Partial Fluorescence Yield XAFS Measurements in Soft X-ray Region Using a Large-Area Silicon Drift Detector

Chihiro Yogi[1], Hideshi Ishii[1], Koji Nakanishi[1], Iwao Watanabe[1],
Kazuo Kojima[2], and Toshiaki Ohta[1]

1) SR Center, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

2) Department of Life Science, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan

Abstract

X-ray absorption fine structure (XAFS) spectra in the soft X-ray region are obtained in the electron and fluorescence yield modes, which are sensitive to surface and bulk, respectively. A micro-channel plate (MCP) can be used as the detector for the total fluorescence yield (TFY) method by applying a sufficiently high negative bias to a grid in front of the MCP. However, this method often suffers from low signal to back ground (S/B) and signal to noise (S/N) ratios. We have introduced a silicon drift detector (SDD) with a large acceptance area of 80 mm^2 in order to perform the highly sensitive partial fluorescence yield (PFY) XAFS experiments. Then the S/N and S/B ratios were improved significantly compared to those in the TFY-XAFS obtained by using the conventional MCP. By introducing the PFY method using the SDD to the ultra-soft XAFS beamline BL-2, XAFS spectra could be collected from a sample in three different modes simultaneously, i.e. PFY, the partial electron yield (PEY) by using an MCP with a retarding grid, and the total electron yield (TEY) by recording the sample current. Since these methods have different detection depths each other, a depth profile can be studied by comparing these three spectra. We demonstrate the performance of the present system applied to the typical cathode materials of lithium ion secondary battery.

1. Introduction

X-ray absorption fine structure (XAFS) analysis in the ultra-soft X-ray region from 50 to 1000 eV has been an important technique to study the local structures and electronic states of many elements in important functional materials, since in this region there exist absorption edges of *K* shell of light elements from Li to C, N, and O and *L* shell of transition metals which are often the key elements. While the XAFS spectra in the hard X-ray region have most conveniently been obtained in the transmission mode, the soft XAFS spectra have normally been obtained by detecting the electrons or fluorescence X-rays due to the difficulty of preparing thin enough samples corresponding to their extremely low transmittance in the soft X-ray region.

In the ultra-soft X-ray beamline BL-2 of the SR Center, Ritsumeikan University, three methods have been used to obtain soft XAFS spectra. They are the total electron yield (TEY) method measuring the sample drain current, the partial electron yield (PEY) method using a micro-channel plate (MCP) with a retarding potential grid, and the total fluorescence yield (TFY) method using the same MCP system with the high enough negative potential at the retarding grid to block all the incoming electrons out.

However, there were serious problems concerning the TFY method using the MCP. The TFY spectra obtained were of low quality, i.e. low signal to background (S/B) and low signal to noise (S/N) ratios. Low probability of fluorescence decay compared to that of the Auger process as the relaxation process of excited species in the soft X-ray region [1] inherently results in low quality FY spectra. In order to improve the quality of FY data, a large-area silicon drift detector (SDD) was introduced to the BL-2 XAFS system. The SDD has a high detection efficiency and is able to discriminate the energy of the detecting X-ray. It therefore works as a detector for the partial fluorescence yield (PFY) method capable of providing high S/B and S/N data.

The present report describes the soft XAFS experiments performed at the BL-2 for the study of lithium ion battery (LIB). The electrodes of LIB are known to be covered by a solid electrolyte interphase (SEI) layer on their surface formed during charge-discharge cycles. Since the SEI formation greatly affects the electrochemical property of electrodes, it is then important to obtain both the bulk and the surface information of the electrodes to investigate the changes of the electrodes during their charging and discharging processes.

The TEY method, the most often used technique for the soft XAFS measurements, is surface sensitive (ca. 10 nm). The PEY method is even more surface sensitive than the TEY method. On the other hand, the PFY method probes a depth of more than 200 nm [1,2] thus it can be called bulk sensitive. After the introduction of the SDD detector to BL-2, three-mode XAFS data, i.e. in PEY, TEY and PFY modes, could be obtained simultaneously at a single scan, from which one can study the depth profile of the LIB electrodes because each mode has different surface sensitivity. Here, the newly introduced SDD will be described and the depth analysis using this system on typical LIB electrode materials, $LiCoO_2$ and $LiMn_2O_4$, will be reported.

2. Experimental

2.1 Outline of large-area SDD

Figure 1 shows the picture of the newly introduced SDD (KETEK, VITUS R100, an acceptance area of 80 mm^2) to the XAFS sample chamber of BL-2. Since a beryllium foil cannot be used as a window because of its low transmission efficiency, a window-less type SDD was selected. In order to prevent the electrons from entering to the SDD, a poly paraxylene (Parylene-N, LEBOW Ltd.) film of 0.1 μm thickness was used as an electron shielding window. The transmission curve of the Parylene-N film is shown in the center of Figure 2. Transmission curves of a beryllium foil of 8 μm thickness and an AP3.3 film (MOXTEK Ltd., a typical window for SDD utilized in the soft X-ray region) are also displayed in Figure 2 for the comparison purpose. Compared to these films, the Parylene-N film has the higher transmission efficiency above 100 eV, especially at lower energies than the absorption edge of carbon (290 eV).

Since the Parylene-N film of 0.1 μm thickness cannot withstand the atmospheric pressure, the SDD detector covered with the film was kept in a vacuum system, which consists of a bellows on an x-stage and a gate valve as shown in Figure 2.

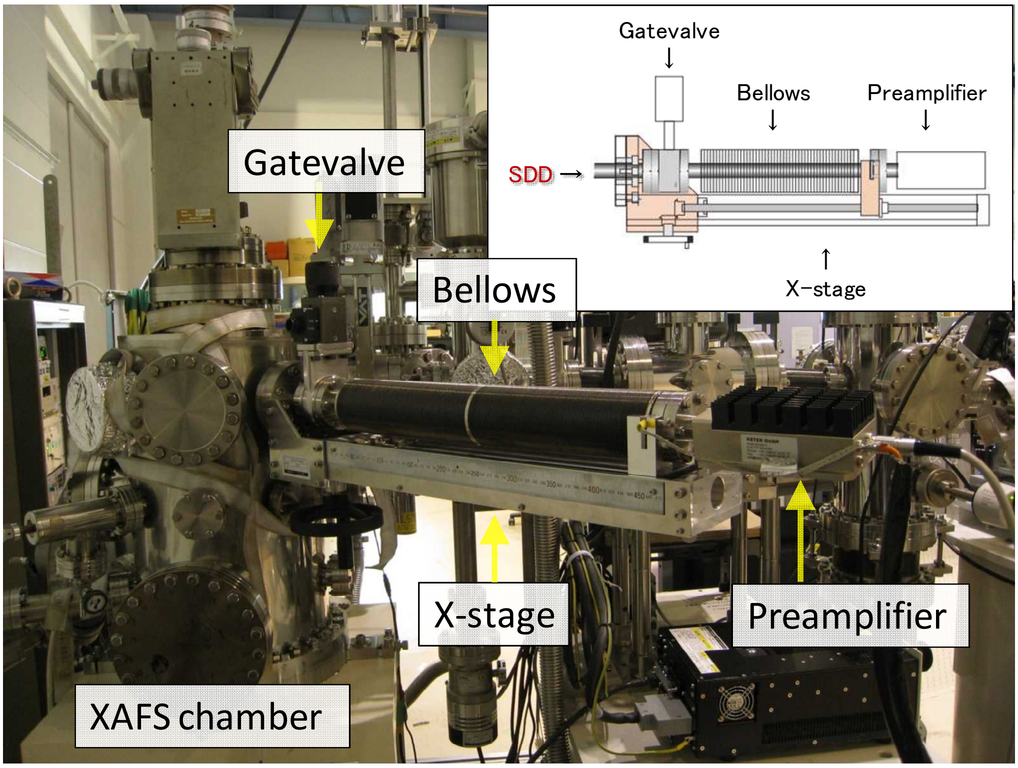

Figure 1. Outline of the large-area silicon drift detector.

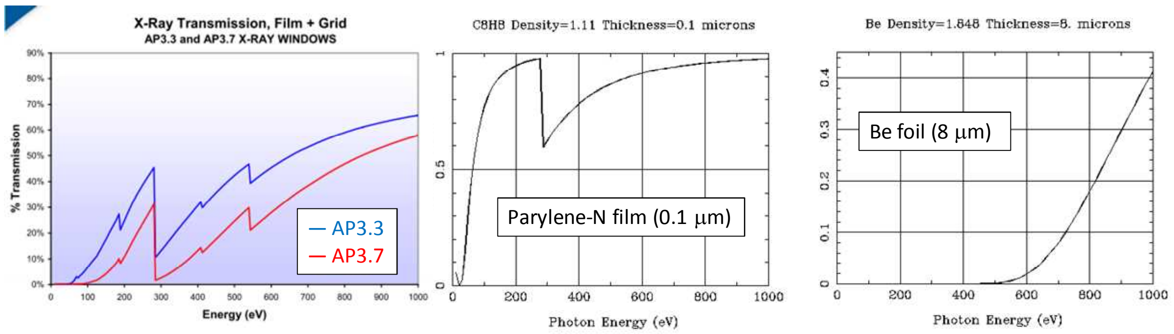

Figure 2. The chemical formula of Parylene-N and transmission curves of Parylene-N film, AP3.3 and beryllium foil.

2.2 Outline of soft XAFS system at BL-2

XAFS measurements were carried out at BL-2 of the SR Center, Ritsumeikan University. The beamline has a VLS grating monochromator equipped with four gratings providing the soft X-ray photons from 40 to 1000 eV. The setup for XAFS measurements is shown in Figure 3. The SDD was installed at 45 degree horizontally and the MCP at about 20 degree vertically from an incident X-ray beam. The three signals for the TEY, PFY and PEY (or TFY) methods were collected simultaneously.

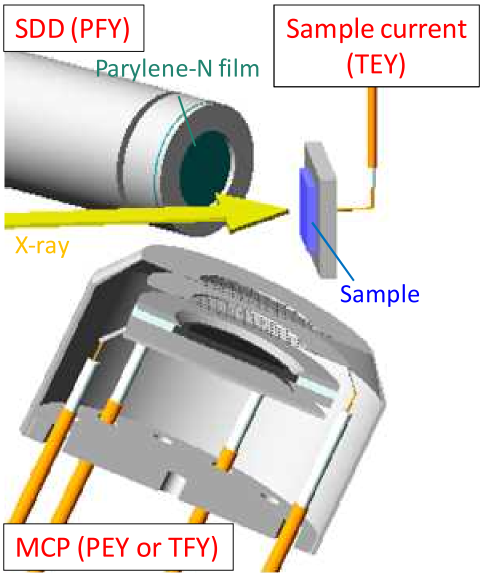

Figure 3. Setup for the simultaneous three-mode XAFS measurement.

2.3 Sample preparation

The composite cathodes, fabricated from mixtures containing 80 wt% of powdered $LiCoO_2$ or $LiMn_2O_4$ as the active material, 10 wt% of acethylene black (Denki Kagaku Kogyo Co.) as a conductive agent, and 10 wt% of polvinylidene difluoride (PVDF, Kureha Co.) as a binder, were employed as the samples for soft XAFS measurements. $LiCoO_2$ composite electrode which had undergone 30 charge-discharge cycles was also used. In the charge-discharge process, lithium metal (Hojyo Kinzoku Co.) was used as the negative electrode and also as the reference electrode. The electrodes were separated by a porous polypropylene film and the electrolyte was 1 mol dm^{-3} $LiPF_6$ in ethylene carbonate/ethylmethyl carbonate (3:7 ratio by volume). All the samples were prepared in an Ar gas glove box with a dew point of lower than -80°C and transferred to the XAFS chamber via a sample transfer vessel [4].

3. Results and discussion

Figure 4 at the left side shows the fluorescence spectrum of $LiMn_2O_4$ electrode excited by the X-ray of 680 eV. The luminescence peaks of C-*K*α, O-*K*α, and Mn-*L*α appear. The energy resolution was evaluated to be 80 eV at 525 eV (O-*K*α) and the peaks of Mn-*L*α and O-*K*α with energy difference of less than 100 eV were clearly separated indicating that the energy-selected fluorescence XAFS, i.e. PFY-XAFS, could be performed on the present sample. At the right side in Fig. 4, Mn $L_{2,3}$-edge XAFS spectrum obtained by using the MCP (TFY mode) is compared with that obtained by using the SDD (PFY mode). The L_3 peak appears in the PFY spectrum but does not in the TFY spectrum since the TFY detects not only Mn-*L*α fluorescence but also O-*K*α. As the absorption increases through the Mn L_3-edge, fewer oxygen atoms are excited and subsequently fewer they emit at the O *K*-edge, resulting in that the TFY detecting the non-energy selected fluorescence are almost unchanged and the peak of Mn L_3-edge is not formed in the spectrum. In contrast, the PFY probing only the increase of Mn-*L*a emission does not perceive the decreases of O-*K*α one, which yields the Mn L_3-edge peak. Furthermore, the S/B and S/N ratios were considerably improved by employing the PFY method. The S/B ratio in the PFY spectrum is more than a thousand times as large as that of TFY data. This result clearly indicates the advantage of using the SDD as the PFY detector in the soft XAFS experiments.

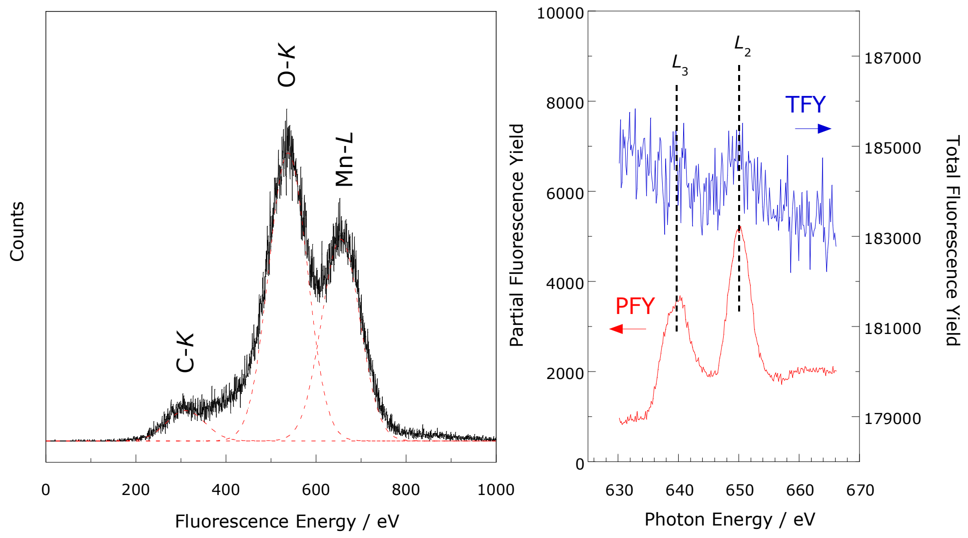

Figure 4. Fluorescence X-ray spectrum (left) and Mn $L_{2,3}$-edge XAFS spectra (right) of the $LiMn_2O_4$ electrode.

Figure 5 shows Co $L_{2,3}$-edge XAFS spectra of $LiCoO_2$ electrode soaked in an electrolyte solution for a day and of the same electrode after 30 charge-discharge cycles. There appear two peaks attributed to Co $L_{2,3}$-edges in every spectrum. It is interesting to see only the TEY indicates the L_3 peak position shift to lower energy after the charge/discharge cycle. The PFY spectra do not change after the cycles indicating that the bulk structure remains the same after the experience of the charge/discharge cycles. Since the TEY is sensitive to the sample surface, the low energy component in the L_3 peak in the TEY spectrum must originate from the Co ion in the SEI or the very surface of the electrode. This result proves that the present method of simultaneous data collection, TEY and PFY, is very powerful to study the mechanism of redox reaction occurring during the charge/discharge process in the electrode material.

The simultaneous three-mode detection of XAFS spectra for the $LiCoO_2$ pristine electrode is demonstrated over the O *K*-edge region as shown in Figure 6. The PFY spectrum has a peak at 526 eV, which is assigned as of the typical $LiCoO_2$. The TEY and PEY spectra have an additional shoulder peak at the higher energy attributed to Li_2O. The intensity of the shoulder peak becomes stronger if more surface sensitive method is used, i.e. the PEY gives bigger shoulder peak than the TEY, indicating that the amount of Li_2O was increased with lowering the detection depth since the surface of electrode could be oxidized following by formation of Li_2O. As like this, to figure out the bulk structure gives more detail information of the surface, thus the 3-mode simultaneous XAFS measurement is a meaningful technique in a surface analysis.

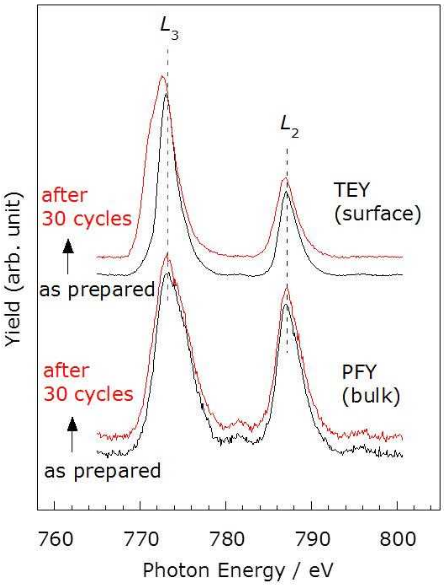

Figure 5. Co $L_{2,3}$-edge XAFS spectra of the $LiCoO_2$ electrode soaked in the electrolyte solution and after 30 charge-discharge cycles.

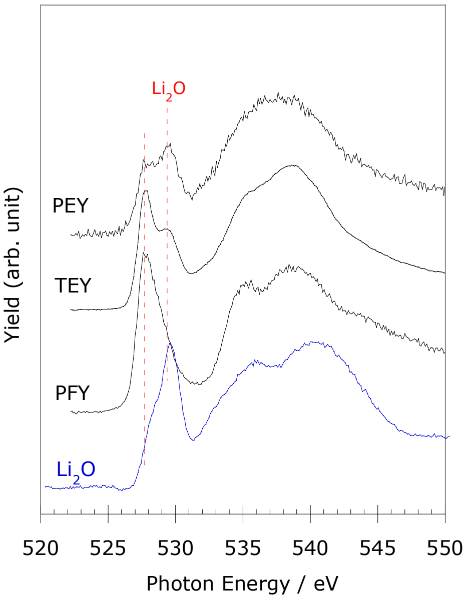

Figure 6. O *K*-edge XAFS spectra of the $LiCoO_2$ electrode obtained by PEY, TEY and PFY methods.

4. Conclusion

A large-area SDD with a window of Parylene-N film of 0.1 μm thickness was introduced to the ultra-soft X-ray XAFS beamline BL-2. The energy resolution of the SDD was about 80 eV at 525 eV (O-*K*α), being able to distinguish the O-*K*α and Mn-*L*α emitted from $LiMn_2O_4$ LIB electrode. Compared to the TFY-XAFS data from the $LiMn_2O_4$ obtained by using the MCP, the PFY data using

SDD were remarkably improved. The introduction of the SDD, in addition to the improvement in the quality of FY-XAFS spectra, enables us to perform the simultaneous three-mode XAFS measurements, PEY, TEY, and PFY. By comparing these three spectra from $LiMn_2O_4$ and $LiCoO_2$, we could distinguish the redox reactions occurring at the surface and in the bulk. We demonstrated the availability of this three-mode XAFS system for the depth profiled XAFS analysis of typical cathode materials of LIB.

Acknowledgement

Author thanks Dr. Tadatsugu Oishi and Mr. Takahiro Fujimoto, Kyoto University, for preparing the electrodes of lithium ion batteries. This work was supported by Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING) project from New Energy and Industrial Technology Department Organization (NEDO) in Japan.

References

[1] J.Stöhr, “NEXAFS Spectroscopy” (1992) (Springer-Verlag, Berlin).
[2] W.S. Yoon et al., J. Power Sources, 174 (2007) 1015.
[3] H. Kobayashi et al., J. Power Sources, 174 (2007) 380.
[4] K.Nakanishi et al., “Mesurement System / Book 2” (InTech., Croatia).