Application of soft X-ray absorption spectroscopy and two-dimensional correlation spectroscopy to the electrochemical reaction in the \( \text{Li}_{1+x} \text{V}_3\text{O}_8/\text{Li} \) cell

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Abstract

This paper demonstrates the use of soft X-ray absorption spectroscopy (XAS) and two-dimensional (2D) correlation spectroscopy in the investigation of the mechanism of solid electrolyte interface (SEI) formation in the \( \text{Li}_{1+x} \text{V}_3\text{O}_8/\text{Li} \) electrode surface during the first lithium insertion–extraction cycle in a \( \text{Li}_{1+x} \text{V}_3\text{O}_8/\text{Li} \) cell. The XAS spectrum of the \( \text{Li}_{1+x} \text{V}_3\text{O}_8 \) electrode showed that LiF forms on the electrode surface during the lithium insertion–extraction process in the \( \text{Li}_{1+x} \text{V}_3\text{O}_8/\text{Li} \) cell. For the further understanding of this process, 2D correlation spectroscopy was applied to the lithium concentration (\( x \))-dependent F K-edge XAS spectra of the \( \text{Li}_{1+x} \text{V}_3\text{O}_8/\text{Li} \) system for the first insertion–extraction process. 2D XAS correlation analysis revealed that F K-edge XAS spectra are strongly influenced by the excitation of the core electron into a bound state.

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1. Introduction

Commercial rechargeable lithium batteries typically use a transition metal oxide as the positive electrode and a carbonaceous material as the negative electrode [1,2]. During the first insertion of lithium into the electrode, a passivating layer forms on the electrode surface. This passivating layer, which is known as the solid electrolyte interface (SEI), generally consists of lithium salts, organic solvent-based compounds, and in some cases, polymeric compounds [1–4]. The SEI plays a key role in the battery performances such as the faradaic efficiency, the cycle life, and irreversible capacity loss [5,6]. The SEI could be instantaneously formed through the contact of the electrode with the electrolyte or forms through the reductive decomposition of the electrolyte on the electrode surface. However, the mechanism of SEI formation is very complex and is not yet completely understood.

The properties of SEI have been identified by various spectroscopic and electrochemical techniques such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and ac impedance spectroscopy [7–10]. Recently, soft X-ray absorption spectroscopy (XAS) has begun to be used in the investigation of the electronic and structural properties of electrode materials and SEIs [11,12]. The major advantage of XAS is its element specificity, which makes possible the identification of the individual components of a composite electrode or even of a complete cell [13]. The peak positions and spectral features of an XAS spectrum can be used to extract useful structural parameters such as the oxidation state of the chemical species, site symmetry, and covalent bond. These
properties of XAS make it a very useful tool for the study of SEIs and electrode materials. Although XAS has many advantages, its application to the study of electrode materials has been limited because a typical electrode contains additives such as plastic binders and carbonaceous materials that often complicate the spectral data. To overcome this limitation, we first applied a two-dimensional (2D) correlation analysis to lithium concentration-dependent XAS spectra, and yield great resolution enhancement [14,15].

The objective of the present study is further extended that 2D correlation analysis can be applied to the complicated electrochemical interfaces combined with soft X-ray absorption spectroscopy. To achieve this objective, Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8} systems in 1.0 M LiPF\textsubscript{6} ethylene carbonate-diethyl carbonate (1:1 by volume) were studied during the first cycle using F K-edge XAS. We also undertake a 2D correlation analysis to obtain the detailed information about the SEI formed on the Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8} electrode.

2. Experimental

Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8}, where \(x\) is the lithium content, powders were prepared by heating a mixture of Li\textsubscript{2}CO\textsubscript{3} and V\textsubscript{2}O\textsubscript{5} at 680 °C as previously described [16,17]. The product was then ground in a freezer mill and sieved using a standard sieve (120 mesh). The resulting fine powder was used as the active material. Cathode electrodes were prepared by the mixing the Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8} powders with 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVdF) dissolved in 1-methyl-2-pyrrolidinone. The mixture were spread on Al foil substrates and pressing. Test cells were fabricated with these electrodes, metallic Li anodes, and polypropylene separators (Celgard 2400) in a glove box filled with Ar gas. A 1.0 M solution of LiPF\textsubscript{6} in ethylene carbonate-diethyl carbonate (1:1 by volume) was used as the electrolyte. Cell performance was evaluated by galvanostatically discharging and charging the cell at a constant current density of 0.2 mA/cm\textsuperscript{2} at room temperature with a WBCS 3000 battery tester system (Won A Tech Corp, Korea).

The F K-edge XAS measurements were performed at the U7 beam line of the Pohang Light Source (PLS). All spectra were obtained ex situ at room temperature. The electrodes were prepared for the XAS measurements in a glove box under highly pure argon atmosphere. After the electrochemical reactions, the electrodes were removed from test cells, and were then washed repeatedly with tetrahydrofuran (THF) to remove electrolyte. The electrodes were dried at 80 °C for 4 h, and were transferred to the XAS system under highly pure argon atmosphere in sealed vessels. The F K-edge XAS data were taken in a total electron yield mode, recording the sample current. The energy resolution was less than 0.2 eV. All spectra were normalized by a reference signal from an Au mesh with 90% transmission. The base pressure of the experimental chamber was of the order of 10\textsuperscript{-8} mbar.

Prior to the 2D correlation calculations, normalization over concentration was applied to all the XAS spectra. In addition, baseline corrections and smoothing of all the XAS spectra were performed before the 2D correlation calculations. Synchronous and asynchronous 2D correlation spectra were calculated using an algorithm based on the numerical method developed by Noda [18,19]. A subroutine named KG2D [20] composed in Array Basic language (GRAMS/386; Galactic Inc., Salem, NH) was employed for the 2D correlation analysis.

3. Results and discussion

Fig. 1 shows the normalized F K-edge XAS spectra obtained from the lithiated Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8} electrode as a function of lithium content during the first cycle over the energy range from 683 to 735 eV. Because the probing depth at these energies is less than 100 Å, the F K-edge near-edge X-ray absorption fine structure (NEXAFS) spectrum mostly originates from properties of the surface species. The F

![Fig. 1. Normalized F K-edge XAS spectra for the electrochemical reactions of lithium with Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8} during the first insertion process (a) and the first extraction process (b). The lithium content (\(x\) in Li\textsubscript{1+x}V\textsubscript{3}O\textsubscript{8}) is as indicated.](image-url)
K-edge spectrum of the pristine Li$_{1+x}$V$_3$O$_8$ electrode, which originates from the polymer binder, polyvinylidene fluoride (PVdF), in the Li$_{1+x}$V$_3$O$_8$ electrode, shows spectral features at ~690 eV due to the fluorine 1s electron to the hole state in the 2p level. The F K-edge XAS spectra of Li$_{1+x}$V$_3$O$_8$ clearly change when the insertion of lithium reaches 1.02 mol ($x = 1.02$). On further insertion of lithium ($x = 2.04, 2.37$ and $2.65$), the relative intensities of the spectral features change but the main spectral positions are approximately unchanged. Also, on extraction of lithium ($x = 0.66$), the main spectral features and positions show no noticeable variation compared to the spectrum of Li$_{1+x}$V$_3$O$_8$ ($x = 1.02$) in the insertion process, which means that the inserted lithium was consumed by irreversible reaction. In addition, the spectrum obtained from the electrochemical reaction is very similar to that of LiF reported by Hudson et al. [21].

This observation can be explained by the presence of the SEI produced by the insertion of lithium into the Li$_{1+x}$V$_3$O$_8$ electrode. Recently, we applied scanning photoelectron microscopy (SPEM) to Li/Li$_{1+x}$V$_3$O$_8$ cell, and obtained intense spectral features corresponding to Li 1s, F 2s, F 2p, and P 2p photoelectron signals in the cycled electrode, which were negligible signals in the pristine electrode [22]. As shown in Fig. 1, the spectral features of the Li$_{1+x}$V$_3$O$_8$ system are relatively close to that of pristine LiF compared to that of pristine Li$_{1+x}$V$_3$O$_8$. This is in good agreement with the previously reported our SPEM result. The F K-edge XAS results give strong support for the formation of an SEI that consists of LiF compounds during the electrochemical insertion of lithium. However, no detailed information about the electrochemical reactions of lithium in the Li$_{1+x}$V$_3$O$_8$/Li cell can be derived from the conventional 1D XAS spectra.

To investigate the mechanism of SEI formation in the Li$_{1+x}$V$_3$O$_8$/Li electrode surface during the first lithium electrochemical insertion–extraction in the Li$_{1+x}$V$_3$O$_8$/Li cell in more detail, we applied 2D correlation analysis to the lithium concentration ($x$)-dependent F K-edge XAS spectra of the Li$_{1+x}$V$_3$O$_8$/Li system for the first discharging–charging process. The synchronous 2D F K-edge XAS correlation spectrum from the first electrochemical insertion process of lithium is displayed in Fig. 2 (a), and a power spectrum extracted along the diagonal line of the synchronous spectrum is also shown at the top of the figure. In the synchronous 2D correlation spectrum, cross peaks are all positive, which reveal that the intensities of the all bands increase simultaneously during this process. The power spectrum presents that bands at 692 and 693 eV show much greater intensity variations compared with other bands. It suggests that several types of compounds such as LiF are formed on the electrode surface due to the reactions of lithium ion. It can also be seen that there are at least four bands in the 690–700 eV region, which are not readily noticeable in the 1D spectra shown in Fig. 1. At these energies, the absorption bands are produced by the core-level excitations, i.e., the excitation of the core electron into a bound state just below the conduction band. These excitations are not easily identified in the spectra [21]. Thus it confirms again that the 2D correlation spectrum often yields greater resolution enhancement than conventional 1D spectra.

The corresponding asynchronous 2D correlation spectrum is depicted in Fig. 2 (b). The sign of asynchronous cross peaks indicate the following sequence of spectral events as the lithium content in Li$_{1+x}$V$_3$O$_8$/Li increases.
During the first insertion process of lithium: 708 → 691 → (697, 699) → 693 → 702 → 717 eV.

We also applied 2D correlation analysis to the first extraction process of lithium. Fig. 3(a) depicts the synchronous 2D F K-edge XAS correlation spectrum from the first electrochemical extraction process of lithium and its power spectrum. Fig. 3(a) presents two very interesting results. One is that there are negative cross peaks at (698, 689), (698, 692), (698, 693), (714, 692), and (719, 698) eV. This shows that the intensities of bands at 698 and 714 eV increase while those at 689, 692, 693, and 719 decrease during the first extraction process. The other interesting result is that bands at both 692 and 698 eV clearly show much greater intensity changes compared with the insertion process. This result indicates that contribution from the excitation of the core electron into a bound state will be very intense in the XAS spectra for the Li1+xV3O8/Li system.

The corresponding asynchronous 2D correlation spectrum is shown in Fig. 3(b). The asynchronous crosspeaks indicate the following sequence of spectral events as the lithium content in Li1+xV3O8/Li increases during the first extraction process of lithium: (720, 707) → 700 → 698 → 693 → 702 → 689 → 691 → 728 eV.

The sequence of spectral events in the extraction process is not concurrent compared with that of the insertion process. This difference can be attributed to the environmental difference between the pristine Li1+xV3O8 and the lithiated sample phase, the spectral feature of which is modified by the surface effect such as SEIs.

4. Conclusion

In this study we successfully applied 2D correlation analysis to the lithium concentration (x)-dependent F K-edge XAS spectra of the Li1+xV3O8/Li system in order to investigate the mechanism of SEI formation in the Li1+xV3O8/Li electrode surface during the first lithium electrochemical insertion–extraction process. The F K-edge XAS spectra of the Li1+xV3O8 electrode showed that LiF forms on the Li1+xV3O8 electrode surface. Also, the 2D correlation analysis of these spectra yielded useful information that is not readily obtainable from 1D spectra. The 2D correlation analysis indicated that the F K-edge XAS spectra are strongly influenced by the excitation of the core electron into a bound state.

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[20] The program can be downloaded from the homepage of Professor Yukihiro Ozaki of Kwansei Gakuin University, Japan. <http://science.kwansei.ac.jp/~ozaki/>.