

## Development of Electrochemical Cell for XAS Measurement of Uranium Ions

Akihiro UEHARA<sup>1,\*</sup>, Toshiyuki FUJII<sup>1</sup>,  
Hajimu YAMANA<sup>1</sup> and Yoshihiro OKAMOTO<sup>3</sup>

<sup>1</sup>Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University,  
2-1010, Asashiro Nishi, Kumatori, Sennan, Osaka, 590-0494, Japan

<sup>2</sup>Quantum Beam Science Directorate, Japan Atomic Energy Agency,  
2-4, Shirakatashirane, Tokai, Ibaraki 319-1195, Japan

### Introduction

In oxygen poor subsurface environments on the disposal nuclear waste, uranium(VI) is likely to be reduced to uranium(IV) by corroding nuclear waste storage containers. Considering the uncertainty of the complexation mechanism and stability of uranium(IV) ions, XAS spectroscopy for in situ speciation is available [1,2]. In order to study coordination circumstance of actinide ions of which oxidation state is controlled, electrochemical cell for XAS measurement was developed.

### Experimental

#### Sample preparation

Uranyl chloride,  $\text{UO}_2\text{Cl}_2$ , hydrate was prepared from Uranyl nitrate hydrate with hydrogen chloride at 623 K. The uranium concentration used in the EXAFS measurements was 0.05 M ( $\text{mol dm}^{-3}$ ).

#### Electrochemical cell

Drawing of electrochemical cell is shown in Fig.1. The cell body consists of acrylic and is sealed by epoxy-acrylic resin. Window size is 30-by-30 mm. Three electrodes consist of reference, working, and counter electrode, respectively, insert to the cell and is sealed with the cell by epoxy-acrylic resin. The liquid volume is 4 ml. Reference electrode is  $\text{Ag}|\text{AgCl}$  containing 1 M  $\text{LiCl}$ , working electrode is Pt wire. Counter electrode is Ag wire containing 1M  $\text{LiCl}$  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.

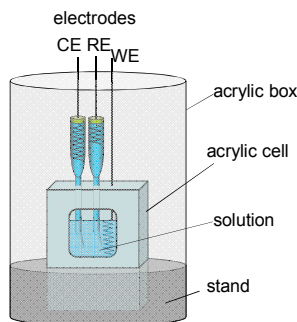


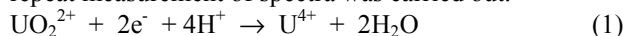
Fig. 1. Electrochemical cell for XAS measurement. CE, RE, and WE are counter, reference, and working electrode, respectively.

#### 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 ( $E_0 = 17.180$  keV) were performed. All the solutions were measured in fluorescence mode using a Ge solid state detector.

### Results

Figure 2 shows the XANES spectra of uranium (0.05 M) in 1 M  $\text{HClO}_4$  solutions. During the electrolysis applying constant current (2 mA) to reduce from uranium(VI) to uranium(IV) as following equation (1), repeat measurement of spectra was carried out.



Edge energy slightly shifted depending on the time of electrolysis. According to the electric charge at the electrolysis,  $\text{U}^{4+}$  was formed quantitatively at No. 26-32 scans. The  $\text{U}^{4+}$  tended to have a larger white-line feature whereas the dioxo coordination of the higher oxidation states produces multiple-scattering that resulted in the shoulder to higher energy of the edge peak itself.

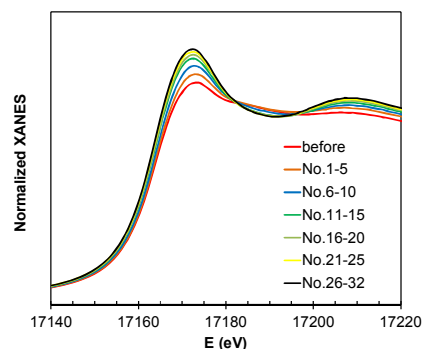


Fig. 2. U  $L_{III}$ -edge EXAFS data. Aqueous solution contains 0.05 M  $\text{UO}_2\text{Cl}_2$  and 1 M  $\text{HClO}_4$  before electrolysis. Controlled current electrolysis by applying 2 mA was carried out for 5 hours. These curves are average of every five scans.

### References

- [1] C. Hennig, et al., *Inorg. Chem.*, 44 (2005) 6655.
- [2] A. Uehara, et al., *Radiochim Acta*, in press.

\*auehara@rri.kyoto-u.ac.jp