

XAFS and TOF–SIMS analysis of SEI layers on electrodes

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Abstract

We have used X-ray absorption fine structure (XAFS) in order to analyze the solid electrolyte interface (SEI) layer on the graphite anode and the LiCoO₂ cathode in a lithium-ion battery. The SEI layers on the electrodes in the propylene carbonate (PC)-based electrolyte containing an ethylene sulfite (ES) additive were analyzed based on the different sulfur oxidation states with sulfur K-edge X-ray absorption near-edge structure spectroscopy (S K-edge XANES), X-ray photoelectron spectroscopy (XPS) and time-of-flight–secondary ion mass spectrometry (TOF–SIMS). The SEI layer on the graphite anode was mainly consisted of a sulfite-type compound with an inorganic film like Li₂SO₃ and an organic films like ROSO₂Li. Furthermore, it was proven that the SEI layer on the graphite anode contained alkyl sulfide species. We also found that the SEI layer on the LiCoO₂ cathode also contained alkyl sulfide species.

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Keywords: Lithium-ion battery; XAFS; S K-edge XANES; TOF–SIMS; SEI

1. Introduction

Battery materials have been studied in order to improve battery performance such as capacity, rate capability and cycle life. For what concerns the electrolyte, some additives have been reported to improve the interface between the electrode and electrolyte [1–11]. In order to analyze the function of the additives, we reported that a lithium-oxy-sulfite film (Li₂SO₃ and/or ROSO₂Li) was formed by the reductive decomposition of the ethylene sulfite (ES) additive on the graphite in a LiPF₆/propylene carbonate (PC) and ES electrolyte [12]. These films contribute to the solid electrolyte interface (SEI) layer, which can transport lithium ion, but prevent electron transfer [9]. Over the past few years, numerous studies have been made on the SEI layer of anodes. There are few studies of the SEI layer on the cathode [13,14].

X-ray absorption fine structure (XAFS) has been used as a technique which analyzes local structure changes and the oxidation states of transition metal oxides in composite cathodes such as LiCoO₂, LiNiO₂, Li(Ni, Co)O₂ and LiMn₂O₄ for Li-ion batteries [15,16]. However, there has been no study on the analysis of the SEI layer using XAFS. X-ray

absorption near-edge structure spectroscopy (XANES) is a sensitive probe of the valency, the coordination geometry and the symmetry of the unoccupied electronic states [17]. Sulfur K-edge X-ray absorption near-edge structure spectroscopy (S K-edge XANES) has been used to study sulfur speciation in various natural systems such as coal [18], asphaltenes [19] and soil humic substances [20]. Sulfur is a good marker of oxidation processes as it is very sensitive to oxidation and exhibits a range of oxidation states from –2 to +6. The S K-edge XANES can provide all the information about state of sulfur in the SEI layer. In contrast, X-ray photoelectron spectroscopy (XPS) and time-of-flight–secondary ion mass spectrometry (TOF–SIMS) can provide surface chemical information about the SEI layer.

The purpose of this study is to clarify the local structure around sulfur atom in the film formed on the graphite anode and the LiCoO₂ cathode in the ES additive electrolyte using S K-edge XANES, XPS and TOF–SIMS.

2. Experimental

The anode was prepared by coating a mixture of graphite (Mitsubishi Power Graphite (MPG), Mitsubishi Chemical Corporation) and poly vinylidene difluoride (PVdF) on a copper foil. The cathode was prepared by coating a mixture

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of LiCoO_2 and acetylene black and PVdF on an aluminum foil. The electrolyte was 1 M LiPF_6/PC solution containing 2–10% ES by weight (Sol-RiteTM, Mitsubishi Chemical Corporation). The cell was galvanostatically charged and discharged at 0.16 mA/cm^2 within the potential range of 3–4.2 V. After one cycle, the cell was disassembled in an Ar glove box. The analytical measurements carried out after sample transfer using an Ar-filled sealed container. The S K-edge XANES measurements were carried out using synchrotron radiation at BL-9C, Photon Factory, High Energy Accelerator Research Organization (Tsukuba, Japan) at 2.5 GeV with an average current of 400 mA [21]. X-rays were monochromatized with a Si(1 1 1) double crystal monochromator and higher orders were reduced with a pair of Ni-coated flat mirrors. The energy of the peaks of Na_2SO_4 was assumed as 2481.95 eV. The measurements of the sulfur standard reagents for identification was carried out by the conversion electron yield method in order to prevent self-absorption of the sample. The SEI layers formed on the electrodes were measured with fluorescence yield under He atmosphere. X-ray photoelectron spectroscopy (XPS; ULVAC-PHI5700ci) was used in order to obtain information about the surface chemical state of the SEI layer. The X-ray source was a monochromatic Al K α source (14 kV, 350 W). TOF-SIMS measurements were performed with TRIFT II (Physical Electronics). The primary ion used a Ga^+ gun (15 kV, 600 pA).

3. Results and discussion

3.1. Charge–discharge tests

Fig. 1 shows the voltage profiles of the first charge–discharge curves of a $\text{LiCoO}_2/\text{graphite}$ -ion cell in PC and ES containing LiPF_6 . A peak was observed at 1.9 V. This peak was not detected in the second cycle and it is due to film formation by reduction of ES additive. For the 2 wt.% ES

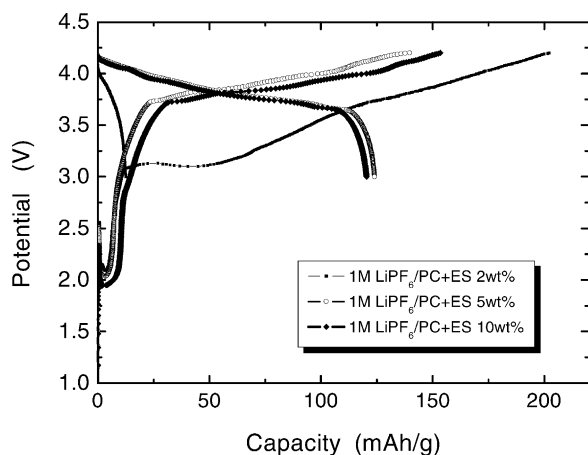


Fig. 1. First charge and discharge curves in 1 M LiPF_6/PC + ES 5% electrolyte using $\text{LiCoO}_2/\text{graphite}$ -ion cell.

additive in the electrolyte, it was difficult to intercalate the lithium ion since the quantity of the additives was not sufficient. It was confirmed that the lithium ion could intercalate into the graphite at a concentration of 5% or more.

3.2. Sulfur analysis with S K-edge XANES

XANES spectroscopy can distinguish the various forms of sulfur because the energy position of the absorption edge in a XANES spectrum strongly correlates with the oxidation level of sulfur in a molecule, shifting to high energy as the oxidation state increases. Fig. 2 shows the S K-edge XANES spectra of some sulfur reagents and the SEI layer formed on the graphite anode and the LiCoO_2 cathode in the 1 M LiPF_6/PC + ES 5% electrolyte. The peak positions are shown in Table 1. The SEI layer formed on the graphite anode had four peaks (2471.9, 2473.3, 2477.6 and 2480.4 eV). The strong peaks at 2477.6 and 2480.4 eV are attributed to Li_2SO_3 and ROSO_2Li as they correspond to the Na_2SO_3 (2477.6 eV) and $n\text{-C}_7\text{H}_{15}\text{OSO}_2\text{Na}$ (2480.5 eV) spectra. The sulfate in Li_2SO_4 was observed at 2482.3 eV as well as Na_2SO_4 . For the S K-edge XANES spectra, the spectra seldom change due to a difference in the counter cation such as Li and Na. The S K-edge XANES spectrum of ES has two peaks at 2476.3 and 2478.1 eV. These peaks were not observed from the SEI layer formed on the graphite in the 1 M LiPF_6/PC + ES 5% electrolyte. On the other hand, it is considered that the peaks at 2471.9 and 2473.3 eV are due to a component with a low valence state. The S K-edge XANES spectrum of Na_2S (–2 oxidation state) has four peaks at 2471.2, 2478.4, 2480.2 and 2482.0 eV. Sulfur has only one peak at 2472.1 eV. The S K-edge XANES spectrum of di-*n*-propyldisulfide (R-S-S-R) showed two peaks at 2471.9 and 2473.4 eV. Moreover, the S K-edge XANES spectrum of diphenyldisulfide (Ph-S-S-Ph) showed peaks at 2472.2 and 2473.9 eV. The S K-edge

Table 1
S K-edge XANES peak energy of standard sulfur reagent and SEI layers on the graphite anode and the LiCoO_2 cathode in 1 M LiPF_6/PC + ES 5% electrolyte

Sample	Peak energy (eV)			
Na_2S	2471.15	2478.35	2480.15	2481.95
S (sulfur)	2472.05			
Na_2SO_3			2477.60	
Li_2SO_4				2482.25
$n\text{-C}_7\text{H}_{15}\text{OSO}_2\text{Na}$				2480.45
Ethylensulfite (ES)		2476.25	2478.05	
Diphenyldisulfide (Ph-S-Ph)	2472.80	2474.15		
Dimethylsulfide ($\text{H}_3\text{C-S-CH}_3$)		2473.25		
Diphenyldisulfide (Ph-S-S-Ph)	2472.20	2473.85		
Di- <i>n</i> -propyldisulfide ($\text{H}_7\text{C}_3\text{-S-S-C}_3\text{H}_7$)	2471.90	2473.40		
PC + ES 5% anode	2471.94	2473.29	2477.62	2480.39
PC + ES 5% cathode	2472.50			2482.25

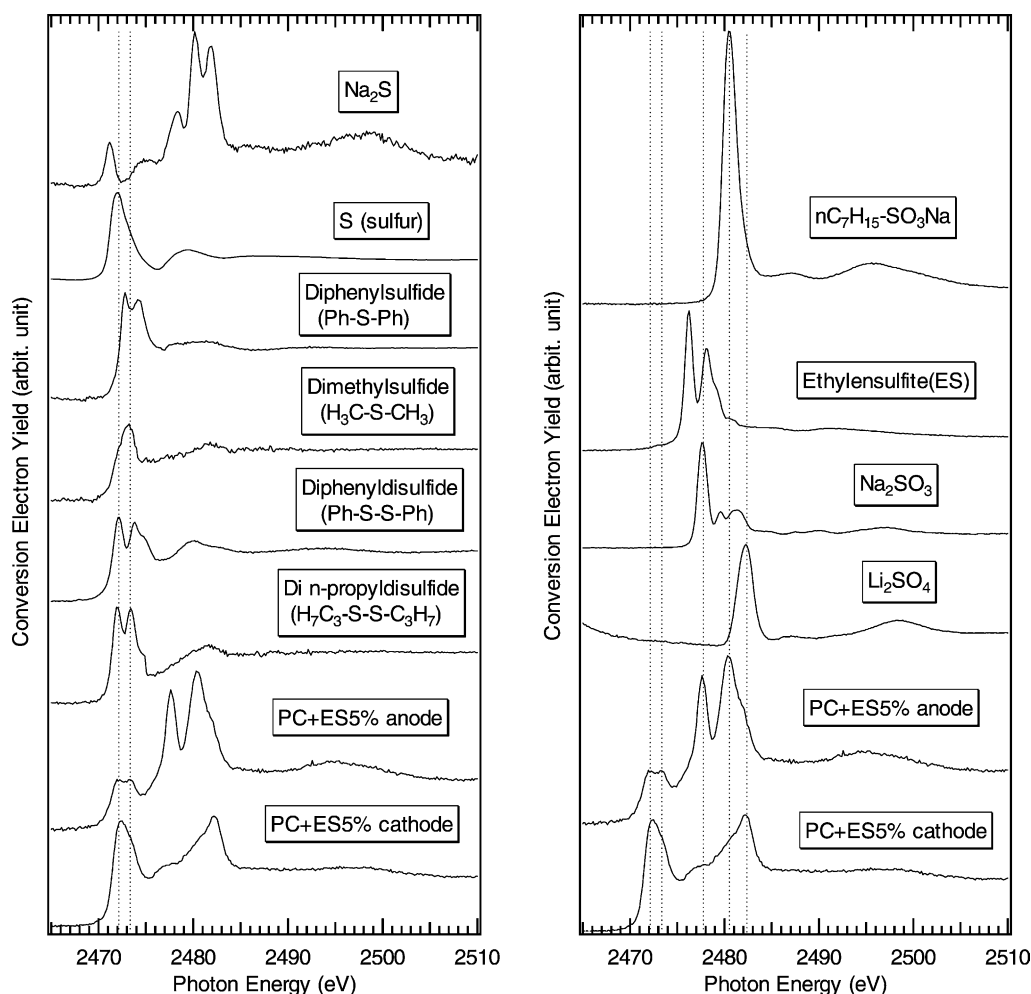


Fig. 2. S K-edge XANES spectra of standard sulfur reagents and SEI layers on the graphite anode and the LiCoO_2 cathode in 1 M $\text{LiPF}_6/\text{PC} + \text{ES}$ 5% electrolyte.

XANES spectrum of dimethylsulfide (C-S-C) showed one peak at 2473.9 eV. The diphenylsulfide (Ph-S-Ph) spectrum has two peaks at 2472.8 and 2474.2 eV. The SEI layer of the graphite anode consists of two peaks at 2471.9 and 2473.3 eV. These peaks are very similar to the R-S-S-R structure. It was found that the SEI layer based on the ES additive contains not only the sulfite (SO_3) components but also the alkyl sulfide (C-S) component. For the SEI layer formed on the LiCoO_2 cathode, the sulfite peak (Li_2SO_3 , ROSO_2Li) at 2477.6, 2480.5 eV was not detected. The S K-edge XANES spectrum of the SEI layer on the LiCoO_2 cathode showed two peaks at 2472.5 and 2482.3 eV. The peak at 2482.3 eV is attributed to Li_2SO_4 . The LiCoO_2 material includes Li_2SO_4 as an impurity, so it is difficult to specify whether the cathode SEI layer contains Li_2SO_4 . The peak at 2472.5 eV is attributed to the C-S component. We found that the SEI layer of sulfide exists on the surface of both electrodes (LiCoO_2 cathode and graphite anode). It is clear that the SEI component of the LiCoO_2 cathode is different from the SEI on the graphite anode. The sulfide species such as R-S-S-R, Ph-S-S-Ph, C-S-C, Ph-C-Ph is solved in the

electrolyte. The S K-edge XANES spectra did not change even if the electrode was washed in the solvent like PC, DMC. Thus, the detected SEI component is different from these sulfide species. We consider that species with S-C bond on the electrode are polymeric compounds.

3.3. Sulfur analysis with S 2p-XPS

XPS is a technique that can provide information on the chemical state of the elements in solids. The kinetic energy of the electrons, the binding energy, is characteristic of both the element and its chemical bonding state. XPS analysis is limited by the escape depth of the electrons, usually about 3–5 nm. Thus, XPS is a surface analysis technique. Fig. 3 shows the XPS spectra of some sulfur standard reagents and the SEI layer formed on the graphite anode and the LiCoO_2 cathode in the 1 M $\text{LiPF}_6/\text{PC} + \text{ES}$ 5% electrolyte. The SEI layer on the graphite anode had peaks around 168.1 and 164 eV. The peaks around 168–169 eV are assigned to Li_2SO_3 , and ROSO_2Li . The peak at 164.5 eV is considered to be reduced sulfur. According to Linderg et al., the organic

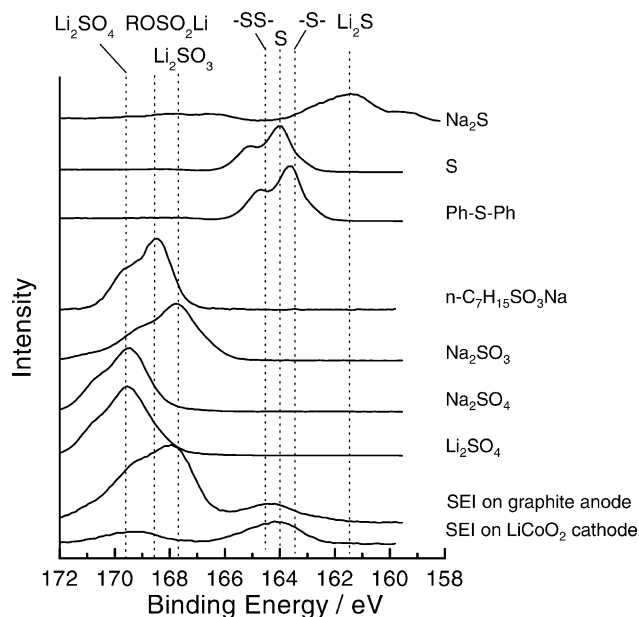


Fig. 3. S 2p XPS spectra of standard sulfur reagents and SEI layers on the graphite anode and the LiCoO₂ cathode in 1 M LiPF₆/PC + ES 5% electrolyte.

sulfide species such as C-S-S-C, S and C-S-C are detected at 164.5, 164.1 and 163.5 eV, respectively [22]. Our measured XPS spectra peaks of Ph-SS-Ph and S were observed at 164.5 and 164 eV. Na₂S (−2 oxidation state) was detected at 162 eV. The peak at 164.5 eV observed from the anode SEI layer can be assigned to the sulfide component. The XPS spectra of the SEI layer on the LiCoO₂ cathode had the peak attributed to the organic sulfide species at 164.3 eV, however a sulfite species was not detected. Based on these results, the SEI layer of the sulfite component could be seen only on the graphite anode. The organic sulfide species, however, could exist on both the anode and the cathode.

3.4. Sulfur analysis with TOF-SIMS

TOF-SIMS can analyze the surface structure and separate the charged ion from the sample based on the mass/electron charge (m/z) using a time-of-flight type mass spectrometer. The analytical depth information is within 2 nm of the top layer. TOF-SIMS has good advantages of high sensitivity and high resolution. As shown in Fig. 4, the peaks of S ($m/z = 31.97$), SO ($m/z = 47.97$), SO₂ ($m/z = 63.96$) and SO₃ ($m/z = 79.96$) were detected in the surface film formed on the graphite anode. The peaks of $m/z = 47.97$ and 63.96 are fragment peaks of SO₃. A peak for SO₄ ($m/z = 95.95$) was not detected. These results suggest that the surface SEI layer on the graphite contains a sulfite species. On the other hand, for the SEI layer on the cathode, no peaks were attributed to SO ($m/z = 47.97$), SO₂ ($m/z = 63.96$), SO₃ ($m/z = 79.96$) and SO₄ ($m/z = 95.95$). The peaks of S ($m/z = 31.97$), PO₂ ($m/z = 62.96$) and PO₃ ($m/z = 78.96$) were detected. The PO_x species may be due to LiPO_xF_y (e.g. LiPO₂F₂, LiPOF₃)

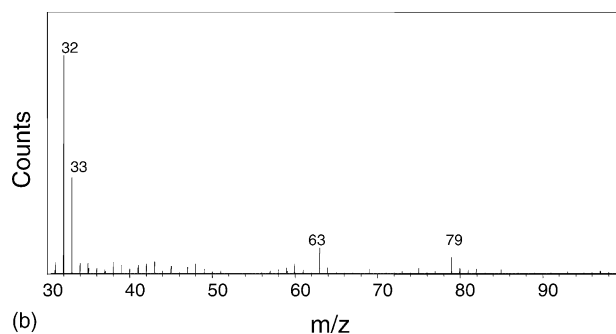
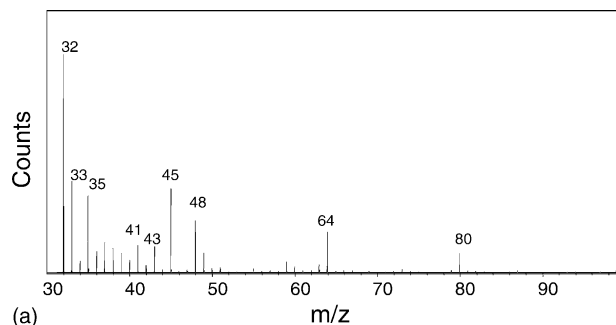


Fig. 4. TOF-SIMS spectra of standard sulfur reagents and SEI layers on the (a) graphite anode, and (b) the LiCoO₂ cathode in 1 M LiPF₆/PC + ES 5% electrolyte. The measurements were done in the negative ion mode.

the peaks of which can be observed from the graphite anode. We found that the SEI layer on the cathode contains an existed sulfur (probably sulfide) species but not a sulfite species.

4. Conclusion

We have used the X-ray absorption fine structure (XAFS) technique in order to analyze SEI layer in the lithium-ion battery. The XAFS measurement has good advantages, for example, it can do an analysis under atmospheric conditions without pretreatment. Thereby, the XAFS measurement can possibly prevent breakdown of SEI layer by vacuum treatment. An in situ measurement would be possible by designing an adequate cell. As another advantage, it can analyze the entire SEI layer compared to the surface analysis by XPS and TOF-SIMS. The ion sputtering method has been used to obtain depth information of the SEI by XPS and TOF-SIMS. The ion sputtering method is useful tool, however, there are some possibilities to reduce the chemical species in the sample by the Ar sputtering.

In this study, we investigated the sulfur component in the SEI layer formed on the graphite anode and the LiCoO₂ cathode by S K-edge XANES spectroscopy, XPS and TOF-SIMS. The SEI layers on the electrodes in the ethylene sulfite additive electrolyte were estimated based on the different S oxidations. It was found that the SEI layer on graphite consists of sulfite compounds such as an inorganic film like Li₂SO₃ and an organic film like ROSO₂Li. Furthermore, it

was proven that the SEI layer on the graphite anode contained alkyl sulfide species. We found that the SEI layer on the LiCoO₂ cathode also contained alkyl sulfide species.

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