

Electrochemical deposition of uranium dioxide in highly concentrated electrolyte at room temperature

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1. Introduction

The calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and similar highly concentrated electrolytes (i.e., 14 M (mol dm^{-3}) LiCl) are of considerable interest as solvents with properties intermediate between those of aqueous solution and molten salts. Activity coefficients, viscosity and structural analyses all indicate that the water molecule in the melts strongly coordinates to the calcium ion showing that this melt is a liquid with the properties of an ionic melt composed of bulky hydrated calcium cations and chloride anions. Namely, this material has advantages such as inorganic-based melt and low melting temperature. 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 the present study, redox reactions of uranium UO_2^{2+} in 14 M LiCl were investigated by electrochemical methods and X-ray absorption spectroscopy. The chemical behavior of uranium ion in the hydrate melt was compared with that in the other solvents such as ionic liquids[2].

2. Experimental

Sample preparation

Uranyl chloride hydrate was dissolved into 14 M LiCl. The uranium concentration used in the EXAFS measurements was 0.05 M. Other chemicals were used without further purification.

Electrochemical cell

Three electrodes consist of reference, working, and counter electrodes, respectively Reference electrode is Ag|AgCl containing 1 M LiCl, working electrode is glassy carbon fiber to enlarge the current density[1,3]. 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

In-situ XAFS was performed by applying a constant potential or current. The 10 scans were collected and averaged, as shown in Fig. 1. The edge jump measured before the electrolysis slightly shifted lower energy depending on the electrolysis (curves 1 to 4). Curve 5, which was measured after the electrolysis, was similar to the spectrum with that of UO_2 solid standard. Also, the solution showed black color afterwards, indicating typical UO_2 deposit. This reaction is not normally observed aqueous acidic solution at room temperature but high temperature ionic liquids.

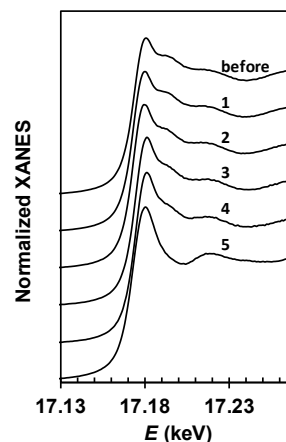


Fig. 1: L_{III} -edge XANES spectra of uranium ions in 14 M LiCl before and after the electrolysis. Ten scans were averaged.

Reference

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