

Spectroelectrochemical Measurement of Uranium Ions in Nitric Acid and Sodium Carbonate Solutions

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Introduction

Understanding the uncertainty of the complexation mechanism and stability of uranium(IV) ions in acidic and basic 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 nitric acid and sodium carbonate solutions is controlled electrochemically, was analysed by XAS measurement.

Experimental

Sample preparation

Uranyl nitrate hydrate was dissolved into 0.1 M HNO₃ and 1 M NaCO₃ solutions. The uranium concentration used in the EXAFS measurements was 0.05 M (mol dm⁻³) for HNO₃ and 0.02M for NaCO₃ solutions. In order to avoid oxidation by O₂ in air, sample preparation was carried out under the Ar atmosphere.

Electrochemical cell

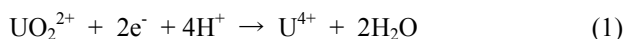
Three electrodes consist of reference, working, and counter electrode, respectively Reference electrode is Ag|AgCl containing 1 M LiCl, working electrode is Pt wire. Counter electrode is Ag wire containing 1M LiCl separated from sample solution by porous film to avoid gas evolution. The cell is stored in containment vessel served as double confinement against radionuclide release. IVIUM compact stat was used for electrochemical measurements.

EXAFS data acquisition and analysis

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.

Results

Figure 1 (a) shows the XANES spectra of 0.05 M uranium (UO₂²⁺) in 0.1 M HNO₃ solutions. During the electrolysis applying constant current (-1 mA) to reduce from UO₂²⁺ to uranium(IV)(U⁴⁺) as following equation (1);



By continuing electrolysis, it was found that UO₂²⁺ was quantitatively reduced to form U⁴⁺. The peak shift of absorption edge in HNO₃ solutions was similar to that in HClO₄ reported previously [1]. On the other hand, when 0.1 M NaCO₃ was used, the following reaction proceeded by applying constant potential (-0.95 V).



One electron reduction of UO₂²⁺ to UO₂⁺ causes a shift in the U L_{III}-edge position from 17.172 to 17.170 keV as shown in Fig. 1 (b), consistent with the shift reported [2].

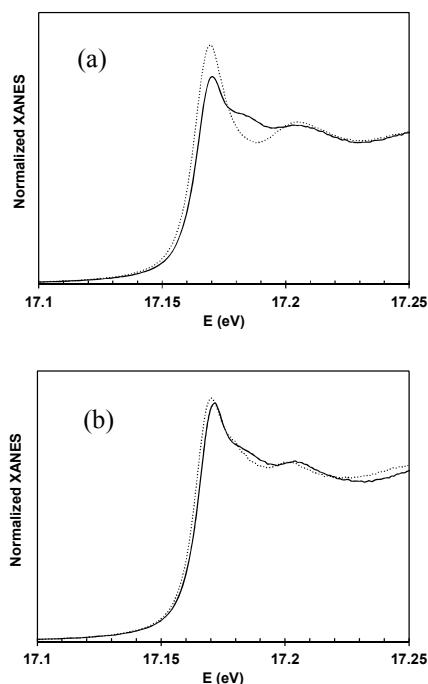


Fig. 1. U L_{III}-edge EXAFS data for (a) 0.05 M UO₂Cl₂ in 0.1 M HNO₃ and (b) 0.02 M UO₂Cl₂ in 1 M NaCO₃: solid line, before, dotted line, after electrolysis.

References

- [1] A. Uehara, et al., KEK activity report 2011.
- [2] TI Docrat, et al., Inorg. Chem., 38 (1999) 1879.

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