Solvent storage-induced structural degradation of LiCoO$_2$ for lithium ion batteries

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Abstract

Spontaneous reactions have been observed between LiCoO$_2$ and electrolyte solvent for lithium ion batteries by characterizing the structural and/or components of the generated species in their gas, liquid and solid states. It is shown that surface coating cannot prevent the dissolution of Li and Co ions from LiCoO$_2$ or the structural degradation of LiCoO$_2$. However, surface modification can suppress the loss of oxygen from LiCoO$_2$. Based on these results, another important aspect of the performance improvement mechanism by surface modification to LiCoO$_2$ and the limitation of surface modification are proposed.
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Keywords: LiCoO$_2$; Lithium ion batteries; Spontaneous reactions; Soakage

1. Introduction

It is well known that surface modification can improve the electrochemical performances of LiCoO$_2$ as positive electrode materials for lithium ion batteries [1]. Cho et al. [2] believed that surface modification suppresses the complicated phase transition of the active material during deep charge and discharge. However, our recent in situ synchrotron X-ray diffraction (XRD) investigation demonstrates clearly that the Al$_2$O$_3$-coated LiCoO$_2$ experiences all the phase transitions that bare LiCoO$_2$ does but with a better structural reversibility even if charged to 4.7 V versus Li$^+$/Li [3].

As the electrode material has to contact with the electrolyte throughout the life of a Li-ion battery, many authors attribute the improved performance of surface modified LiCoO$_2$ to the coating layer that separates the active material from the electrolyte and prevents the escape of Li$^+$ ions at discharged states [4,5]. Indeed, Ostrovskii et al. [6] reported that spontaneous reactions can occur on the surface of LiNi$_{0.8}$Co$_{0.2}$O$_2$ and LiMn$_2$O$_4$-based electrodes during storage in electrolytes. However, they failed to show the structural degradation of the electrode material due to lithium ion extraction or identify the

source of Li for the surface species. Therefore, the mechanism of performance improvement of surface modified LiCoO$_2$ is still not clear.

The purpose of this work is to show the presence of spontaneous solvent (electrolyte)/electrode reactions and their impact on the structural and electrochemical performance of the electrode. We are trying to understand the improvement mechanism from another point of view rather than to emphasize how severe these spontaneous reactions are in a practical battery. Therefore, commercial LiCoO$_2$ is nano-sized solely to promote the spontaneous reactions.

2. Experimental

Commercial LiCoO$_2$ (Cellseed^{TM} with average particle size of 5–6 μm) was high-energy ball-milled in ethanol and nano-sized LiCoO$_2$ particles (ca. 200 nm) were obtained. Part of the nano-sized powder was annealed at 500 °C for 4 h in air to eliminate most of the microstructural defects generated during ball milling and to make the powder sufficiently dry. The rest of the powder was surface-coated with Al$_2$O$_3$ as described below.

Nano-sized LiCoO$_2$ was mixed with NH$_4$OH in distilled water. Al(OH)$_3$ was deposited on the surface of LiCoO$_2$

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particles when $Al(NO_3)_3$ solution was slowly added into the stirred mixture. The mixture was then filtered and flushed with distilled water three times and stored in an oven of 130 °C for 12 h. Later the dried $Al(OH)_3$-coated $LiCoO_2$ was heated at 500 °C for 4 h. This is expected to dehydrate $Al(OH)_3$ and to obtain dry Al_2O_3-coated nano-$LiCoO_2$. Transmission electron microscopy analysis indicated that the thickness of the Al_2O_3 coating layer on nano-$LiCoO_2$ particles was ca. 10 nm.

Battery-grade ethylene carbonate (EC) and dimethyl carbonate (DMC) were mixed (1:1 v/v) in an Ar-filled glove box at room temperature. Then the EC/DMC mixture (4 mL) and the nano-$LiCoO_2$ (300 mg) were mixed and sealed in a stainless steel (SS) container with a rubber cover (2.5 mm thick) in the glove box. The mixture was stirred for 7 days at room temperature. By puncturing the rubber cover with an injector, 100 μL of the gas ion the sealed container was transferred into an HP-Plot Q fused silica capillary column for gas chromatography and mass spectroscopic (GC–MS) analysis. Then the container was opened in the glove box and the liquid and solid in it were separated for later analysis. Finally, the solid was dried in the vacuum chamber of the glove box for 24 h before it was characterized with various techniques.

Inductively coupled plasma (ICP) technique was used to determine the Co/Li atomic ratio in both the liquid and the solid. The solid species were then sealed between two pieces of glass in the glove box and characterizing with Raman spectroscopy (Renishaw R-1000; Ar^+ laser, 514.5 nm excitation; resolution set at 3 cm^{-1}). Finally electrode sheets were prepared by standard method with nano-$LiCoO_2$ as the active material, carbon black as the conductive additive and PVDF as the binder (85:10:5 w/w/w). Button type nano-$LiCoO_2$/Li cells were assembled in the glove box with 1 M $LiPF_6$ dissolved in EC/DMC (1:1 v/v) electrolyte and Celgard 2300 polypropylene film as the separator. These cells were galvonostatically cycled between 2.5 and 4.3 V (versus Li^+/Li) on a Land 2001 battery tester at a current density of 0.1 mA cm^{-2}.

3. Results and discussion

Fig. 1 shows the GC spectrum of the generated gas of Al_2O_3-coated $LiCoO_2$ soaked in solvent EC/DMC. The strongest line in the spectrum is from $Ar + N_2$ because $LiCoO_2$ and the solvent were sealed into the container in the Ar-filled glove box and some N_2 in air could enter the injector during sample transference from the sealed container into the GC column. Besides that, carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethylene (C_2H_4), water (H_2O), ethane (C_2H_6) and oxygen (O_2), in the order of their abundances from high to low, are also detected in the gas sample. In order to make sure that the detected H_2O and O_2 are from the gas in the SS container rather than from air during sample transference, GC–MS spectra of air were recorded by simply injecting similar volume of air (100 μL) in the room
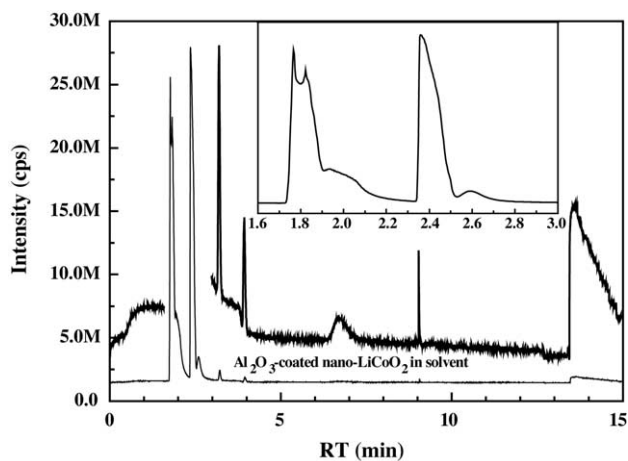

Fig. 1. Typical GC spectrum of gas species generated on $LiCoO_2$ soaked in EC/DMC (Al_2O_3-coated nano-$LiCoO_2$ here). The vertical scale is only for the bottom GC plot while the horizontal scale is for both the bottom and the middle plots; the inset is a selected part of the middle plot.

into the column. It is found that the abundances of O_2 and H_2O (with N_2 from air as the reference) in air are about 30% lower than in the sealed container. GC–MS analysis is carried out to the gas from the soaked commercial and bare nano-$LiCoO_2$ as well. It is found that the main generated species in these three samples are the same but their contents are lower than that of Al_2O_3-coated $LiCoO_2$. In addition, the abundance of O_2 in Al_2O_3-coated nano-$LiCoO_2$ is lower than in the other two samples. Yang et al. [7] examined the products of carbon electrode cycled in different electrolytes for lithium ion batteries. According to their mass spectral analysis, CO_2 is the main product of EC decomposition. DMC is decomposed into CO and CH_4 while diethyl carbonate (DEC) is decomposed into CO and C_2H_6. Our results show that CO and C_2H_6 can also be produced from EC and/or DMC decomposition on $LiCoO_2$.

The Co/Li atomic ratios in the solids and in the corresponding liquids of bare and Al_2O_3-coated $LiCoO_2$ are shown in Table 1. As $LiCoO_2$ is the only source of lithium in this system, the low Co/Li atomic ratio in the liquid and high Co/Li ratio in the solid indicate that simply soaking $LiCoO_2$ in the solvent can result in obvious lithium dissolution and make its structure degraded. Considering that some lithium ions might be solvated with the Co^{3+}-oxidized solvent molecules and deposit on the particle surfaces, the actual Co/Li ratio within a $LiCoO_2$ particle should be higher than shown here.

Table 1
Comparison of Co/Li atomic ratios in the solid and liquid of EC/DMC soaked nano-$LiCoO_2$

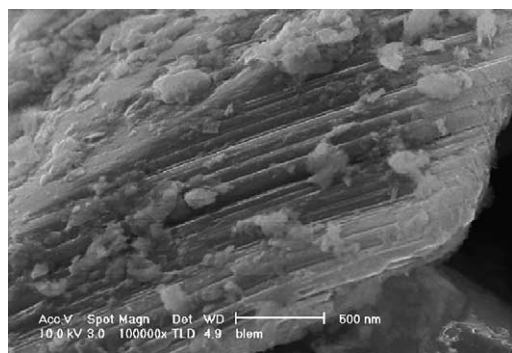| Condition	Co/Li in solid	Co/Li in liquid
Non-soaked	1:1.00	–
Bare and soaked	1:0.78	1:12.4
Coated and soaked	1:0.61	1:18.4

Fig. 2. Surface morphology of commercial $LiCoO_2$ soaked in EC/DMC solvent.

It has been believed that an important role of the surface coating is to prevent Li^+ escape from the positive electrode material and keep its good electrochemical stability upon cycling [4,5]. However, Table 1 shows the opposite results: the Al_2O_3 coating layer on $LiCoO_2$ does not prevent the escape of lithium ions. Rather, the Co/Li atomic ratio in the solid of Al_2O_3-coated $LiCoO_2$ is even higher and the abundances of most of the generated gas species are higher in $Al_2O_3/LiCoO_2$ solvent system than in bare $LiCoO_2$/solvent system. These results are well reproducible, demonstrating that surface coating cannot suppress the electrode/electrolyte (solvent) reactions. This explains that the improved electrochemical performance of surface modified $LiCoO_2$ fails after about 20 cycles of galvonostatic cycling [8]. There must be some other reasons for the improved electrochemical performances of surface modified $LiCoO_2$.

Fig. 2 shows the surface morphology of commercial $LiCoO_2$ soaked in solvent EC/DMC. The surface of commercial $LiCoO_2$ is very smooth and "clean" prior to soakage (see Fig. 1 in Ref. [8]). However, many straight stripes or furrows are formed and the surface is covered with a very rough layer. The size of the randomly distributed fragments is over 100 nm. The straight stripes correspond to the 2-D layered structure of hexagonal $LiCoO_2$. The bumpy surface demonstrates the formation of thick and rough surface films on the particles. These features are typical of corroded surfaces.

Lithium loss by solvent soakage will definitely lead to structural degradation of $LiCoO_2$. XRD was carried out to characterize the solvent-soaked bare and Al_2O_3-coated nano-$LiCoO_2$ (Fig. 3). Besides the residual $LiCoO_2$, Co_3O_4, Co_2O_3 and Li_2CO_3 are also detected. Li_2CO_3 has been observed on solvent- and electrolyte-soaked $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles in our previous report [9]. However, it seems that no authors have reported the formation of Co_2O_3 and Co_3O_4 in solvent- or electrolyte-soaked $LiCoO_2$ or electrochemically cycled $LiCoO_2$ electrodes. Further study by Raman spectroscopy confirms the existence of Co_2O_3 and Co_3O_4 in both systems and indicates that the content of the residual $LiCoO_2$ is lower in Al_2O_3-coated nano-$LiCoO_2$ than in bare nano-$LiCoO_2$ (Fig. 4). Mean-
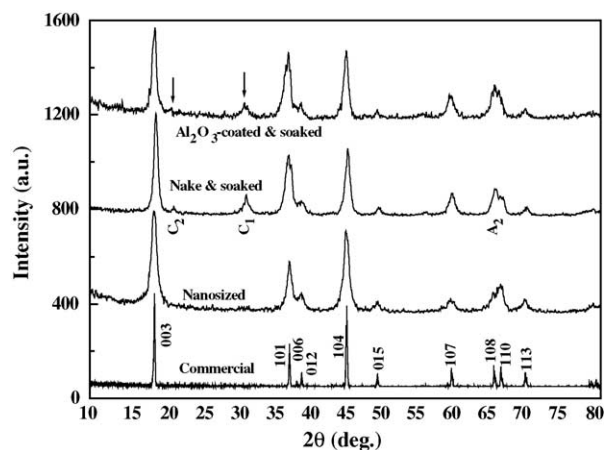

Fig. 3. Comparison of (a) the XRD patterns of commercial $LiCoO_2$, high-energy ball-milled $LiCoO_2$, solvent-soaked nano-$LiCoO_2$ and Al_2O_3-coated nano-$LiCoO_2$: A for Co_3O_4, B for Co_2O_3 and C for Li_2CO_3. The footnotes (1, 2 or 3) are for the first three strongest diffraction lines of each product in the order of their intensity from high to low.

while, it is also found that the content ratio of Co_2O_3/Co_3O_4 is higher in Al_2O_3-coated nano-$LiCoO_2$ than in bare nano-$LiCoO_2$. Calculation to the XRD patterns of the soaked materials indicates that the a values of the bare and Al_2O_3-coated nano-$LiCoO_2$ are 2.8188 and 2.8197 Å, respectively, while the c values of the bare and Al_2O_3-coated nano-$LiCoO_2$ are 14.0364 and 14.0780 Å, respectively. Compared with the lattice parameters of nano-$LiCoO_2$ prior to soakage ($a = 2.8214$ Å and $c = 14.0379$ Å), these parameters do not show obvious changes. This implies that a core-and-shell structure is formed in the $LiCoO_2$ particle. The shell is Li-rare while the core is still Li-rich. The lithium content in the core is similar to that of pristine $LiCoO_2$. Suppose that there was no lithium ion in the shell (composed of Co_2O_3 and Co_3O_4) and the core was still $LiCoO_2$, the thickness of
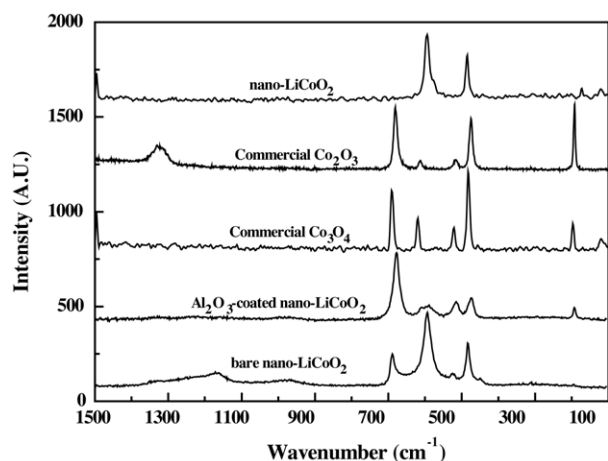

Fig. 4. Comparison of the Raman spectra of commercial, nano-scaled and solvent-soaked nano-$LiCoO_2$ and other commercial cobalt oxides. *Note*: The solvent soaked nano-$LiCoO_2$ bare or Al_2O_3-coated, have been exposed to air for several days; without exposure to air, the characteristic peaks of $LiCoO_2$ cannot be observed.
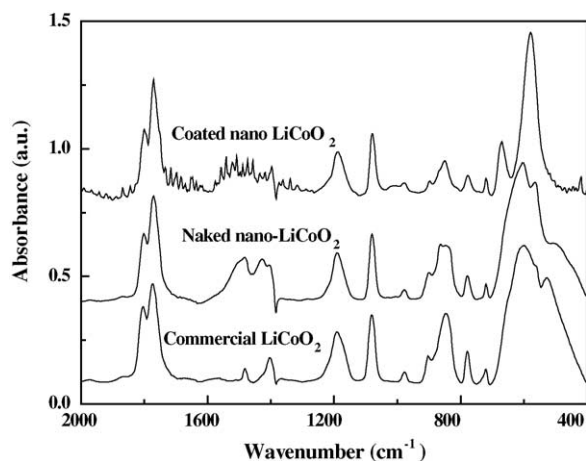
Fig. 5. FTIR spectra of fresh solid species on various $LiCoO_2$ soaked in the electrolyte.

Fig. 6. Renishaw Raman spectra of $LiCoO_2$ materials covered with surface films kept in dry Ar for 7 days.

the shell should be over 15% of the particle diameter for the coated $LiCoO_2$. In comparison, the thickness of the shell of the bare nano-$LiCoO_2$ is much smaller.

The charge/discharge profiles of the nano-$LiCoO_2$ and solvent-soaked nano-$LiCoO_2$, bare and Al_2O_3-coated have been recorded. Only a capacity of about $40\,mA\,h\,g^{-1}$ is obtained for the Al_2O_3-coated nano-$LiCoO_2$ in the first cycle while the discharge capacities are $90\,mA\,h\,g^{-1}$ for the non-soaked nano-$LiCoO_2$ and $40\,mA\,h\,g^{-1}$ for the soaked bare nano-$LiCoO_2$, respectively, under the same conditions. This is understandable as neither Co_2O_3 nor Co_3O_4 is electrochemically active for lithium storage above 2.5 V versus Li^+/Li. The other reason for the low capacity is the poor contact due to severe aggregation of the nano-$LiCoO_2$ particles. In the subsequent cycles the capacity of the nano-$LiCoO_2$ material decreases with cycling.

Fig. 5 shows the FTIR spectra of fresh solid species on various $LiCoO_2$ soaked in the electrolyte. It is seen that the IR spectra of the surface species on different substrates are similar to each other, indicating that surface modification does not influence the composition of the surface film on $LiCoO_2$. This is consistent with the observation of the surface film on $LiCoO_2$ soaked in the solvent. The composition of the surface film is found quite similar to that of repeatedly reported solid electrolyte interphase (SEI) on the electrode and will not be further discussed here. However, it is worth pointing out that LiF is detected in the solid ($775\,cm^{-1}$ band), indicating that $LiPF_6$ is decomposed during storage. However, no vibration bands related to P–F bonding are detected.

Fig. 6 shows the Raman spectra of $LiCoO_2$ materials covered with surface films. The dependence of the thickness of the surface film on the specific surface area of the material in the electrolyte is less obvious than in the corresponding $LiCoO_2$ materials soaked in the solvent. In addition, the thickness of the surface film on corresponding $LiCoO_2$ in electrolyte is estimated to be smaller than on $LiCoO_2$ soaked in the solvent because the characteristic bands of $LiCoO_2$ can easily be recognized at 592 and $483\,cm^{-1}$, respectively.
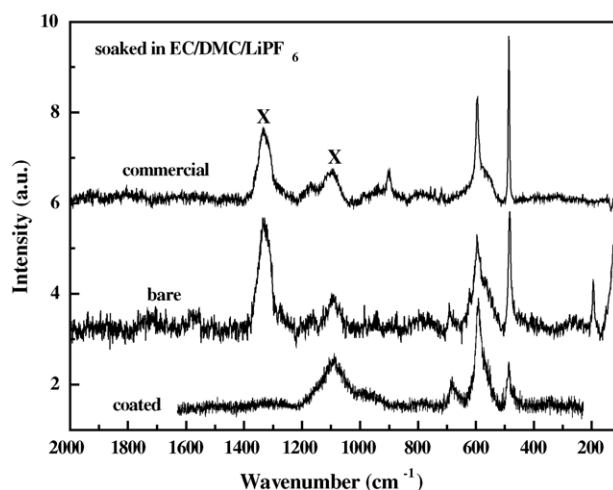
Different from solvent-soaked $LiCoO_2$, lithium dissolution is significantly suppressed in the electrolyte, implying that the concentration difference of the Li^+ ions in and out of the $LiCoO_2$ particles is one of the driving forces for lithium dissolution. As a result, the structural degradation of $LiCoO_2$ is less severe in the electrolyte than in the solvent. Similar to the case of $LiCoO_2$ soaked in the solvent, bare $LiCoO_2$ is mainly degraded to Co_3O_4 while the Al_2O_3-coated nano-$LiCoO_2$ is mainly degraded to Co_2O_3. Finally, it seems that the influence of $LiCoO_2$ particle size on the structural degradation is also less pronounced in the electrolyte than in the solvent.

Finally as a complimentary to the above discussion on the nano-sized $LiCoO_2$, Fig. 7 shows the surface morphology of commercial $LiCoO_2$ soaked in the electrolyte. Clearly the soakage-induced corrosion is still obvious but significantly suppressed. Grid-like as well as stripe-like structures are observed (Fig. 7a). Meanwhile, a thick surface film can be observed on the particle surface. Amazingly, layer cleavage is observed in the particle as shown in Fig. 7b. This is direct evidence of Li^+ extraction (lithium escape leads to strong repulsion between the neighboring O–Co–O slabs). Due to severe aggregation and small size of the nano-$LiCoO_2$ particles, the surface morphology of bare and coated nano-$LiCoO_2$ is not available. However, considering the strong spontaneous reactions between the positive and the solvent or electrolyte, the structural degradation of nano-$LiCoO_2$ is expected to be more severe.

The following reactions are supposed to take place upon soaking nano-$LiCoO_2$ in the solvent. The Co^{3+} ions in the $LiCoO_2$ attack and oxidize the carbonate groups of the solvent molecules due to their acidic/nucleophilic properties and are reduced to Co^{2+}. This will bring about two effects. On one hand, the reduction of Co^{3+} leads to the degradation of $LiCoO_2$ to Co_2O_3 and/or Co_3O_4 and the dissolution of some Li^+ and Co^{3+} ions into the liquid. On the other hand, the Li^+ ions in the liquid are solvated and combine with the Co^{3+}-oxidized solvent molecules to form RCO_2OLi. The
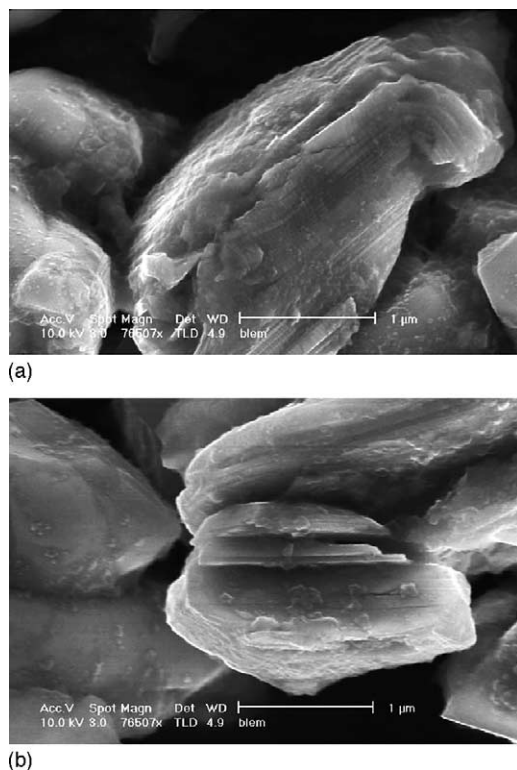
Fig. 7. Surface morphology (a, upper) and layer cleavage (b, lower) of commercial $LiCoO_2$ particles soaked in 1 M $LiPF_6$ dissolved in EC/DMC for 7 days.

great difference of the Li^+ ions concentration in $LiCoO_2$ and in the solvent facilitates the above reaction. As the Li^+ ions leave the lattice due to their large concentration gradient in and out of the $LiCoO_2$ particle, it is understandable than a core-and-shell structure is the most possible for the soaked $LiCoO_2$. Out of the shell is the surface film composed of various Li-containing compounds.

4. Conclusions

The above results show that $LiCoO_2$ is not stable and Li^+ ions can be chemically extracted from $LiCoO_2$ in the EC/DMC solvent. Dissolution of Li^+ ions from $LiCoO_2$ leads to the formation of electrochemically inactive Co_2O_3 and

Co_3O_4 and capacity falling. The dissolved Li^+ ions combine with the Co^{3+}-oxidized solvent molecules and form a thick surface film out of the shell structure. Comparative study shows that surface modification to $LiCoO_2$ does not prevent Li^+ ion dissolution from the material. Rather the Al_2O_3 coating layer promotes the dissolution of Li^+ and Co^{2+} from $LiCoO_2$. This is a severe limitation of Al_2O_3-based (and probably the Al^{3+}-based) surface modification. However, surface coating suppresses the escape of oxygen from $LiCoO_2$. Therefore, the improved electrochemical performance of $LiCoO_2$ by surface modification cannot be simply attributed to the suppression of Li^+ or Co^{2+} ion dissolution from the active material. Although the above results are obtained on nano-$LiCoO_2$ soaked in electrolyte solvent, they also offer some revelation about the stability of micro-$LiCoO_2$ (and probably other lithium transition metal oxide material) in a practical battery. Finally, this study demonstrates the necessity of optimizing the electrolyte/electrode matching.

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