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The effect of Al_2O_3-coating coverage on the electrochemical properties in $LiCoO_2$ thin films

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Abstract The electrochemical properties of nanoscale Al_2O_3-coated $LiCoO_2$ thin films were examined as a function of the coating coverage. Al_2O_3-coated $LiCoO_2$ films showed enhanced cycle-life performance with increasing degree of coating coverage, which was attributed to the suppression of Co dissolution and F^- concentration in the electrolyte. Moreover, an Al_2O_3-coating layer with partial coverage clearly improved the electrochemical properties, even at 60 °C or with a water-contaminated electrolyte. Even though metal-oxide coating on $LiCoO_2$ has been actively investigated, the mechanisms of nanoscale coating have yet to be clearly identified. In this article, surface analysis suggested that the Al_2O_3-coating layer had transformed to an $AlF_3\cdot3H_2O$ layer during cycling, which inhibited the generation of HF by scavenging H_2O molecules present in the electrolyte.

Keywords Li-ion battery · $LiCoO_2$ · Al_2O_3 ·
Nanoscale coating · H_2O scavenge

Introduction

Recently, hexagonal $LiCoO_2$ cathode materials have been used in most commercial lithium-ion batteries on account of their simple preparation, high specific capacity, and good electrochemical properties [1]. However, Li_xCoO_2 is typi-

cally charged up to ~4.2 V vs. Li ($Li_{0.5}CoO_2$), yielding a specific capacity below ~140 mAh/g. Further increased charge cutoff voltage results in significant deteriorations of $LiCoO_2$. This is attributed to structural changes in the unit-cell volume [2], increased cobalt dissolution into the organic electrolyte [3], loss of oxygen [4], formation of electrochemically resistive surface films [5], etc.

An effective method of resolving the problem of capacity fading at high cutoff voltage is thermal treatment [6, 7] or coating the surface of cathode with various materials (metal oxide, metal phosphate, or other materials) [8–22]. It was previously reported that a nanoscale metal-oxide coating on the surface of cathode improved the electrochemical properties at high cutoff voltages and current rates [8–13, 17–21]. Thackeray et al. reported enhanced capacity and stability in cycling by coating ZrO_2 on $LiMn_2O_4$, and speculated that the enhanced performance of spinel was attributed to its ability of ZrO_2 particles to neutralize the HF component from the electrolyte [23]. Myung et al. also reported that a metal-oxide coating layer on $Li_{1.05}Ni_{0.4}Co_{0.15}Mn_{0.4}O_2$ acted as an HF scavenger, and they suggested the following reaction: $Al_2O_3+6HF\rightarrow2AlF_3+3H_2O$ [24, 25]. However, H_2O generated from the reaction between Al_2O_3 and HF regenerates HF in the electrolyte, and the same things happen again consequently. My group reported that metal-oxide coating on $LiCoO_2$ can affect lattice expansion during cycling [8, 9]. Some other researchers suggested that a partial or non-uniform coating still improved the electrochemical properties of powder materials [26, 27]. My group recently reported that Al_2O_3-coated $LiCoO_2$ thin film with even 50% coating coverage showed enhanced cycle-life performance with no evidence of mechanisms [28], and Al_2O_3 coating on $LiCoO_2$ powder was also carefully investigated by Fey et al. [29, 30]. These results were correlated with the

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suppression of Co dissolution during electrochemical cycling. However, the mechanisms of metal-oxide coating have yet to be clearly identified.

Characterizing the intrinsic properties of $LiCoO_2$ powders is complicated, because the powder geometry consists of polymer binders and carbon blacks for the required electronic conduction among the ~10 μm powders. Therefore, thin-film geometry is appropriate for investigating the intrinsic properties of nanoscale coating on $LiCoO_2$, because it has only a cathode and metal-oxide electrolyte interface, and is insensitive to the coating thickness on cycle-life performance [10]. In this article, thin-film $LiCoO_2$ cathodes were examined by distinctly controlling the coating coverage, cycling temperature, and level of water contamination in order to clarify the scavenge mechanisms.

Experimental section

$LiCoO_2$ thin films were deposited on thermally oxidized Si (100) substrates using RF magnetron sputtering of a $LiCoO_2$ target. A Pt current collector was deposited onto a TiO_2 adhesion layer, and the $LiCoO_2$ film was deposited on the Pt layer. An approximately 600-nm-thick $LiCoO_2$ was deposited at a pressure of 20 mTorr with an Ar/O_2 ratio of 3/1 after presputtering for 1 h. To obtain high-quality $LiCoO_2$, all films were annealed at 700 °C in an oxygen atmosphere at 20 mTorr for 30 min. The 10-nm-thick Al_2O_3 thin films with a coating coverage ranging from 25% to 100% were deposited on top of the crystallized $LiCoO_2$ films by reactive sputtering of an Al target. The Al_2O_3-coating patterns with 75%, 50%, and 25% coverage consisted of 1,000, 360, and 150 μm squares, respectively, with a distance of 150 μm between the nearest squares. After Al_2O_3 deposition, the coated and bare samples were heat-treated at 400 °C for 2 h in an oxygen atmosphere.

Beaker-type half cells were used to evaluate the electrochemical properties. The cells were made up of Li-metal sheets as a counter and reference electrode, a $LiCoO_2$ cathode with an active area of ~1 cm^2 as a working electrode, and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, 1/1 vol.%, water impurities of less than 20 ppm) (Cheil Industries, Inc.) as the electrolyte. The cells were electrochemically cycled over the voltage range of 2.75 and 4.4 V by applying a current density of 0.4 mA/cm^2 (= 12 C) at 25 °C and 60 °C. At all the charge/discharge cutoff steps, the cell voltages were potentiostated until the current decreased to 10% of the charge/discharge rate with a time limit of 10 min. The charge-transfer resistance of cathodes with the bare and coated $LiCoO_2$ films was measured by electrochemical impedance spectroscopy (EIS) from 10 mHz to 100 kHz with an ac signal amplitude of 5 mV. The EIS

was measured at a 4.2 V charged state with a current less than 1 $μA/cm^2$, during the initial cycle, and after the tenth, 40th, and 80th cycles.

Inductively coupled plasma–mass spectroscopy was used to measure the extent of cobalt dissolution into the electrolyte, after floating the 4.6 V charged cathodes for 12 days at 25 °C. The fluorine-ion concentration in the electrolyte was measured by ion chromatography (IC, Dionex 500). The effects of water impurities on the electrochemical properties of $LiCoO_2$ were examined by cycling the cells at 25 °C with a 200 ppm water-contaminated electrolyte. The compounds on the surface of cathode materials were examined using a time-of-flight secondary-ion mass spectroscopy (ToF-SIMS, PHI7200) surface analyzer equipped with a 7.9 keV Cs ion source and pulse-electron flooding.

Results and discussion

The electrochemical performance was examined by cycling the Al_2O_3-coated $LiCoO_2$ thin films with a surface coverage ranging from 0% to 100%. Figure 1 shows the cycle-life performance of the bare and Al_2O_3-coated $LiCoO_2$ films, excluding the capacity at constant-voltage mode. The Al_2O_3-coated $LiCoO_2$ films show improved capacity retention with increasing coating coverage. Non-linearity of charge and discharge capacities above 70 cycles is attributed to the slower kinetics of Li^+ de-intercalation in
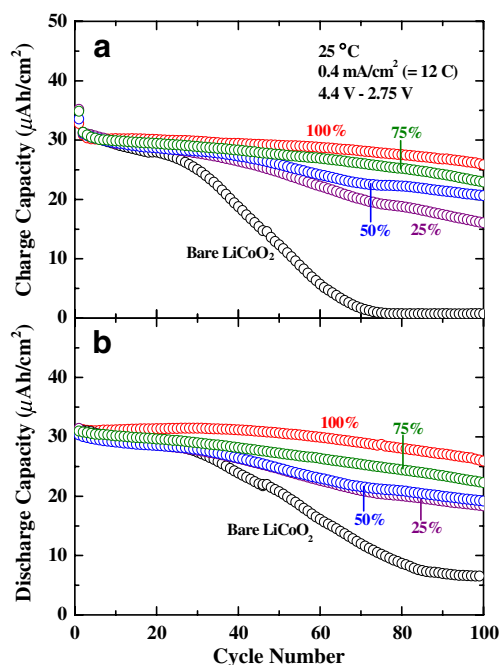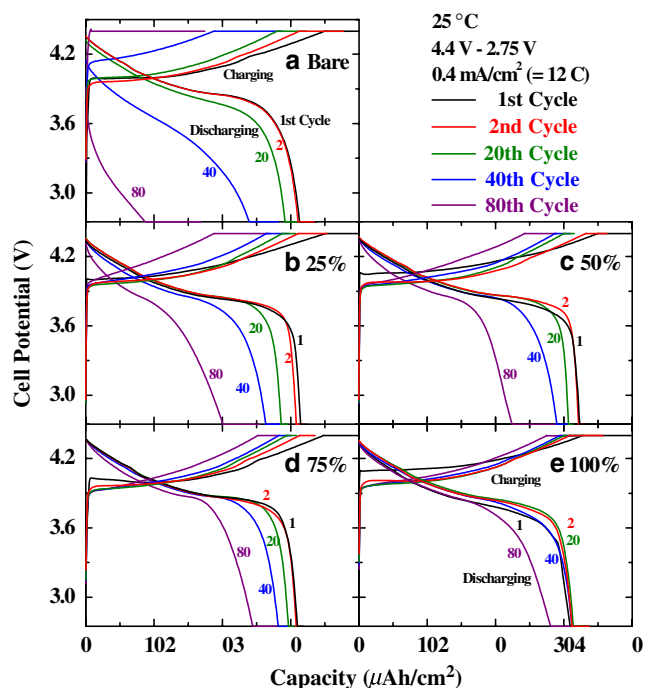

Fig. 1 **a** The charge- and **b** discharge capacity retention of bare and Al_2O_3-coated $LiCoO_2$ thin films (charged to 4.4 V at 12 C) as a function of coating coverage ranging from 25% to 100%
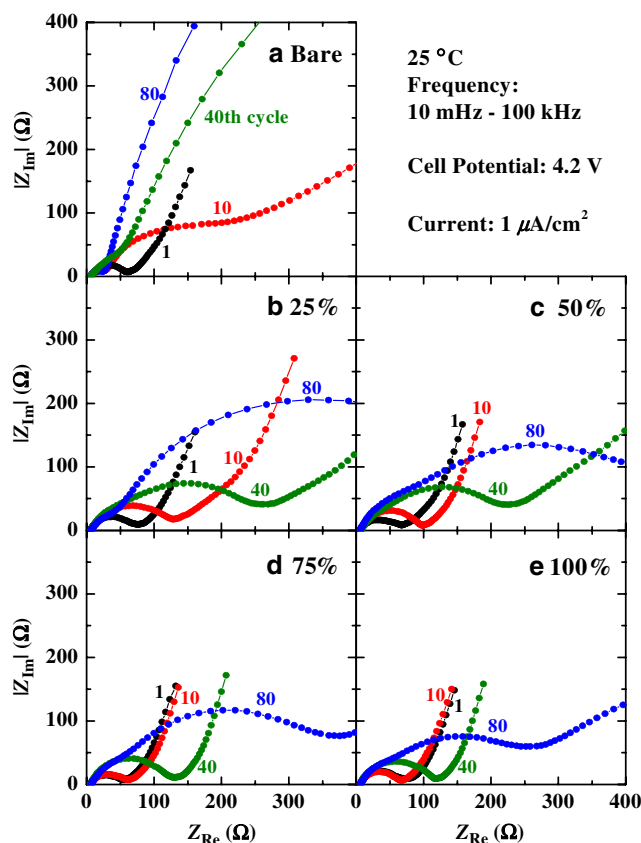
bare $LiCoO_2$ than Li^+ intercalation, as observed by a galvanostatic intermittent titration technique, since the extra capacity from the constant-voltage mode (at 4.4 and 2.75 V) is not included [10, 15].

The voltage profiles of the bare and Al_2O_3-coated $LiCoO_2$ thin films with various degrees of surface coverage (observed at 25 °C) are shown in Fig. 2. Compared with the profiles of the bare $LiCoO_2$, a slight increase in polarization is observed in the initial cycle of the Al_2O_3-coated cathodes. From the second cycle, the polarization in the charge and discharge processes of the coated sample becomes less significant [10, 15].

In order to correlate the cycle-life performance of thin-film $LiCoO_2$ with the electrode kinetics, EIS analysis of both the bare and Al_2O_3-coated $LiCoO_2$ films with different degrees of surface coverage was carried out after cycling, as shown in Fig. 3. Before the EIS measurements, all cells were cycled at 0.4 mA/cm^2 between 4.4 and 2.75 V, and potentiostated at 4.2 V until the current density had decreased to 1 μA/cm^2. All the $LiCoO_2$ thin films during the first cycle show similar charge-transfer resistance (R_{ct}), indicating that R_{ct} at the interface of the Al_2O_3-coating layer and $LiCoO_2$ film is comparable to that of the electrolyte and $LiCoO_2$ film during the initial cycle. However, R_{ct} of the bare $LiCoO_2$ significantly increases with increasing number of cycles compared with the coated $LiCoO_2$ films. These impedance spectra are consistent with the cycling performance of bare and fractional Al_2O_3-
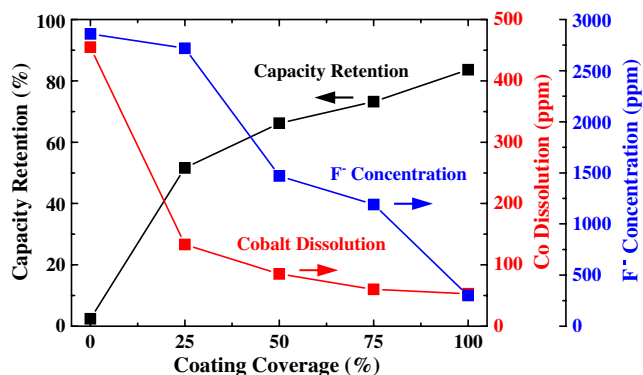

Fig. 3 EIS of the **a** bare and Al_2O_3-coated $LiCoO_2$ films with **b** 25%, **c** 50%, **d** 75%, and **e** 100% surface coverage

coated $LiCoO_2$ films, because the increase in R_{ct} is closely related to a deterioration of the electrochemical properties of the cathode during cycling.
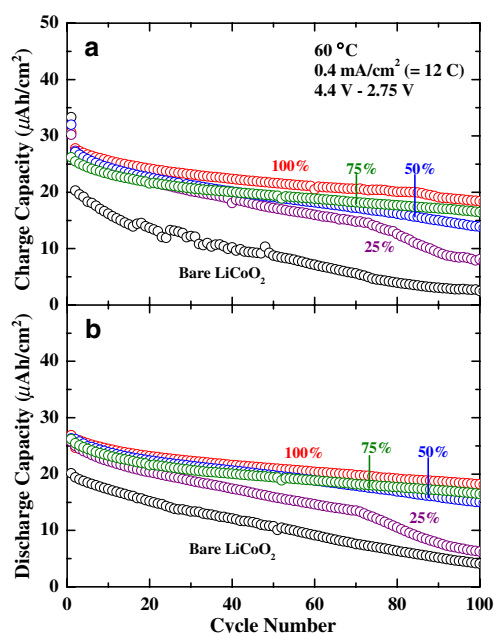
The effect of Al_2O_3-coating coverage on the HF generation was examined by measuring the F^- concentration in the electrolyte. The amount of F^- decreases with increasing Al_2O_3-coating coverage. Moreover, the Al_2O_3 coating with 100% coverage effectively inhibits F^- generation (~300 ppm), which is much smaller than the F^- concentration (~2,900 ppm) from the uncoated $LiCoO_2$ samples. It was reported that the decomposition of a $LiPF_6$-based electrolyte with water leads to the formation of HF ($LiPF_6 \rightarrow LiF + PF_5$ and $PF_5 + H_2O \rightarrow POF_3 + 2HF$), which accompanies Co dissolution from $LiCoO_2$ [31, 32]. The amount of Co dissolution into the electrolyte from the uncoated $LiCoO_2$ thin film is ~460 ppm, while that from the Al_2O_3-coated $LiCoO_2$ film with 100% coverage is ~50 ppm, as shown in Fig. 4. There is a strong correlation between the amount of Co dissolution from the Al_2O_3-coated $LiCoO_2$ with different degrees of surface coverage and the charge-capacity retention after 100 cycles (shown in Fig. 1a). Although it is difficult to analyze the amount of scavenged water by the Al_2O_3-coating layer, the improved

Fig. 2 Voltage profiles of the **a** bare and Al_2O_3-coated $LiCoO_2$ films with **b** 25%, **c** 50%, **d** 75%, and **e** 100% surface coverage

Fig. 4 The charge-capacity retention after 100 cycles from Fig. 1a, and the Co dissolution and F⁻ concentration in the electrolyte from bare and Al₂O₃-coated LiCoO₂ films with different coverage, after an initial 4.6 V charge and being immersed for 12 days at 25 °C

electrochemical properties even with partial coverage indicate an interaction between the coating layer and the electrolyte, which inhibits the HF generation by water scavenging.

Figure 5 shows the cycle-life performance of the bare and Al₂O₃-coated LiCoO₂ thin films with different coverage ratios at 60 °C. The Al₂O₃-coated LiCoO₂ films with 25% coverage show rapid capacity fading after ~70 cycles at 60 °C. However, the initial capacity and the capacity retention of the Al₂O₃-coated LiCoO₂ at 60 °C increase with the increasing Al₂O₃-coating coverage. The Al₂O₃ coating with a coverage ranging from 50% to 100% shows excellent cycle-life performance at the elevated temperature.

The cycle-life performances of the bare and Al₂O₃-coated LiCoO₂ films with 200 ppm water-contaminated electrolytes at 25 °C were examined as a function of the surface coverage, as shown in Fig. 6. The initial capacity and the capacity retention with water impurities increase with the increasing Al₂O₃-coating coverage. The Al₂O₃ coating even with partial coverage appears to inhibit the Co dissolution from acidic HF which occurs in the electrolyte.

In order to clarify the mechanisms of how an Al₂O₃ coating effectively enhances the electrochemical properties of LiCoO₂ films under severe conditions, such as elevated temperature and additional water, the level of electrolyte decomposition was analyzed by measuring the amount of F⁻ in the electrolyte. As shown in Fig. 7a, the F⁻ concentration in the electrolyte of the Al₂O₃-coated LiCoO₂ with full coverage samples is extremely low compared with that of the bare samples. The Al₂O₃ coating appears to suppress Co dissolution from LiCoO₂, even at an elevated temperature and additional water impurity. This is correlated with the capacity retention of LiCoO₂ as a function of the coating coverage, as shown in Fig. 7b.

To investigate the reactions between the Al₂O₃ coating and electrolyte with water contamination, the surface was examined by SIMS after 60 cycles in an electrolyte containing 200 ppm of water. In Fig. 8, the marked lines indicate the calculated ratios of mass/charge for $AlOF_2^-$ (80.97 Th, Th=1 hydrogen atomic mass/electron charge), AlF_4^- (102.98 Th) and $CoOH^+$ (75.94 Th), respectively. A fragment of $CoOH^+$, which is attributed to cobalt dissolu-

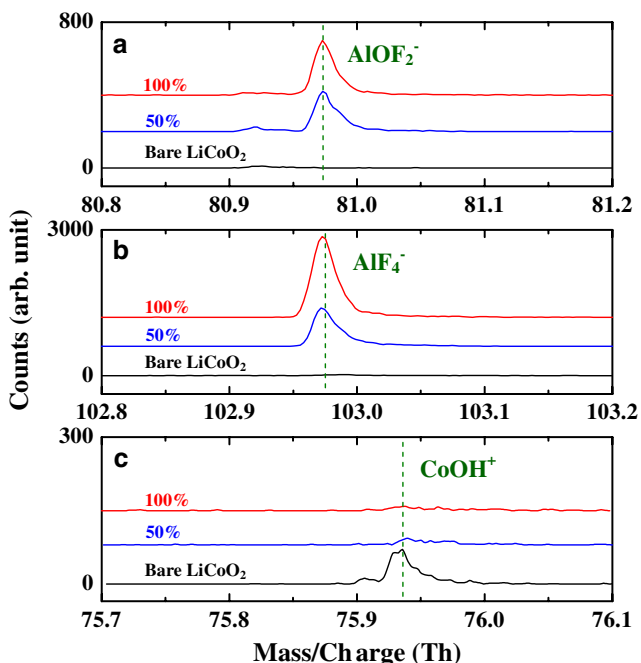**Fig. 5** **a** The charge- and **b** discharge capacity retention of bare and Al₂O₃-coated LiCoO₂ films at 60 °C
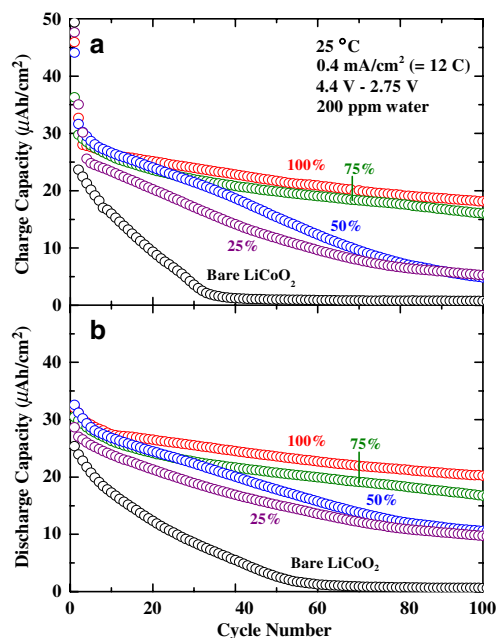
Fig. 6 **a** The charge- and **b** discharge capacity retention of bare and Al₂O₃-coated LiCoO₂ films at 25 °C with 200 ppm water-contaminated electrolyte
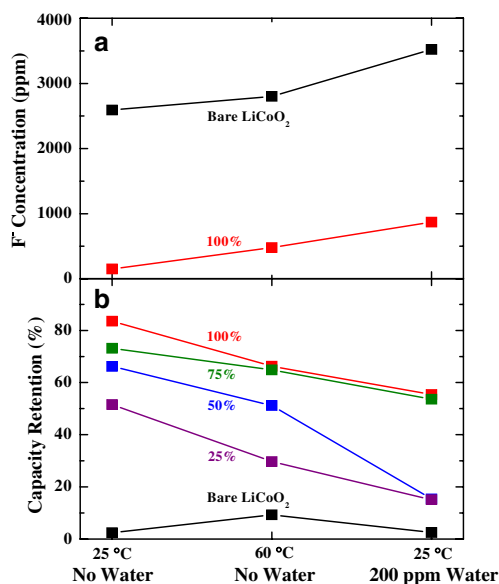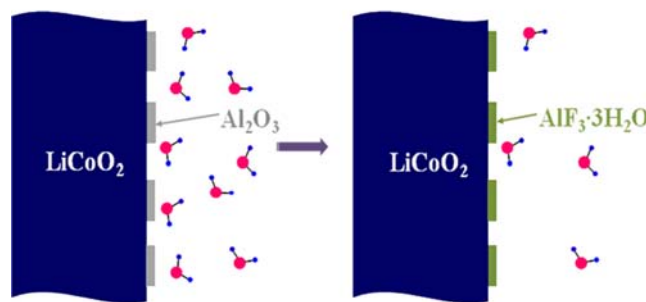
Fig. 7 **a** The F$^-$ concentration in the electrolyte from bare and Al$_2$O$_3$-coated LiCoO$_2$ films with 100% coverage, after an initial 4.6 V charge and being immersed for 12 days at 25 °C, 60 °C, and 25 °C with 200 ppm water, respectively. **b** The charge-capacity retention of Al$_2$O$_3$-coated LiCoO$_2$ films, after 100 cycles at 25 °C (Fig. 1), 60 °C (Fig. 5), and 25 °C with 200 ppm water (Fig. 6)

Fig. 9 Schematic figure of H$_2$O scavenging by Al$_2$O$_3$-coating layer

tion from LiCoO$_2$ was observed on the surface of the bare LiCoO$_2$ films. However, the amount of CoOH$^+$ on the surface decreased significantly even with a 50% Al$_2$O$_3$ coating, as shown in Fig. 8c.

Kleist et al. reported that bulk Al$_2$O$_3$ powders react with HF and H$_2$O in an electrolyte to form AlF$_3$·3H$_2$O complexes at room temperature after 3 days [Al$_2$O$_3$+6HF+3H$_2$O→2(AlF$_3$·3H$_2$O)], which was confirmed by the sharp X-ray diffraction peak widths [33]. Density-functional theory calculations also showed that AlF$_3$·3H$_2$O complexes were energetically favorable compared to AlF$_3$ and water, by ~2 eV/AlF$_3$ [34]. With these studies, the SIMS data of AlOF$_2$$^-$ and AlF$_4$$^-$ suggest that an Al$_2$O$_3$-coated layer scavenges H$_2$O molecules, which improves the electrochemical properties of LiCoO$_2$ cathodes (Fig. 9).

Conclusions

This study examined the electrochemical properties of nanoscale Al$_2$O$_3$-coated LiCoO$_2$ thin films as a function of the coating coverage. These results were attributed to the suppression of Co dissolution and decomposition of LiPF$_6$ by extensive cycling. It was found that AlF$_3$·3H$_2$O was formed from the Al$_2$O$_3$-coating layer by a reaction with HF and H$_2$O, thereby scavenging H$_2$O molecules in the electrolyte and consequently decreasing the amount of HF. The enhanced electrochemical properties with various degrees of coating coverage were correlated with the affinity of metal fluoride to scavenge H$_2$O impurities in the electrolyte. It still remains a question that how many H$_2$O molecules can be scavenged by Al$_2$O$_3$ coating, and what the effective partial-coating thickness is. In addition, direct evidence of AlF$_3$·3H$_2$O with reaction kinetics between Al$_2$O$_3$ coating layer and HF/H$_2$O also needs to be clarified experimentally.

Fig. 8 SIMS spectra of bare and Al$_2$O$_3$-coated LiCoO$_2$ thin films, after 60 cycles with 200 ppm of water impurities in the electrolyte

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