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X-ray Absorption Spectroscopy Analysis of SEI Formation on Graphite Anodes in Lithium-Ion Batteries

Takeru Hamada[1], Daisuke Shibata[2], Chengchao Zhong[1], Keiji Shimoda[3], Ken-ichi Okazaki[2] and Yuki Orikasa[1]

1) *Department of Applied Chemistry, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
2) *Research Organization of Science and Technology, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
3) *Ritsumeikan Global Innovation Research Organization, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

Soft X-ray absorption spectroscopy (XAS) was used to study the chemical species in the solid electrolyte interphase (SEI) formed on graphite anodes in lithium-ion batteries. Li K-edge XAS, for which limited SEI studies exist, was measured. By directly probing the chemical state of SEI-related compounds with Li, C, and F K-edge spectra, we identified lithium fluoride as the dominant SEI component and confirmed that it remains stable after charge-discharge cycling. The spectra also suggest that LiF exists in a defective or amorphous state, which may contribute to the excellent cycling stability of graphite anodes.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in electric vehicles, portable devices, and other energy storage applications. Graphite, the most widely used anode material, has a theoretical specific capacity of 372 mAh g^{-1} and operates at low potentials (0.07-0.23 V vs. Li/Li^+)[1]. Although the capacity is limited due to the intercalation of lithium between graphite layers [2], the excellent cycling performance has broadened the application range of the technology.

The solid electrolyte interphase (SEI) formed at the anode/electrolyte interface plays a key role in the long-term stability of LIBs [3, 4]. This thin layer, typically tens of nanometers thick, is formed mainly by reductive decomposition of the electrolyte during initial charging and acts as a passivation that suppresses further electrolyte reduction. Despite its importance, elucidating the formation mechanism, structure, and chemical composition of the SEI remains challenging.

Soft X-ray absorption spectroscopy (sXAS) is a powerful tool for probing the electronic states of surface layers containing light elements. Since the SEI contain light elements such as Li, C, O, and F [5], sXAS is ideally suited for their analysis. Previous C K-edge XAS studies by Augustsson et al. revealed the presence of organic lithium compounds - including lithium oxalate, succinate, and lithium methoxide in SEI [6] - while F K-edge studies by Xia et al. identified lithium fluoride as the major inorganic component [7]. However, SEI studies using Li K-edge XAS (approximately at 55 eV) have been rare [8], largely due to instrumental limitations. Recent advances have enabled the acquisition of reference spectra for various lithium compounds [9, 10], demonstrating the feasibility of fingerprinting.

In this study, Li, C and F K-edge sXAS was applied to graphite anodes after charge-discharge cycling. By comparing the resulting spectra, we analyze the distribution of inorganic salts and organic species within the SEI and clarify the dominant SEI phases.

2. Experimental

Meso carbon microbeads (MCMB, MTI) were used as the active material for graphite electrodes. A slurry containing MCMB and poly(vinylidene fluoride) (PVdF, Kureha) in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 9:1 (MCMB:PVdF) was cast onto copper foil using a film applicator. The coated sheets were dried in air at 80 °C for 1 h and then under vacuum at 80 °C overnight, followed by calendering at 2.5 kN, which served as the working electrode. A 13 mm diameter working electrode and a 15 mm diameter lithium foil counter electrode (Honjo) were used. CR2032 type two-electrode cells were assembled in an argon-filled glove box. Celgard separators and 1.0 mol dm^{-3} $LiPF_6$ in ethylene carbonate/ethylmethyl carbonate (EC/EMC = 3:7 v/v; Kishida Chemical) were used. Cells were charged and discharged at 25 °C between 0.005 V and 3.0 V at 0.1 C (based on the theoretical capacity of 372 mAh g^{-1}).

After the cycling, the cells were disassembled in the glove box. The working electrodes were washed with dimethyl carbonate (DMC, Kishida Chemical) and dried under vacuum. The electrode sheets were mounted on carbon tape and transferred to the measurement chamber in the beamline without air exposure. Li, C, F K-edge XAS were measured at beamline BL-2 of the Ritsumeikan University SR Center in total electron yield (TEY) mode.

3. **Results and Discussion**

Fig. 1 shows the charge-discharge profile of the graphite electrodes. The obtained charge-discharge capacity is about 310 mAh g^{-1}, and no cycle degradation is observed. This indicates that the cells used in this study also reflect the charge-discharge behavior of a generally stable graphite electrode.

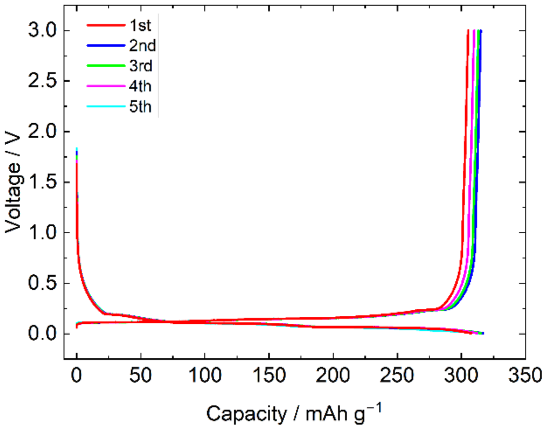

Fig. 1 Charge-discharge profile of graphite electrodes at the rate of 0.1C based on the theoretical capacity of 372 mAh g^{-1}.

Fig. 2 shows the C K-edge XAS of the graphite electrodes after charge-discharge compared to that of the electrode sheet before electrolyte immersion. The characteristic graphite π^* peak at 285.5 eV can be observed for the pristine electrode [11] and disappeared after cycling, indicating the formation of an overlying SEI layer. This result suggests that the sXAS of the cycled electrodes mainly contains the information of the SEI film other than graphite. SXAS using the total electron yield mode extracts information on the surface of a few nanometers[12], suggesting that SEI has a thickness greater than this. Two peaks were identified in the cycled electrodes, mainly around 287 eV and 289 eV, which are similar to the peak positions of the reported organolithium compounds[6]. These peaks did not change with cycling.

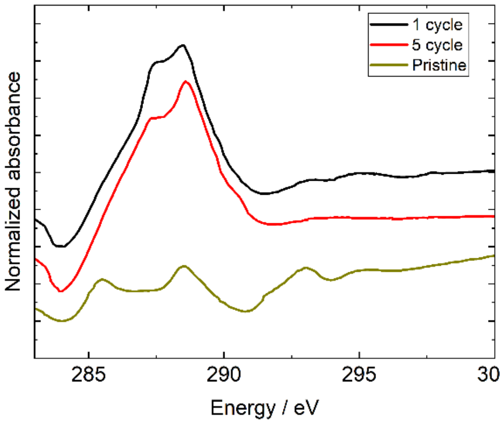

Fig. 2 C K-edge X-ray absorption spectra of the cycled graphite electrodes and the pristine electrode.

Fig. 3 shows the Li K-edge XAS of graphite electrodes after charge-discharge and LiF. LiF shows a large peak at 61.9 eV and also has a peak at 70 eV. The reported Li K-edge XAS of Li_2CO_3, Li_2O and LiOH do not have both peaks at these two energies simultaneously [13]. The spectra of graphite electrodes after charge-discharge cycling are similar to the shape of LiF, indicating that LiF is the main component of the lithium compound in SEI. However, compared to the spectrum of LiF, the pre-edge peak around 61 eV is not clear. This indicates that the LiF contained in SEI has defects or amorphous-like structure. On the other hand, the organic compound-derived peaks seen in the C K-edge were not observed. There are two possible reasons for this. The first is that LiF is very abundant as a lithium compound in SEI, and the second is that the Li K-edge is low energy and the components may be distributed in the SEI thickness direction.

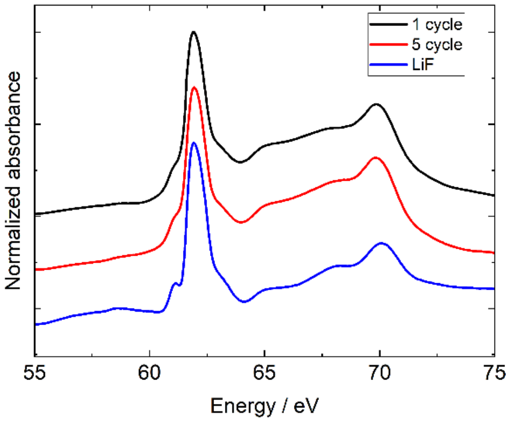

Fig. 3 Li K-edge X-ray absorption spectra of the cycled graphite electrodes.

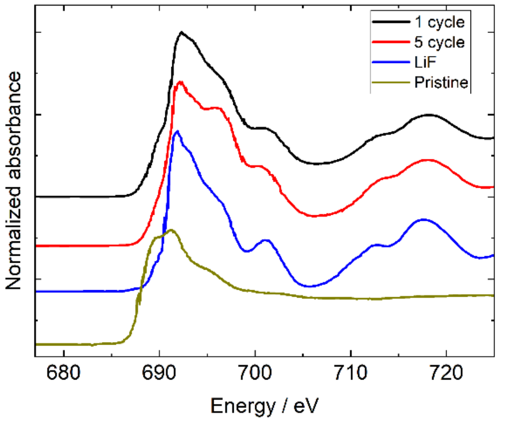

Fig. 4 F K-edge X-ray absorption spectra of the cycled graphite electrodes and the pristine electrode.

Fig. 4 shows the F K-edge XAS of the cycled graphite electrode, the electrode sheet before electrolyte immersion, and LiF. The peak of the pristine electrode can be assigned to the PVDF binder without LiF before the charge-discharge. LiF has a sharp peak at 692 eV and a broad shoulder around 697 eV. This shape is also seen in the cycled graphite electrodes. Therefore, the main component of fluorine-derived SEI is LiF. The observed XAS structure is also stable after 5 cycles. These results indicate that the SEI in the graphite electrodes with the conventional $LiPF_6$ salt has a large LiF-derived component and is stable at the graphite-electrolyte interface at 25 °C.

4. Conclusions

The chemical states of lithium compounds in the SEI layer formed on the graphite electrode were analyzed by soft X-ray absorption spectroscopy including Li K-edge. The obtained results show that the main lithium compound in the SEI is LiF, and no significant change in its composition was observed after 5 cycles; LiF may contain defects or amorphous states, which may contribute to the stability of the confirmed peaks derived from organolithium compounds, but no clear organolithium compound signals were detected in the Li K-edge. This suggests that the main component of the lithium compound in the SEI is LiF, and the spatial distribution of the component may also be affected.

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