

## An in-situ X-ray spectroelectrochemical measurement of uranium ions in basic carbonate 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. These oxidation states are prone to change via oxidation and disproportionation reactions depending on the proton and oxygen concentration. In the present study, coordination circumstance of uranium ions of which oxidation state in basic carbonate 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<sup>-3</sup>) Na<sub>2</sub>CO<sub>3</sub>. The uranium concentration used in the EXAFS measurements was 0.05 M. In order to avoid oxidation by O<sub>2</sub> 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. 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<sub>III</sub>-absorption edge were performed. All the solutions were measured in fluorescence mode using a Ge solid state detector.

### 3. Results

To prepare U(V), in-situ XAFS was performed in 1 M Na<sub>2</sub>CO<sub>3</sub> solution by applying a constant current at -0.1 mA for 19,000 s. For this experiment, a platinum wire electrode was used as the working electrode. According to the chronopotentiogram by constant current electrolysis, the electrode potential was -0.96 V vs. SSE after 4,100 s. This rate is more than the 120 mV negative of the standard potential of the UO<sub>2</sub><sup>2+</sup>|UO<sub>2</sub><sup>+</sup> couple in the

carbonate solution (-0.492 V vs. NHE[1]), which means that over 99% of the total concentration of uranium was reduced to form UO<sub>2</sub><sup>+</sup> based on the Nernst equation. Figure 1 shows the XANES spectra before and after electrolysis. The edge jump slightly shifted from 17.164 to 17.163 keV, and the spectra were similar to those reported previously [2,3]. The solution was light yellow before the electrolysis and colorless and transparent afterwards, which is typical of UO<sub>2</sub><sup>+</sup>. The *k*<sup>3</sup> weighted EXAFS spectra and their corresponding FT for the uranyl carbonate complexes that were obtained before and after electrolysis. The EXAFS oscillation pattern of UO<sub>2</sub><sup>2+</sup> is different from that of UO<sub>2</sub><sup>+</sup>. It has been reported that UO<sub>2</sub><sup>2+</sup> and UO<sub>2</sub><sup>+</sup> carbonate complexes form bidentate-coordinated tricarbonato complexes i.e., [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup> and [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>5-</sup>, respectively.

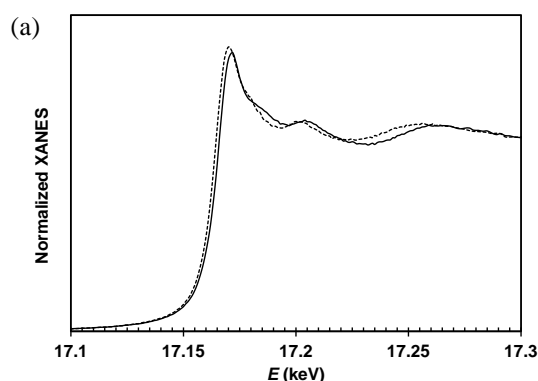


Fig. 1. L<sub>III</sub>-edge XANES spectra of uranium ions in 1 M Na<sub>2</sub>CO<sub>3</sub> before (solid line) and after (dotted line) the electrolysis. Five scans were averaged.

### References

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