Local Structural Analyses of Liquids by Soft X-Ray Absorption Spectroscopy

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Soft X-ray absorption spectroscopy (XAS) is an element specific method to reveal local structures of liquids with the K-edges of C, N, and O. We have developed a liquid flow cell for XAS of liquids in transmission mode, where liquid thickness is controllable from 20 to 2000 nm.[1)] Local structures of several liquid samples have been investigated from the precise energy shift analyses of XAS peaks with the help of inner-shell calculations.[2,3)]

1. Microheterogeneity in Aqueous Acetonitrile Solution

In microheterogeneity (MH), two liquids are mixed in macroscopic scale but are inhomogeneous in microscopic scale. We have investigated one of the simplest MH systems, aqueous acetonitrile solution, by using XAS. Molecular interactions of acetonitrile were measured in C and N K-edges, and those of solvent water were separately observed in O K-edge. The energy shifts of the C≡N π^* peaks in C K-edge XAS show three concentration regions and especially a phase transition-like behavior. By comparing the energy shifts of XAS peaks with the inner-shell calculations, we have revealed that the MH state emerges when small acetonitrile clusters are formed by surrounding water with dipole interactions. By increasing the molar fraction of water, the MH state is diminished when the small acetonitrile clusters are taken into hydrogen bond network of water.

References

1) M. Nagasaka *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **224**, 93–99 (2018).
2) M. Nagasaka *et al.*, *Z. Phys. Chem.* **232**, 705–722 (2018).
3) M. Nagasaka *et al.*, *J. Phys. Chem. Lett.* **9**, 5827–5832 (2018).

Award

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Spectro-Microscopic Analysis of Lithium in an Electrode of a Lithium-Ion Battery

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Nowadays, lithium is an important element especially used for a secondary battery. To analyze chemical state and distribution of lithium in the battery, a scanning transmission X-ray microscope (STXM) will be a promising tool but an absorption edge in low energy, 55 eV, makes it difficult. Then, main issues are contamination of spectra by a lot of higher harmonic lights from a monochromator and extremely short focal length of an optical element, a Fresnel zone plate (FZP). Recently, we overcame these issues by designing a new FZP and succeeded to have an access to Li K-edge by STXM at BL4U. Parameters of the new FZP are as follows; diameter of 240 μm, outermost zone width of 60 nm, gold pattern of 100 nm thick on a silicon substrate of 200 nm thick. The new FZP works as not only a focusing device of the X-rays but also as a filter for higher harmonics above 100 eV by Si L-edge (99 eV) absorption. From evaluation of the new FZP, intensities of the higher harmonics light from 2nd to 5th orders for Li K-edge range are suppressed less than 1% of the 1st order light. Then, spatial resolution is below 85 nm at 90 eV.

An ultra-thin section of an electrode of a lithium-ion battery was measured around Li K-edge. The X-ray absorption spectra of $LiCO_3$ were obtained.

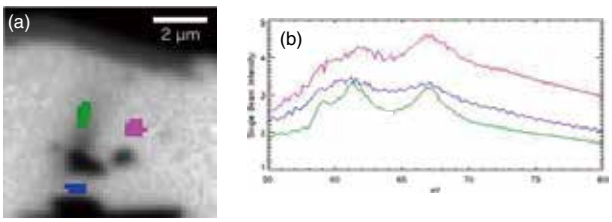

Figure 1. (a) Optical density image of an electrode of a lithium ion battery and (b) X-ray absorption spectra.

Reference

1) T. Ohigashi, in preparation.