

Soft X-ray Absorption Spectroscopic Studies with Different Probing Depths: Effect of an Electrolyte Additive on Electrode Surfaces

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Abstract

A solid electrolyte interphase (SEI) formed on a model LiCoO₂ electrode was analyzed by using an ultra-soft X-ray absorption spectroscopy (XAS) system, BL-2 of SR Center, Ritsumeikan Univ. The spectral data of Li K-, B K-, C K-, O K-, and Co L-edges for the SEI film on the electrode were collected using three detection methods with different probing depths. The electrode was prepared by a pulsed laser deposition method. All the spectral data consistently indicated that the SEI film containing lithium carbonate was instantly formed just after the soak of the electrode in the electrolyte solution and that it decomposes during the repeated charge-discharge reactions. The decomposition of the SEI film seems to cause the reduction in lithium ion battery cycle performance and an additive of lithium bis(oxalate) borate (LiBOB) increases the cycle life. From the XAS spectra it is concluded that some of the Co ions at the electrode surface are reduced to Co(II) by the charge-discharge reaction and this reaction can be suppressed by the addition of LiBOB and that the SEI film decomposition during the reaction can also be prevented by LiBOB.

1. Introduction

Lithium ion battery (LIB) is a promising energy storage device due to its high volumetric and gravimetric energy density. While the current LIB technology is adequate for portable electronic applications, the increasing demand from electric vehicle applications requires further improvement of anode and cathode materials in terms of safety, power and cycle life. It is well known that films called solid electrolyte interphase (SEI) formed at the surface of the electrodes originate from the decomposition of the solvent and/or electrolyte during the initial charge process.¹⁾ Although the SEI prevents further decomposition of electrolyte solution and improves cycle performance, it slowly grows during repeated charge-discharge cycles leading to increased impedance of the electrode-electrolyte interphase, and then the capacity of the battery fades away. Since its chemical nature and morphology play a crucial role in the battery performance, many investigators have focused their effort on its characterization and improvement.

The use of additives in an electrolyte is an effective approach to improving the SEI properties.²⁾ Lithium bis(oxalate) borate (LiBOB) has received significant attention as the additive since it forms a stable SEI with superior thermal stability and better performance concerning safety.³⁻⁵⁾ The LiBOB additive works at the negative electrode. Some studies have shown that LiBOB also works at the positive electrode.⁶⁻⁹⁾ Although the SEI layers formed on the electrode surfaces in the electrolyte solutions containing LiBOB have been studied by XPS and FT-IR techniques, the details are still remained unclear.¹⁰⁻¹⁴⁾

X-ray absorption spectroscopy, XAS, using synchrotron radiation is sensitive to the electronic state and coordination structure of the element of interest in a sample. The spectrum of each compound has a unique feature in terms of energy position, shape and intensity of the resonances.^{15,16)} The XAS over the soft X-ray region (40 – 1000 eV) is possible to obtain the spectra of Li K-, C K-, O K-, and the first transition metal L-edges. These elements are main constituent of the SEI and B K-edge can also be an important target because the aim of this report is to find the role of the LiBOB additive in the SEI film.

The XAS spectra were collected for the LIB electrodes by using a total electron yield (TEY) and a fluorescence yield (FY) methods. These methods have different probing depths; ~ 10 nm for TEY, depending on the escape depth of electrons, and ~200 nm for FY, depending on the X-ray attenuation length in materials, respectively.^{17,18)} Surface sensitivity of the EY method can be increased by introducing partial electron yield (PEY) technique (~ 2, 3 nm), which does not detect low energy secondary electrons escaped from deeper part of the sample. When the spectral data from these three yield methods are obtained for a same sample, it is possible to analyze depth profiles non-destructively on the SEI-formed electrode surface. Since the fluorescence emission as a radiative process of atomic relaxation is of a low yield process over the soft X-ray energy region, the FY method gives us the spectra with lower signal-to-noise ratio compared to the EY method. In order to improve the quality of the FY data, we have introduced a large acceptable-area (80 mm²) silicon drift detector (SDD).¹⁹ The FY spectra obtained by using the large area SDD are comparable in quality to those of EY. The detectors are arranged to the sample chamber so that the all PEY, TEY and FY data can be collected simultaneously at the same part of the sample.

The XAS spectroscopy using the above three detection modes was applied to LiCoO₂ electrode surface in the present study. The LiCoO₂ electrode used was composed of polycrystalline LiCoO₂ thin film having a flat structure in nanometer scale and similar electrochemical properties to those of composite electrodes containing graphite as an electrical conductor and polyvinylidene fluoride (PVDF) as a binder.²⁰

2. Experimental

LiCoO₂ thin film was fabricated by a pulsed laser deposition (PLD) method on a flat platinum substrate. The structure and electrochemical properties are described in the previous report.²⁰ Its cycle performance as the cathode was evaluated by the cyclic voltammetry (CV) using a three-electrode cell with lithium metal as counter and reference electrodes. The electrolyte solutions used contained 1 mol dm⁻³ LiClO₄ in ethylene

carbonate (EC) / diethyl carbonate (DEC) (1:1 (v/v)) mixed solvent. The aim of the present experiments is to study the effect of 0.1 wt% lithium bisoxalatoborate (LiBOB) additive to the above electrolyte solutions on the formation of SEI film and thus the performance of the electrode.

Figure 1 shows the decrease in discharge capacity after charge-discharge cycles. After 20 cycles, the electrode retained only 60% of its initial capacity. However, it could be increased to more than 90% by adding LiBOB. It is important to know the role of the additive concerning the SEI film formation.

Soft X-ray absorption spectroscopy at Li K-, O K-, C K-, and Co L-edges was used to characterize the electrode surfaces. The spectra were obtained at the beam line BL-2 of Ritsumeikan University SR Center (Shiga, JAPAN). Three electrodes were prepared; a pristine, a soaked in the electrolyte solution, and a 20-cycled electrodes. The electrodes soaked and cycled as the cathode were rinsed with dimethyl carbonate and dried in an argon filled glove box where the dew point was lower than -70 °C. To avoid the exposure of the samples to the air, they were transferred to the high vacuum sample chamber of BL-2 via a transfer vessel filled with argon gas.²¹ The XAS spectra were obtained in three different modes simultaneously; the partial fluorescence yield (PFY) mode with a silicon drift detector (KETEK, VITUS R100 with a 0.1 μm Parylene-N film window), the total electron yield (TEY) mode (sample current mode), and the partial electron yield (PEY) mode (using a micro-channel plate (MCP) applying an appropriate retarding voltage in front of the MCP).¹⁹ In the case of Li K-edge XAS, the MCP was employed as a total fluorescent yield (TFY) detector applying high enough retarding voltage for electrons.

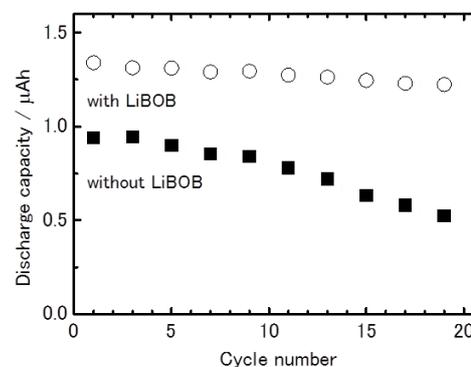


Figure 1. Cycle performance of LiCoO_2 electrode with and without LiBOB.

3. Results and Discussion

Figure 2(a) shows Co $L_{2,3}$ -edge XAS spectra obtained by the TEY method of the pristine electrode, LiCoO_2 and CoO powders as reference spectra. The peaks at 780.0 and 794.6 eV were attributed to L_3 - (pertaining to the electronic transition of $\text{Co}2p_{3/2} \rightarrow \text{O}2p\text{-Co}3d(e_g)$ hybrid states) and L_2 - ($\text{Co}2p_{1/2} \rightarrow \text{O}2p\text{-Co}3d(e_g)$ hybrid states) edges. These two peaks appear at the same energies for both the pristine electrode and LiCoO_2 , indicating Co ions in the electrode exist as Co^{3+} .²²

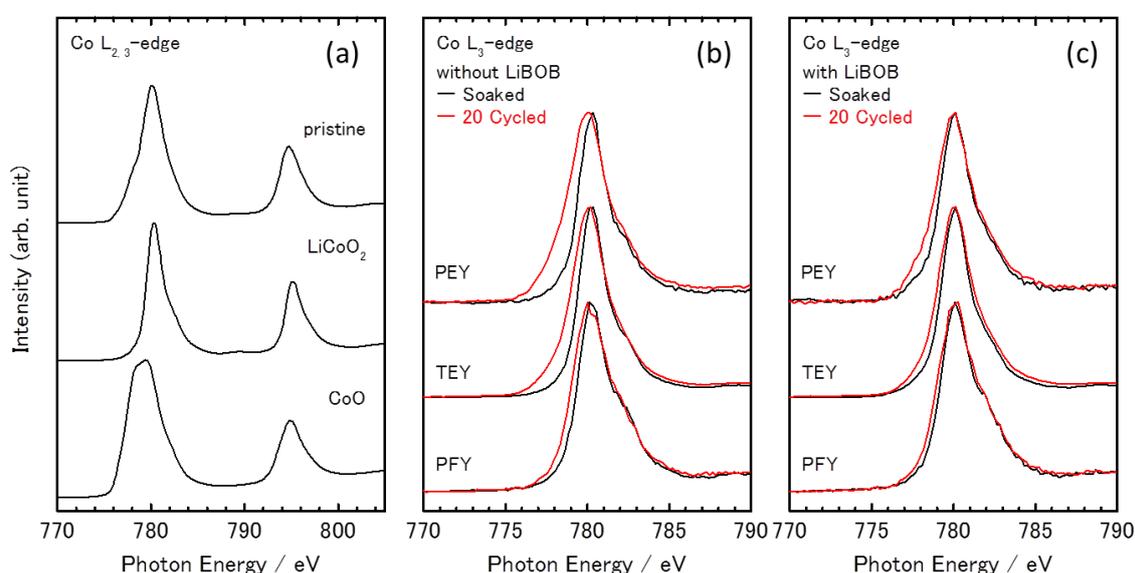


Figure 2. Co $L_{2,3}$ -edge spectra of the pristine electrode, LiCoO_2 and CoO powders (a), of the soaked- and 20-cycled- LiCoO_2 electrode in the electrolyte solution without (b) and with 0.1 wt% LiBOB (c).

Figures 2(b) and (c) show the comparisons of Co L_3 -edge spectra for the soaked and 20-cycled electrodes without and with the LiBOB additive, respectively. Small peak shift or the appearance of a lower energy component than 780 eV caused by the cycles in the surface sensitive PEY and TEY spectra in Fig.2(b) indicates that the charge-discharge reaction causes some of the Co^{3+} ions at the electrode surface to be reduced to Co^{2+} .²³ However if the LiBOB is added, the reduction is effectively suppressed as shown in Fig.2(c). The PFY spectra in Fig.2(b) indicates that almost no reduction of Co ions occur in

the bulk phase. The effect of LiBOB addition again very effectively suppresses the reduction in the bulk as shown in the PFY spectra of Fig.2(c). It can be concluded then that the LiBOB additive prevents not only the bulk phase of the electrode but the surface phase from the reduction of the Co ions by the charge-discharge reactions.

Figure 3(a) shows O K-edge XAS spectra of the pristine electrode and the reference compounds, LiCoO_2 , Li_2CO_3 , and CoO collected in TEY mode. The pre-edge peak A at 529.8 eV is attributed to the transition from $\text{O}1s$ to $\text{O}2p\text{-Co}3d(e_g)$ hybrid states and the broadened peak over the higher energy region (higher than 535 eV) is to σ^* transitions. The spectra for the soaked and 20-cycled electrodes in the electrolyte solution without the additive are displayed in Fig.3(b). In these spectra a peak B_1 at around 533 eV appears which can be assigned to be of lithium carbonate. This peak is most strongly observed in the PEY mode and most weakly in the PFY. This result means Li_2CO_3 is formed on the electrode surface just after the soak. In addition to the Li_2CO_3 detection by the surface sensitive PEY and TEY modes, these modes also detect a peak A at 529.8 eV assigned to bulk LiCoO_2 , indicating that the SEI layer composed of Li_2CO_3 is very thin.

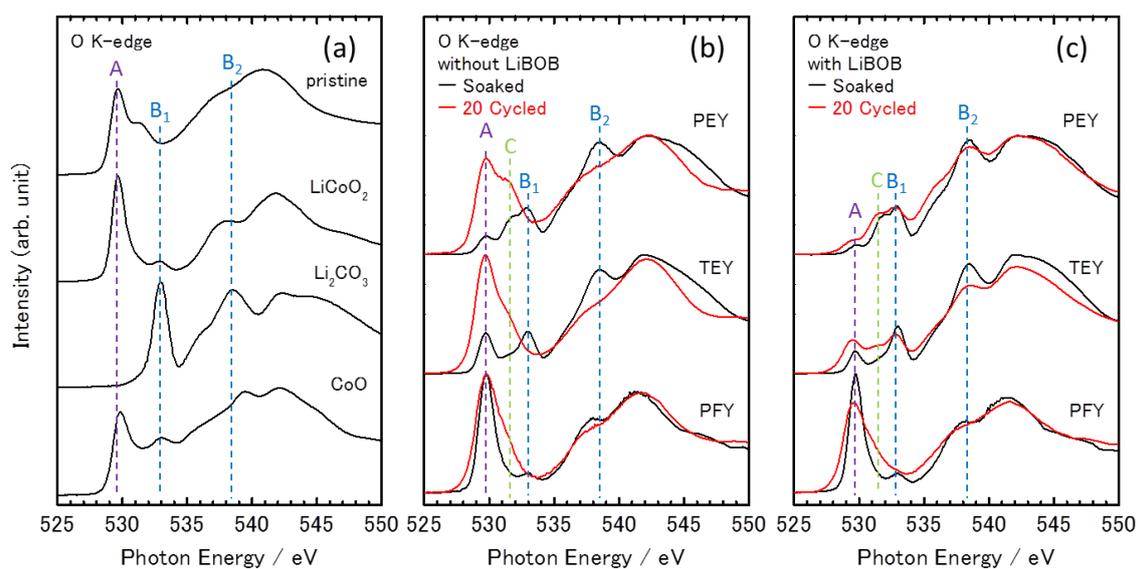


Figure 3. O K-edge spectra of the pristine electrode, LiCoO_2 , Li_2CO_3 , CoO powders (a), the soaked- and 20-cycled- LiCoO_2 electrode in the electrolyte without (b) and with 0.1 wt% LiBOB (c).

By comparing the spectra in Fig.3(b) for the soaked (black) and the 20-cycled electrode (red), it is obvious that the surface structure changes significantly after the charge-discharge reactions as indicated in the spectra obtained by the EY modes. This structure change is effectively suppressed by adding LiBOB as shown in Fig.3(c).

Careful inspection of the PEY and TEY spectra in red in Fig.3(b), the data obtained without the additive, indicates that after the cycles the peak B₁ of Li₂CO₃ disappears and a peak C at 531.8 eV strongly appears as a shoulder. The peak C at 531.8 eV is known to be of organic carbonyl.²⁴ Therefore, the charge-discharge reaction seems to remove the surface Li₂CO₃ and produce organic carbonyl compound at the surface possibly as a decomposition product of the solvent. Since the peak A of LiCoO₂ appears the most strongly even after the cycles, the carbonyl film formed at the surface must be very thin.

If the LiBOB is added to the electrolyte, the effect of charge-discharge reaction is quite different. The most surface sensitive PEY spectrum for cycled in Fig.3(c) has strong peaks B₁ of Li₂CO₃ and C of carbonyl, and a small peak A of LiCoO₂. The O K-edge results altogether conclude that the additive protects the SEI film composed of Li₂CO₃ and carbonyl compound against the attack of the charge-discharge reaction and that without the additive the SEI film can be easily decomposed and only very thin carbonyl film remains after the reaction. Since the peaks originated from CoO appear at almost the same energies as those of LiCoO₂, it is impossible to discuss the Co ion reduction by using O K-edge spectra.

The Li K-edge energy region spectra obtained in the TEY mode for the pristine electrode and references, LiCoO₂, Li₂CO₃ and CoO powders, are shown in Fig. 4(a). The spectrum for LiCoO₂ shows a sharp peak A at 61.5 eV which is characteristic of ionic lithium^{15,25} and the other broad peaks corresponding to Co M-edge transitions. All of these peaks are also observed in the spectrum of the pristine electrode. Figures 4(b) and (c) show the comparisons of the soaked and 20-cycled electrodes. The features in the TEY spectra of electrodes soaked in the electrolytes both with and without LiBOB are just the same as that of Li₂CO₃. This result is in accord with those of O K- and C K-edge XAS data indicating

Li_2CO_3 is generated on the electrode surface after the soak. Here again the addition of LiBOB protects the SEI film composed of Li_2CO_3 from the decomposition by the charge-discharge reaction. The TFY spectra of the electrodes seem to contain at least two components, i.e. of Li_2CO_3 and LiCoO_2 . Since the TFY mode over the Li K-edge energy region is relatively surface sensitive, its spectral data can contain the information both on the bulk LiCoO_2 and the SEI film containing Li_2CO_3 .

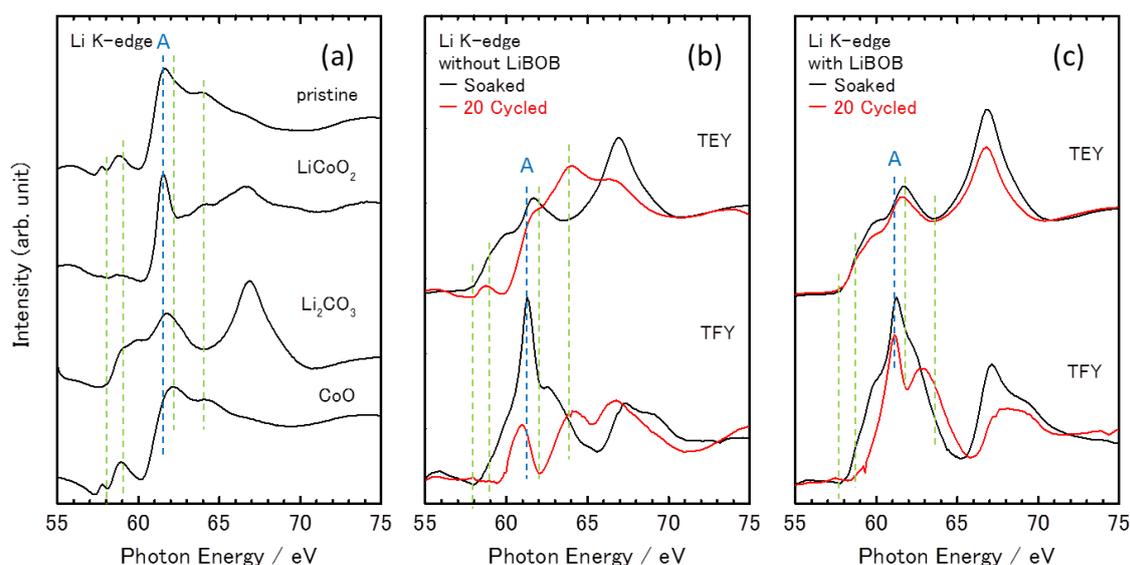


Figure 4. Spectra over the energy region for Li K- and Co M-edges of the pristine electrode, LiCoO_2 powder, and reference samples of Li_2CO_3 and CoO (a), and the soaked- and 20 cycled- LiCoO_2 electrode in the electrolyte without (b) and with 0.1 wt% LiBOB (c).

Figure 5(a) shows C K-edge XAS spectra of CoCO_3 , Li_2CO_3 and graphite as references collected by TEY mode. The peak A at 285.5 eV is attributed to a double bond carbon ($\text{C}=\text{C}$) and peak B at 290.8 eV is to carbonate (CO_3^{2-}). The comparison of TEY and PEY spectra of the soaked and 20-cycled electrode cycled in the electrolyte solutions without and with LiBOB are shown in Fig.5(b) and (c), respectively. First, all the soaked spectra show a peak B of carbonate (290.8 eV), a peak C of C-H (288 eV) and a peak A of $\text{C}=\text{C}$ (285.5 eV) regardless of the LiBOB addition, implying the decomposition of electrolyte solution at the electrode surface and the generation of carbonates and alkyl

compounds.²⁶ The peak C assigned to alkyl compounds does not change much with cycles.

The behavior of peak B in Fig.5(b) indicate that the carbonyl (from solvent) and carbonate (of lithium salt) present at the surface of soaked electrode almost disappear at the surface (PEY result) after the charge-discharge reactions. While the results given in Fig.5(c) show that the LiBOB additive prevents the surface composition change by the reactions, so the surface is covered by LiCO₃ SEI securely.

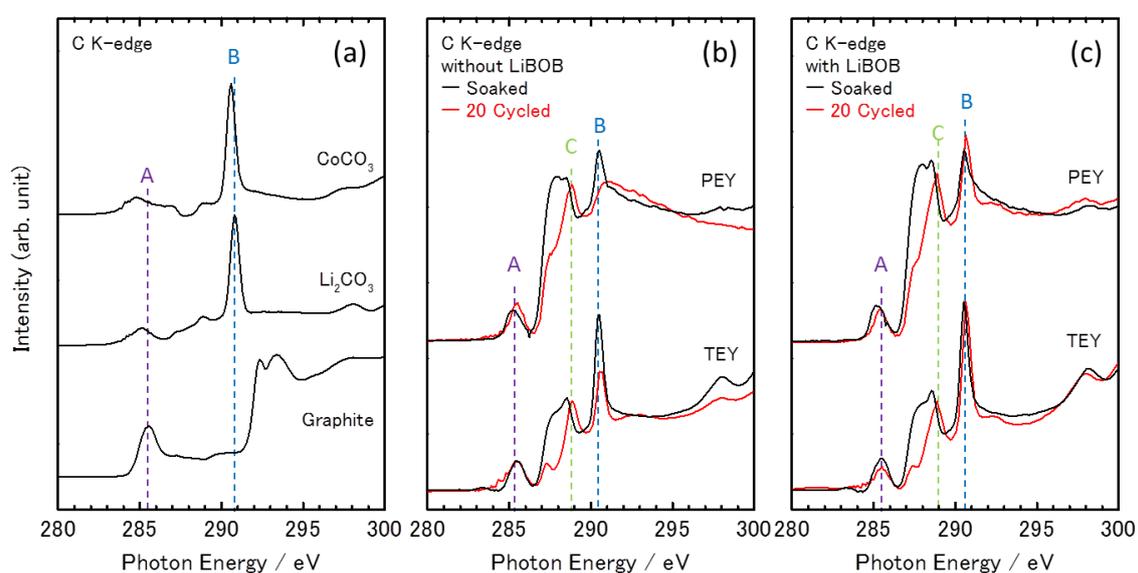


Figure 5. C K-edge spectra of graphite, Li₂CO₃ and CoCO₃ as references (a), soaked- and 20 cycled-LiCoO₂ electrode in LiClO₄ EC/DEC containing no 0.1 wt% LiBOB (b), and the same but containing 0.1 wt% LiBOB (c).

Figure 6 shows B K-edge TEY spectra of the electrode. The electrolyte solution contained LiBOB. The peak at 194 eV, corresponding to a four coordinated boron compound,²⁷ did not appear just after the soak but appeared after the charge-discharge cycles. This result indicates that the electrode does not absorb LiBOB and that B containing decomposition product of LiBOB with four-coordinated structure accumulates on the electrode surface. This B containing decomposition product must be protecting the SEI layer.

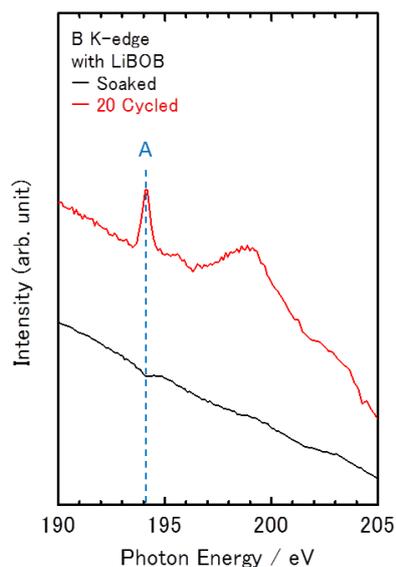


Figure 6. B K-edge XAS spectra (TEY) of LiCoO₂ electrode soaked and cycled in an electrolyte solution, 1 mol dm⁻³ LiClO₄ in EC/DEC, containing 0.1 wt% LiBOB.

4. Conclusions

The effect of LiBOB addition to the electrolyte on the SEI layer formed on a LiCoO₂ thin film electrode was investigated using soft X-ray XAS analysis. PEY, TEY and FY methods were used to collect the spectra simultaneously. These methods have different probing depths. At the surface of the electrode Co ion was reduced to Co²⁺ after 20 cycles of charge-discharge reactions and that by adding the LiBOB the reduction was suppressed. From the O K- and C K-edge results it was found that without the LiBOB the SEI layer formed on the electrode surface by a soaking process was degraded during the charge-discharge reactions, leading to the reduction of LiCoO₂ electrode surface by the solvent. B K-edge XAS spectra for 20-cycled electrode showed a peak characteristic of four-coordinated boron compound indicating its formation in the SEI layer. This boron species seems to protect the SEI layer from degradation during the charge-discharge cycles resulting in longer cycle life.

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