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

Akihiro UEHARA1,*, Toshiyuki FUJII1,**, and Yoshihiro OKAMOTO2,***
1Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University,
2-1010, Asashi Nishi, Kumatori, Sennan, Osaka, 590-0494, Japan
2Quantum Beam Science Directorate, Japan Atomic Energy Agency,
2-4, Shirakatashirane, Tokai, Ibaraki 319-1195, Japan

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$_4^{4+}$ 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](image-url)