

Characterization of uranium species in molten salt: An application of synchrotron-based XAFS spectroscopy

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Abstract

Synchrotron-based X-ray absorption spectroscopy has been applied to determine the changes in bulk oxidation state of uranium oxides in molten salt. From an analysis of XANES data, one can determine the changes in bulk oxidation-state of U compounds in salts(LiCl/KCl). XAFS spectroscopy is a powerful tool for probing the changes in valence state and structure of uranium compounds in molten salt as well as in non-crystalline form and doped in other matrices.

1. Introduction

X-ray absorption spectroscopy is becoming an important research tool for studying actinides behavior in various fields^{1,2,3}. Recently, an interesting electrochemical reduction method of metal to metal in molten salt medium has been introduced⁴. We're currently applying similar approach to the reduction of uranium oxides in molten LiCl/KCl media. This reaction is essentially a direct removal of oxygen from uranium oxides, so called 'oxygen pumping' process. During the course of a reaction, changes in and around the uranium atom, especially in oxidation states, are expected. A non-destructive and element-specific method is required to probe such changes. To identify the species of uranium in this process, we applied synchrotron-based x-ray absorption

fine structure (XAFS) spectroscopy.

2. Experimental

A series of XAFS measurements have been carried out for different solid phase uranium samples taken from the electrochemical reduction process of U_3O_8 in molten LiCl electrolyte⁵.

XAFS Measurements: In XAFS experiments, an intense monochromatic x-ray beam from a synchrotron source is required. The XAFS (XANES/EXAFS) spectra were obtained using synchrotron radiation on the 7C beam line of the Pohang Accelerator Laboratory (PAL), in Korea. The spectra were recorded at the uranium L_{III} edge (17,166 eV) in fluorescence mode. The measurements were carried out at room temperature and normal pressure. The measured spectral data were processed using the WINXAS program⁶.

3. Results and Discussion

The XAFS spectrum includes the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions. Each one has different molecular information for elements of concern in the samples. Figure 1 shows the U- L_{III} edge XAFS spectra for various uranium samples.

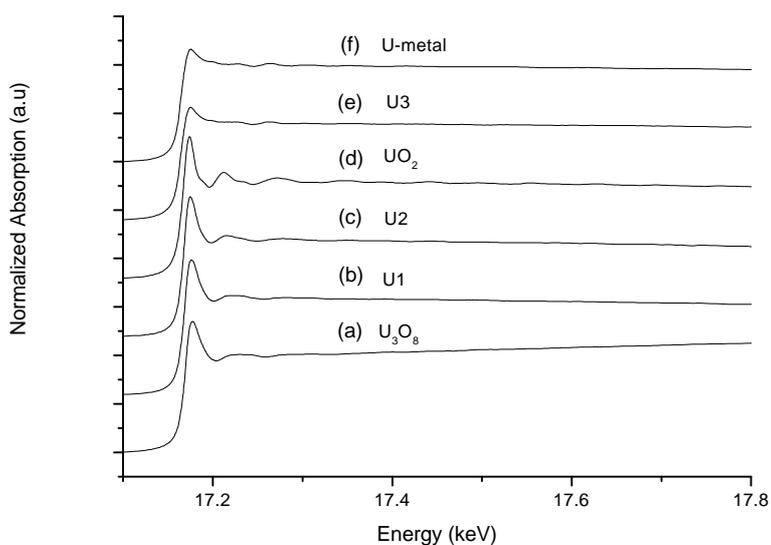


Figure 1. The U-L_{III} edge XAFS spectra of uranium samples (a) U₃O₈, (b) U1, (c) U2, (d) UO₂, (e) U3, (f) U-metal : (a), (d), (f) are model samples (U₃O₈, UO₂, U-metal) and (b), (c), (e) samples (U1, U2, U3) are taken from electrochemical reduction of U₃O₈ in molten LiCl electrolyte.

XANES Spectra: It is generally known that the energy of an x-ray absorption edge increases with increasing valence state. That originates from the reduced shielding (desheilding) of the core electrons from the nucleus. This increase in the binding energy of the core levels is apparently measured by shifts absorption edge features in XANES spectrum that can be correlated to differences in the oxidation states of uranium in the samples. Figure 2 shows the background-corrected XANES spectra for uranium samples. The position of the edge, corresponding to the electron binding energy, shifts to higher energy values as the absorbing atoms are oxidized. It appears at a slightly higher energy for U₃O₈ (a), mixed-valent compound, compared with UO₂ (d), consistent with the net formal oxidation state of the former oxides (5.3) being greater than that of UO₂. Our results show that U-L_{III} edge is shifted to lower energy side, which indicates the reduction in relative valence. (Figure 2) The edge shift between two oxidation states is not large. However, by utilizing the edge shift, XANES spectra can be used as a sensitive probe for the slight changes in valence states^{7, 8}. The bulk oxidation states of samples U1 and U2 appear in between U₃O₈ and UO₂, indicating the partial reduction of U₃O₈ as the reduction process taking place in molten LiCl electrolyte. The edge shift value for U2 was larger than that of U1, indicating much reduction, oxygen removal, has taken place for U2. This agrees with the experimental fact that U2 was obtained from an electrochemically more reduced compared to U1. When reduction process is almost completed, it has the same XANES spectral pattern as U metal. (See (e), (f) in Figure 2). As there were no discernible matrix (LiCl/KCl) effects on the position of the absorption edge, it was dependent predominantly on oxidation state of uranium. By using this advantage, synchrotron based XAFS spectroscopy proved to be a powerful method for the characterization of non-crystalline, very low concentration samples such as environmental samples with trace amount elements^{9, 10}.

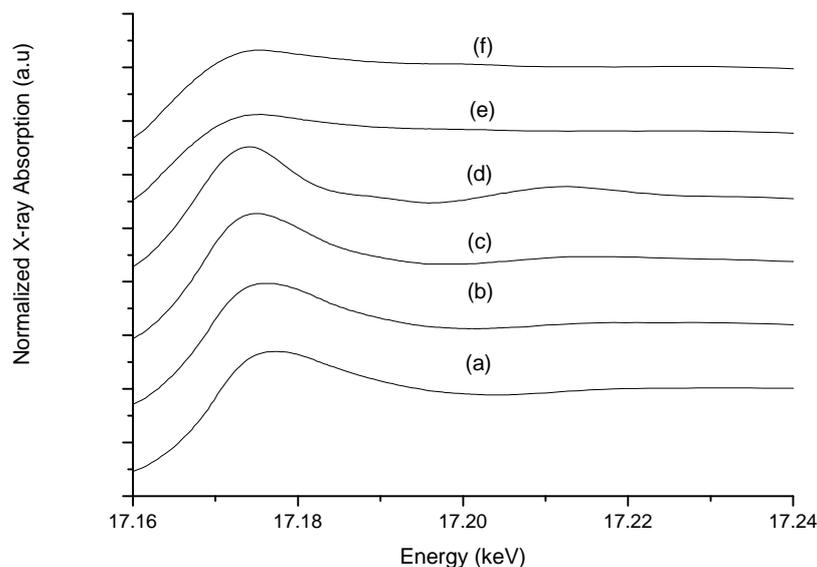


Figure 2. The U-L_{III} edge XAFS spectra of uranium samples. Sample notation is the same as in Figure 1.

Besides the oxidation state information, XANES spectra provide some structural information as well. Fine structure in the near edge region of the spectrum (to perhaps 40 eV above the absorption threshold) results from resonant transitions to bound energy levels associated with molecular orbitals, and from multiple scattering of photoelectrons with very low kinetic energies. These effects are sensitive to orbital hybridization and to the symmetry of the local environment of the absorbing atoms. The ‘white line’, the first strong feature of the absorption edge, varies in intensity from compound to compound and has no obvious dependence on oxidation state; this is most likely due to its sensitivity to the local environment. This can be used as a rough fingerprint for certain species. As was shown in Figure 1 and 2, (a)-(c) and (e)-(f) are roughly close each other in structural and valence point of view in and around uranium atom.

4. Conclusions

In order to get the information on the reduction mechanism of uranium oxides in molten LiCl electrolyte, we have studied the X-ray absorption fine structure (XAFS) at the U-L_{III} edge of a series of uranium samples in related solid phases. The position of the

absorption edge shifted in negative energy side as the reduction processes are taking place from uranium U_3O_8 to U metal. From an analysis of the XANES data, we determined the changes in bulk oxidation-state of U compounds associated with salts(LiCl/KCl). XAFS spectroscopy was proved to be useful for probing the changes in the valence state and structure of the uranium compounds in poorly-ordered form and doped in other matrices.

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