

# Electrochemical Behavior of Uranium(VI) in Ionic Liquid

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## 1. Introduction

Ionic liquids have attracted attention in the field of nuclear fuel cycle because they have several attractive properties such as an amazing ability to dissolve organic and inorganic compounds and a wide electrochemical window suitable for aqueous and non-aqueous reprocessing applications. Ionic liquids are being evaluated as an alternative to the conventional diluent, n-dodecane, in aqueous reprocessing, and as a substitute to the traditional high-temperature molten salts in the non-aqueous reprocessing of spent nuclear fuels [1, 2]. In this work, as a part of the research to recover uranium from spent nuclear fuel using ionic liquid, the electrolytic reduction of uranyl nitrate in ionic liquid, 1-butyl-3-methylimidazolium chloride (bmimCl), was studied. The electrochemical behavior of uranium(VI) in bmimCl was investigated within the temperature range of 343-373 K through cyclic voltammetry (CV).

## 2. Experimental

### 2.1 Chemicals and equipment

All the chemicals used in this study were of analytical grade and used without further purification. Ionic liquid, bmimCl, was procured from C-TRI, Korea. To remove the water and volatile impurities, bmimCl was kept for more than 3 hours under a reduced pressure at 373 K, and the residual water concentrations measured using a Karl Fisher moisture content meter (Metrohm 831 KF Coulometer) were below 100 ppm. The uranyl nitrate was procured from Merck.

### 2.2 Experimental method

All electrochemical experiments were carried out in a three-electrode cell. For cyclic voltammetric

measurements, a glassy carbon (cylindrical, SA = 0.07 cm<sup>2</sup>) and a platinum wire were used as a working electrode and a counter electrode, respectively. As a quasi-reference electrode, a platinum wire was used. Cyclic voltammograms of the ionic liquid solutions were recorded using ZIVE SP2 (WonATech) equipped with Smart Manager program.

## 3. Results and discussion

The cyclic voltammogram for the reduction of U(VI) in bmimCl on a glassy carbon working electrode at the potential sweep range of 50 ~ 500 mV/s is shown in Fig. 1. It is seen that the cathodic peak potential  $E_p^c$  is virtually constant with increase of scan rate and the anodic-to-cathodic peak current ratio,  $i_p^c/i_p^a$ , is unity. However, the difference in the value of  $|E_p^c - E_{p/2}^c|$  is twice larger than the value required for the reversible process (32.5 mV at 343 K) indicating that the reduction of U(VI) in bmimCl at glassy carbon electrode is not only controlled by diffusion but also charge transfer kinetics.

The ionic liquid, bmimCl, exhibits an electrochemical window of 2.7 V with a cathodic stability of up to -1.4 V (vs. Pt), which is sufficient for enabling the reduction of uranyl ions. The cyclic

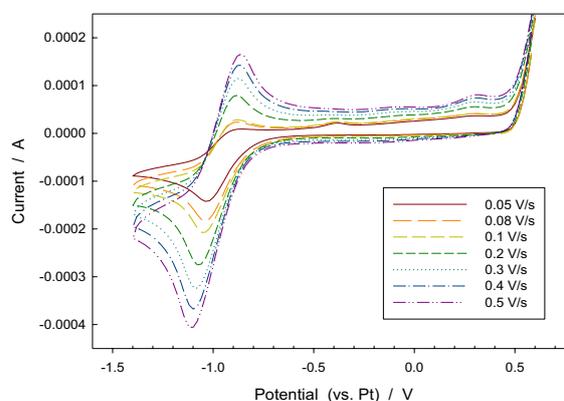


Fig. 1. Cyclic voltammogram of uranyl nitrate in bmimCl at various sweep rates.

voltammogram of  $\text{UO}_2(\text{NO}_3)_2$  in bmimCl consists of a reduction wave occurring at the peak potential of  $-1.05$  V owing to the reduction of U(VI) and an oxidation wave occurring at the peak potential of  $-0.90$  V. The result from the CV experiments at various scan rates and temperatures indicates that a reduction of uranyl ions takes place through a quasi-reversible single-step two-electron transfer reaction.

The relation between the cathodic peak current and the scan rate for an irreversible reduction reaction is given by Eq. (1).

$$i_p^c = 0.496nFCAD^{1/2} \left( \frac{\alpha n_\alpha Fv}{RT} \right)^{1/2} \quad (1)$$

The linear dependence of cathodic peak current ( $i_p^c$ ) on square root of scan rate ( $v^{1/2}$ ) was shown in Fig. 2, which confirms that the reduction of U(VI) in bmimCl is diffusion controlled and the diffusion coefficient can be determined from the slope by Eq. (1) and the value  $\alpha n_\alpha$  can be obtained from Eq.(2).

$$|E_p^c - E_{p/2}^c| = \frac{1.857RT}{\alpha n_\alpha F} \quad (2)$$

The diffusion coefficient of U(VI) in bmimCl was calculated to be  $0.69 \times 10^{-7}$   $\text{cm}^2/\text{s}$  at 343 K and at the scan rate of 0.10 V/s. Besides, the diffusion coefficient at other temperatures (353-373 K) were also determined, and the resultant values increase with temperature increment.

The diffusion coefficient is related to temperature by Arrhenius equation shown in Eq.(3).

$$D = A e^{-E_a/RT} \quad (3)$$

where  $E_a$  is the activation energy which can be obtained from the plot of  $\ln D$  against  $1/T$ . Effect of temperature on the cyclic voltammogram of U(VI) in bmimCl is shown in Fig. 3. It is seen that  $i_p^c$  increases and the peak potential  $E_p^c$  shifted towards

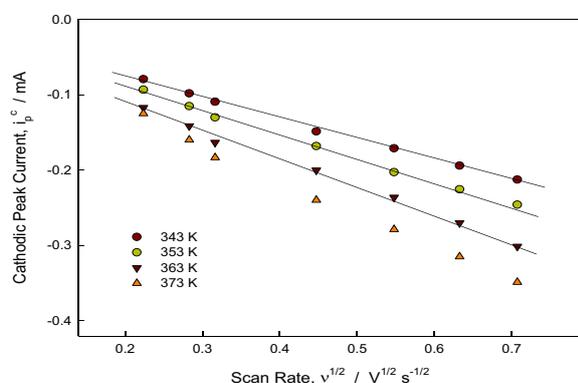


Fig. 2. Plot of cathodic peak currents against square root of scan rate at different temperatures for the reduction of U(VI) in bmimCl.

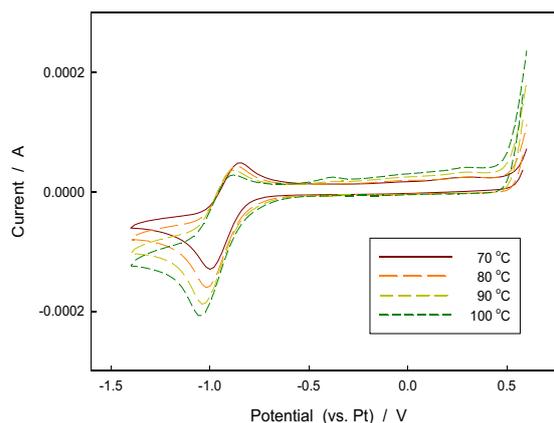


Fig. 3. Cyclic voltammogram of uranyl nitrate in bmimCl at various temperatures.

positive potential with increase of temperature. From the slope of the straight line of Arrhenius plot of Eq.(3), the energy of activation for the diffusion of U(VI) in bmimCl was found to be 43 kJ/mol.

#### 4. Conclusion

The cyclic voltammogram of  $\text{UO}_2(\text{NO}_3)_2$  in bmimCl consists of a reduction wave occurring at the peak potential of  $-1.05$  V owing to the reduction of U(VI) and an oxidation wave occurring at the peak potential of  $-0.90$  V. The result from the CV experiments at various scan rates and temperatures indicates that a reduction of uranyl ions takes place through a quasi-reversible single-step two-electron transfer reaction. The diffusion coefficient and the activation energy of U(VI) in bmimCl was found to be on the order of  $10^{-8}$   $\text{cm}^2/\text{s}$  and 43 kJ/mol, respectively.

#### REFERENCES

- [1] P. N. Pathak, "N,N-Dialkyl amides as extractants for spent fuel reprocessing - an overview", *Journal of Radioanalytical and Nuclear Chemistry*, 300, 7-15 (2014).
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