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An in-situ X-ray spectroelectrochemical measurement of uranium ions in perchlorate solution

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1. Introduction

Uranium forms various oxidation states in aqueous solution (trivalent to hexavalent), and it is important to estimate the chemical state of uranium ions in the fields of nuclear fuel cycles and environmental science. In-situ X-ray spectroelectrochemistry can be used to determine the relative concentrations of the species at an applied potential, even if sample solutions contain other redox-active species or there is an overlying optical transition that prohibits the direct determination of the concentrations. EXAFS spectra may undergo Fourier transform into frequency space, providing a radial distribution function. The resultant "R-space" clearly distinguishes UO_2^{2+} from U^{4+} via the presence of a peak (U-O_{ax}) that corresponds to the two axial oxygen atoms of the linear UO_2^{2+} complex.

2. Experimental

Sample preparation

Uranyl chloride hydrate was dissolved into 1 M (mol dm^{-3}) $HClO_4$. The uranium concentration used in the EXAFS measurements was 0.05 M. In order to avoid oxidation by O_2 in air, sample preparation was carried out under the Ar atmosphere. Other chemicals were used without further purification.

Electrochemical cell

Three electrodes consist of reference, working, and counter electrode, respectively Reference electrode is Ag|AgCl containing 1 M LiCl, working electrode is glassy carbon fiber to enlarge the current density[1]. Counter electrode is Ag wire containing 1M LiCl separated from sample solution by porous film to avoid gas evolution. The cell was stored in containment vessel. IVIUM compact stat was used for electrochemical measurements.

EXAFS data acquisition

EXAFS measurements were carried out at BL27B beam-line of the Photon Factory in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. EXAFS measurements based on the U L_{III}-absorption edge were performed. All the solutions were measured in fluorescence mode using a Ge solid state detector.

3. Results

To prepare U(IV), in-situ XAFS was performed by applying a constant current or potential for 5,200 sec. The 5 scans were collected and averaged, as shown in Fig. 1 (a). The fourier transform for the uranyl complexes were obtained before and after electrolysis, and are shown in (b) of Fig. 1. Figure 1 (a) shows the typical peaks corresponding to a single scattering path from the axial oxygen atoms of the linear UO_2^{2+} unit (U-O_{ax}) and oxygen atoms of the hydrated water in the equatorial plane perpendicular to the UO_2^{2+} axis (U-O_{eq}) at $R + \Delta$ = 1.25 and 1.92 Å, respectively.

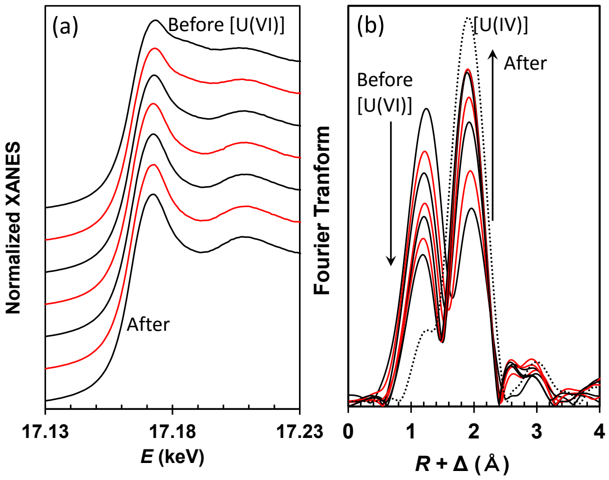

Fig. 1: (a) L_{III}-edge XANES spectra of uranium ions in 1 M $HClO_4$ before and after the electrolysis and (b) Fourier transform. Five scans were averaged.

The edge jump before the electrolysis slightly shifted lower energy than that after the electrolysis, and the spectra were similar to those reported previously. The solution showed light yellow before the electrolysis and green colour afterwards, which is typical of U^{4+}. This result in Fig. 1 (b) indicates that the U-O_{ax} bond of UO_2^{2+} was replaced by water molecules to form U^{4+} by the electrolysis.

Reference

[1] A. Uehara et al., Radiochim. Acta, 104 (2016) 1-9.

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