## Study on electrorefining of uranium focusing on anodic dissolution

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#### Abstract

For several decades, the pyrometallurgical treatment of spent nuclear fuel has been extensively studied due to its relatively low processing cost and proliferation resistance of nuclear fuel cycles. In pyrometallurgical treatment, electrorefining is one of the most important processes. However, a detailed knowledge of electrochemical reactions during electrorefining process, which is of the essence in realising high-throughput applications, has not been satisfactorily gleaned yet. Under this circumstance, this work aims at investigating the kinetics of uranium dissolution at anode during electrorefining process. For this purpose, we established the electrochemical method for estimating the electrochemical active area of uranium at anode by employing cyclic voltammetry, then investigated the variation of electrochemical active area with time. The rate-determining step (RDS) of uranium dissolution was precisely determined by analysing the impedance spectra measured at different current densities. From the above results, the relative portion of each resistance, e.g., mass transport resistance, ohmic resistance and charge transfer resistance, in electrorefining process was quantitatively estimated.

## Introduction

For several decades, the pyrometallrugical treatment of spent nuclear fuel has been extensively investigated because of its relatively low processing cost as well as its proliferation resistance of the nuclear fuel cycles [1,2]. Recently, it has become one of the important requirements to recover long-lived nuclides, since a geological disposal of high-level waste is encountering big difficulties in obtaining public acceptance. In addition, the recovered uranium and transuranic (TRU) elements can be re-utilised as a fuel source. Hence, the recovering of long-lived nuclides is awakening new interest in the fuel cycle process for the partitioning and transmutation of transuranic elements [3].

There are similar but unique researches conducted by several institutions in various countries using their own strategies, i.e. IFR fuel cycle at ANL, DOVITA process at RIAR and the OMEGA programme at CRIEPI [4]. The Korea Atomic Energy Research Institute (KAERI) has also developed an electrorefining system using PWR surrogate spent fuels. However, to realise the practical applications of electrorefining, the efficiency should be improved.

In recent study [5], it has been reported that the anodic process predominantly controlled the overall electrorefining rate. However, the results are qualitative and quite experimentally oriented, so that it is very difficult to completely or straightforwardly grasp the kinetic property of the anodic process. In this respect, the present work aims at determining the basic data about uranium dissolution and at elucidating the mechanism of anodic dissolution using various electrochemical techniques.

#### Experimental

#### Cell configuration

A three-electrode electrochemical cell was employed for the electrochemical measurement as shown in Figure 1. The uranium cylindrical pellet with 10 mm in diameter and in thickness was used as the working electrode. A 304L stainless steel and Ag/AgCl were used as the counter and reference electrodes, respectively. High purity LiCl-KCl eutectic (41.5-58.2 mol.%) salt purchased from Sigma-Aldrich was used as an electrolyte. For the electrochemical experiments, the uranium tri-chloride (UCl<sub>3</sub>) was extracted as molten LiCl-KCl by an oxidation reaction between the depleted U metal in the anode basket and CdCl<sub>2</sub> in the electrolyte. All the chemicals were handled in a glove box in which both the oxygen and moisture contents in the argon atmosphere were maintained at lower than 10 ppm.





The 304L stainless steel cell with a proper insulation device was located in a stainless steel thermowell which was heated externally with an electric furnace attached to the floor of a glove box, and the temperatures were controlled at 500°C.

## Electrochemical measurements

Prior to the electrochemical measurements, the electrode were cycled 10 times from -1.5 to V(Ag/AgCl) at a scan rate of 100 mV s<sup>-1</sup> to activate the working electrode. The current vs. potential curve for uranium dissolution was measured at the current range of 5 to 100 mA by employing galvanostatic intermittent titration technique.

To evaluate the kinetic parameters during uranium dissolution, the cyclic voltammograms (CV) were obtained at the current range of -30 to 30 mA with a scan rate of 10 mV s<sup>-1</sup>. The impedance spectrum was measured at the applied potential of -0.4 V(Ag/AgCl) by applying an ac-amplitude of 10 mV<sub>rms</sub> over the frequency range from 100 kHz to 1 Hz. Ten data points of the measured impedance spectra were taken every decade of the logarithmic frequency.

#### **Results and discussion**

In general, the current-vs.-potential curve is very important to understand the electrochemical properties of the electrochemical reaction. Figure 2 shows the plots of the electrode potential against the applied current measured on the uranium pellet by employing galvanostatic intermittent titration technique (GITT).





In Figure 2(b), the electrode potential is linearly proportional to the logarithm of the applied current at applied currents higher than 50 mA, which is represented by the Butler-Volmer equation. At applied current lower than 40 mA, on the other hand, the Figure 2(a) exhibits a linear relationship between the potential and the current, representing ohmic behaviour. From the results, it is reasonable to think that the uncompensated ohmic resistance significantly affects the anodic process rather than the charge transfer resistance at the lower current.

In order to investigate the kinetic properties during the anodic dissolution, the cyclic voltammograms (CV) were measured at regular intervals of 0.5 h up to 2.5 h during the galvanostatic dissolutions from 50 to 200 mA. Figures 3(a) and 3(b) show the changes of the open-circuit potential (OCV) difference and relative active area with dissolution time. As the



Figure 3: Variations of (a) the open-circuit potential (OCV) and (b) relative active area with dissolution time, measured from the U pellet by employing cyclic voltammetry (CV)

applied current increased, the concentration of  $U^{3+}$  increased, hence the value of OCV decreased. On the other hand, the relative active area did not show a certain tendency. From Figure 3(b), it can be supposed that the surface roughness increased with decreasing applied current due to the selective dissolution of uranium pellet. In addition, the increase in the relative active area at large current may originate from the larger decrease of pellet size as compared with the increase of surface roughness.

Next, the ac-impedance spectrum was measured to elucidate the mechanism of uranium dissolution. In general, ac-impedance spectroscopy has widely been used to identify the various reaction steps and to determine the rate-determining step (RDS), since it provides an exceptionally powerful tool for separating the dynamics of several electrode processes with different relaxation times [6]. Figure 4(a) shows the Nyquist plot of the impedance spectrum measured on the uranium pellet at the applied potential of -0.4 V(Ag/AgCl). Here, the value of -0.4 V(Ag/AgCl) was selected from the point that showed the Butler-Volmer behaviour in the current-vs.-potential curve.



# Figure 4: (a) Nyquist plot of the impedance spectrum obtained from the U pellet at the applied potential of -0.4 V(Ag/AgCl), and (b) the equivalent circuit used for the complex non-linear least squares (CNLS) fitting

In Figure 4(a), the impedance spectrum consists of only a depressed arc. To quantitatively analyse the measured impedance spectrum, the equivalent circuit was constructed as shown in Figure 4(b). Here,  $R_u$  represents the uncompensated ohmic resistance,  $R_{ct}$  the charge transfer resistance,  $C_{dt}$  the double layer capacitance, and  $Z_w$  denotes the Warburg impedance, respectively.

To evaluate each resistance explicitly, the measured impedance spectrum was analysed using a complex nonlinear least squares (CNLS) fitting method based upon the equivalent circuit of Figure 4(b). In Figure 4(a), it is found that the impedance spectrum measured experimentally was quite well fitted with that calculated theoretically. The resulting values of  $R_u$ ,  $R_{ct}$  and  $R_w$ , which is the diffusion resistance in the Warburg impedance, were determined to 3.71, 0.38 and 0.01  $\Omega$  cm<sup>2</sup>, respectively. From the results, it is concluded that the uranium dissolution occurs under the mixed control of interfacial charge transfer and diffusion, but the rate of charge transfer predominantly affects the overall uranium dissolution.

## Conclusions

In this work, the kinetics of uranium dissolution at anode during electrorefining process was investigated using various electrochemical methods such as cyclic voltammetry and ac-impedance spectroscopy. The results are summarised as follows:

- From the current-vs.-potential curve, it is found that the uncompensated ohmic resistance is quite larger than the charge transfer resistance at lower currents, hence the kinetic analysis of the uranium dissolution should be performed at potentials higher than -0.4 V(Ag/AgCl).
- From the analysis of the cyclic voltammograms (CV) measured during the uranium dissolution, the lower the applied current is, the larger the surface roughness.
- From the analysis of the impedance spectrum obtained at -0.4 V(Ag/AgCl), the uranium dissolution proceeds under the condition where interfacial charge transfer is kinetically coupled with diffusion through the electrolyte. However, the effect of charge transfer on the overall dissolution reaction is more dominant than that of diffusion.

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