In-situ Spectroelectrochemical Measurement of Uranium Ions in Chloric Acid Solution

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1. Introduction
Understanding the uncertainty of the complexation mechanism and oxidation state (III, IV, V and VI) of uranium ions in aqueous solutions is important in the assessment of environmental impact on the disposal nuclear waste as well as the development of chemical separation of actinide ions. In the present study, coordination circumstance of uranium ions of which oxidation state in chloric acid solution is controlled electrochemically, was analyzed by in-situ XAS measurement.

2. Experimental
Sample preparation
Uranyl chloride hydrate was dissolved into 1 M (mol dm⁻³) HCl. The uranium concentration used in the EXAFS measurements was 0.05 M. In order to avoid oxidation by O₂ 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. 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 served as double confinement against radionuclide release. 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 LIII-absorption edge were performed. All the solutions were measured in fluorescence mode using a Ge solid state detector.

3. Results
Figure 1 (a) shows the XANES spectra of 0.05 M uranium (UO₂²⁺) in 1 M HCl before, during, and after electrolysis. Fourier transforms taken over \( k = 2.5 - 11.5 \) Å⁻¹ was shown in Fig. 1 (b). Constant current (-1 mA) was applied to reduce from UO₂²⁺ to uranium(IV)(U⁴⁺) as following equation (1);

\[
\text{UO}_2^{2+} + 2e^- + 4H^+ \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O}
\]  (1)

By continuing electrolysis, it was found that UO₂²⁺ was gradually reduced to form U⁴⁺ because of the peak shift of absorption edge which was also observed in HClO₄ reported previously [1]. Peak at \( R + \Delta = 1.2 \) Å corresponding to the bond of U=O for UO₂²⁺ decreased by the electrolysis because of the formation of U⁴⁺. On the other hand, peak at 1.9 Å corresponding to the bond of U-OH₂ increased because of the increasing coordination number of H₂O to U[2].

Fig. 1. (a) U LIII-edge EXAFS data for 0.05 M UO₂Cl₂ in 1 M HCl. (b) Fourier transforms taken over \( k = 2.5 - 11.5 \) Å⁻¹ Each spectrum is averaged one of 5 scans.

References
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