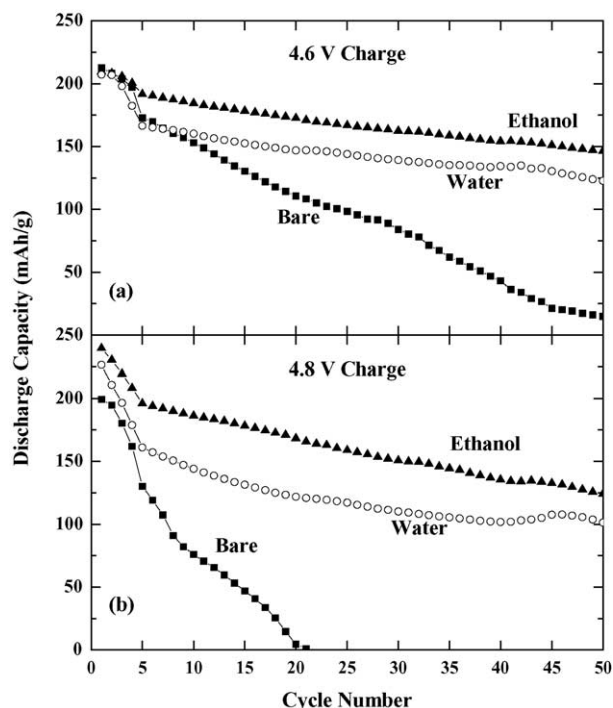
profiles of the bare and $AlPO_4$-coated $LiCoO_2$ cathodes prepared in water and ethanol, respectively. Fig. 5 shows that the coating improves the discharge rate capability, and the coated cathode prepared in ethanol led to better capacity retention at higher C rates than that prepared in water. The irreversible capacity (the difference of the 1st charge/discharge capacity) of the bare cathode ($\sim$25 mAh/g) is obviously larger than the $\sim$8 mAh/g of the coated cathodes at 4.6 V charge cutoff. At a 4.8 V charge cutoff, that of the bare cathode increases to $\sim$50 mAh/g, while the coated cathodes show $\sim$10 mAh/g. A charging voltage to 4.8 V led to more severe change to the

Fig. 3. TEM images of (a) coated $LiCoO_2$ prepared in water and (b) coated $LiCoO_2$ prepared in ethanol.
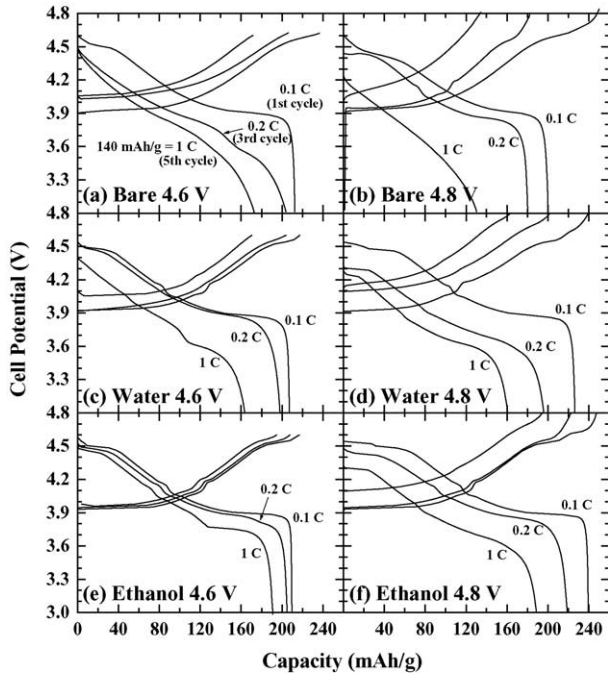
Fig. 5. Plots of the first-, third-, and fifth-cycle voltage profiles of bare and coated LiCoO$_2$ prepared in water and ethanol, in the voltage range of 4.6–3 V and 4.8–3 V. Same charge and discharge rates were used for each cycling steps.
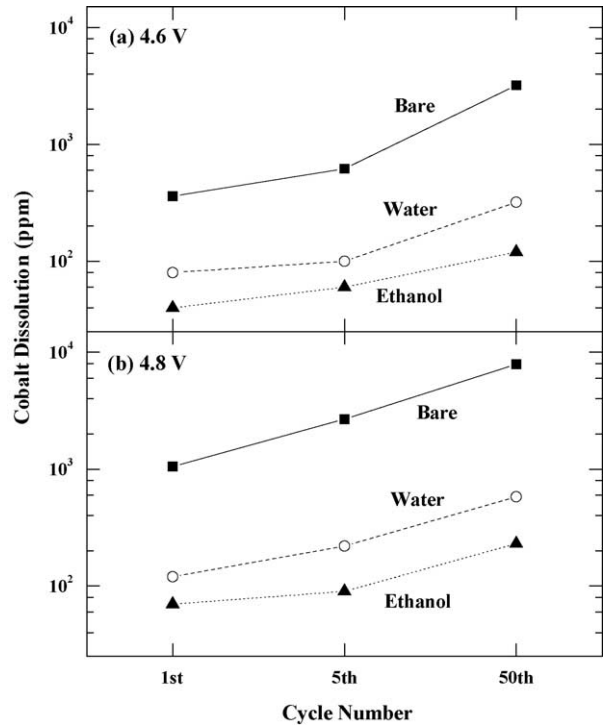

Fig. 6. Amounts of Co dissolution from the bare and coated electrodes at (a) 4.6 V and (b) 4.8 V charge cutoffs in the coin-type half cells (Li/LiCoO$_2$).

lattice constant *c*, up to ~7% [26,40], and such an abrupt structural change was reported to induce the electrochemical grinding between the particles, eventually resulting in Co dissolution and increasing the interfacial resistance [41].

After the 1st cycle, the Co dissolution of the bare cathode are ~350 and ~1000 ppm, respectively, at the 4.6 and 4.8 V charge-cutoff voltages (as shown in Fig. 6), while those of both coated cathodes (in water or ethanol) are almost the same, ~60 and ~90 ppm, respectively at 4.6 and 4.8 V. After 50 cycles, the extent of Co dissolution in the bare cathode at the 4.6 and 4.8 V cutoff voltages are much larger than those in the coated cathodes, indicating that the enhanced capacity retention of the AlPO$_4$-coated cathodes (Figs. 4 and 5) is well correlated with the Co dissolution. TEM images of both coated cathodes showed a similar coating thickness. The decreased Co dissolution of AlPO$_4$-coated cathode prepared in ethanol (compared to that prepared in water) is believed to be from the crystallinity difference.

The coated cathode prepared in ethanol exhibits a smaller irreversible capacity than that prepared in water. Moreover, the capacity drop in the bare and AlPO$_4$-coated cathode prepared in water is larger than that prepared in ethanol when the C rate increases from 0.1 C (1st cycle) to 1 C (5th cycle), for both 4.6 and 4.8 V cutoffs. This indicates that the large irreversible capacity and capacity drop are related to the decreased Li diffusivity in the LiCoO$_2$, as shown in Fig. 7. The improved Li diffusivity of the coated sample prepared in ethanol is due to decreased Co dissolution compared to that prepared in water. Co dissolution comes with the disso-

lution of Li, and thus local structure damage was expected with Co dissolution. Hence, Li diffusion may be hindered in this area. The difference between the coated cathode in water and ethanol may be related to the crystallinity of the coating layer. Hence, optimum thickness is required in powder geometry. On the other hand, the Li diffusivity of the bare cathode exhibits much lower Li diffusivity than the coated samples after cycling, suggesting that Co dissolution plays a prominent role in reducing the diffusivity.

According to Aurbach et al, upon cycling or storage, the capacity loss of LiCoO$_2$ electrodes cycled to 4.2 V is caused
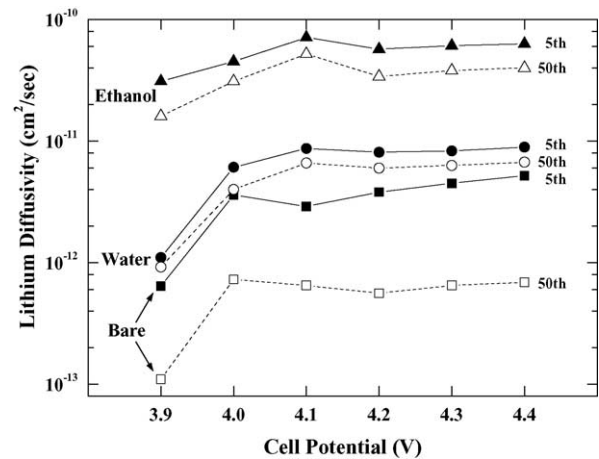

Fig. 7. Li diffusivities of the bare and coated electrodes at the 5th cycle and at the 50th cycle (after 46 cycles at 1 C rate).
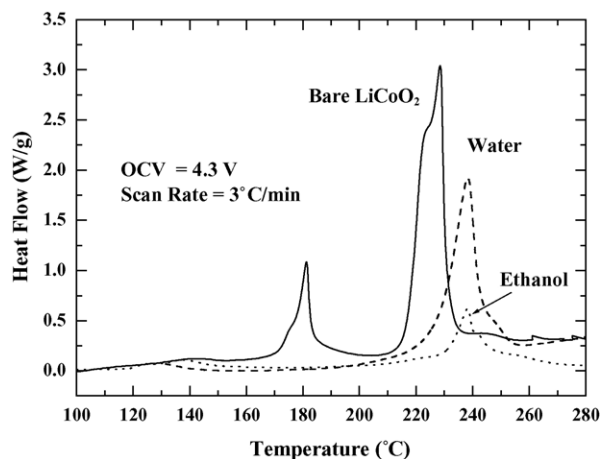
Fig. 8. DSC scans of the bare and AlPO$_4$-coated LiCoO$_2$, after charging to 4.3 V. The total exothermic heat of the AlPO$_4$-coated LiCoO$_2$ prepared in ethanol is smaller by one order of magnitude, compared to that of the bare one.

by the formation of surface films that cover the particles and may electronically isolate them from each other and from the current collector [42]. When LiCoO$_2$ is cycled to 4.5 V, such an electronically resistive surface film may form even faster and cause quicker capacity loss than when the electrode is cycled to 4.2 V [43]. In addition, Co dissolution was accompanied from the Li$_x$CoO$_2$ structure, resulting in the loss of Li insertion/extraction sites. This leads to a decrease of Li diffusivity in Li$_x$CoO$_2$. However, our results clearly showed much higher Li diffusivity of the coated cathodes, along with excellent capacity retention during cycling than the bare cathode. This indicates that formation of the electrically resistive film on the cathode was much suppressed. However, more detailed studies will be needed to investigate crystallinity effect on the cycling improvement.

The AlPO$_4$-coated LiCoO$_2$ has excellent thermal properties in comparison to the bare one. As shown in Fig. 8, the DSC results of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ show less generation of exothermic heat (an indication of oxygen generation from cathode decomposition). In particular, the exothermic reaction is the most important factor for the thermal stability of Li secondary batteries [34,35]. This is because the reaction accelerates oxygen evolution from the decomposing LiCoO$_2$, causing a temperature increase and thermal runaway of the cell [34]. Accordingly, the cathode material that has the slowest reaction with the electrolyte is the most promising candidate for the safety of Li secondary batteries. Chemical composition of Li and Co in LiCoO$_2$ before AlPO$_4$ treatment was analyzed and compared it with after AlPO$_4$ treatment. Both results show that mole ratio of Li to Co was 1.0. Thermal stability of the cathode is closely related to the exothermic reaction with the electrolytes, and therefore, it is important to minimize such reaction. This result is very consistent with our previous result that AlPO$_4$ suppresses the exothermic reaction with the electrolytes [34–36]. In addition, Omanda et al. showed that coating with SiO$_x$ on

LiNiCoO$_2$ suppressed the exothermic reaction with the electrolytes [44].

The total heats evolved from the AlPO$_4$ nanoparticle-coated LiCoO$_2$ prepared in water and ethanol are ∼470 and ∼140 J/g, respectively while that of the bare one is ∼770 J/g (from 100 to 280 °C). In addition, the exothermic reaction of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ with the electrolyte is initiated at higher temperatures: ∼220 and ∼230 °C in the coated LiCoO$_2$ prepared in water and ethanol, respectively, and ∼170 °C in the bare sample. As a result, the AlPO$_4$ nanoparticle-coated LiCoO$_2$, especially prepared in ethanol, has an excellent thermal stability compared to the bare one. These outstanding thermal behaviors of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ may be related to many phosphate compounds that are very stable against both the chemical and thermal reactions, probably due to the strong covalent P−O bonding [45,46].

4. Conclusions

The electrochemical properties and phase transitions of the coated LiCoO$_2$ above 4.6 V were affected by the solvent used for the AlPO$_4$-nanoparticle synthesis. The capacity retention of the coated LiCoO$_2$ powders prepared in ethanol was better than that prepared in water. The AlPO$_4$-coating layer prepared in water or ethanol can suppress Co dissolution effectively, so the electrochemical properties of the coated cathodes are much better than the bare cathode. The difference between the coated cathodes prepared in water or ethanol correlated with the suppression of the Li-diffusivity decay. In addition, the DSC results of the AlPO$_4$ nanoparticle-coated LiCoO$_2$ from ethanol exhibited less generation of exothermic heat and a higher onset temperature than the bare cathode or coated from water. Further studies are needed to clarify the involved mechanisms of nanoscale coating layer, with impedance spectroscopy, X-ray photoelectron spectroscopy, etc.

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