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Electrochemical behavior of actinide ions in LiCl–KCl eutectic melts

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Abstract

The electrodeposition and dissolution of uranium and plutonium in LiCl–KCl eutectic salt on tungsten and molybdenum working electrodes were investigated by cyclic voltammetry at 723, 773 and 823 K. It is suggested from the voltammograms that the electrodeposition and dissolution of U and Pu, U^{3+}/U and Pu^{3+}/Pu, may be quasi-reversible, while the redox reaction of U^{4+}/U^{3+} is reversible. The adsorption and desorption peaks of U and Pu on W and Mo working electrodes, respectively, caused by underpotential deposition, were observed. © 1998 Elsevier Science S.A.

Keywords: Cyclic voltammogram; Electrodeposition; Molten salt; Plutonium; Underpotential deposition; Uranium

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1. Introduction

A pyrochemical method is proposed as an advanced reprocessing technique for nuclear fuels such as metal [1] and nitrides [2,3]. In the electrorefining process, actinide elements are dissolved at the anode and deposited again at the cathode. Many studies have been conducted on the electrochemical reactions of U^{3+}/U, U^{4+}/U^{3+} and Pu^{3+}/Pu in molten chloride salts by e.m.f. measurements, chlonopotentiometry and voltammetry [4–13]. However, meaningful comparison of these results is difficult because of the variety of experimental conditions, including electrolyte composition, solute concentration, temperature, reference electrode and working electrode.

Voltammetry is a powerful method for understanding not only the energetics but also the dynamic features of electrochemical redox reactions. In addition, voltammetric measurements can be applied over a wide potential range. In the present study, the electrodeposition and dissolution of U and Pu in LiCl–KCl eutectic salt were investigated by cyclic voltammetry in the temperature range from 723 to 823 K.

2. Experimental

The electrochemical cell used for the voltammetric studies is shown in Fig. 1. Molybdenum (Mo) and tungsten (W) wires of 1.0 mm diameter served as working electrodes. The wires were encased in alumina tubes in such a way that an apparent surface area of 0.479 cm^2 was exposed to the molten salt. A silver–silver chloride electrode with 1.0 wt% AgCl in the LiCl–KCl eutectic salt was used as the reference electrode. The counter electrode used was made of Mo or glassy carbon. The temperature of the molten salt was measured to ±1.0 K using a calibrated

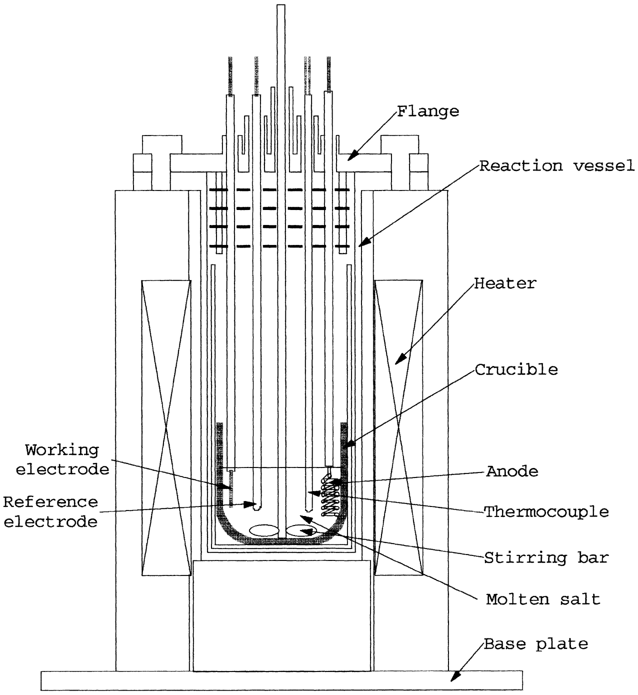

Fig. 1. The electrochemical cell.

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Chromel-Alumel thermocouple. Cyclic voltammograms were obtained using a voltammetric analyzer BAS CV-50W at scan rates from 0.01 to 0.5 V s^{-1}.

Polarographic-grade LiCl–KCl eutectic and $CdCl_2$ salts were obtained from the Anderson Physics Laboratory, and Cd (99.999%), Mo (≥99.95%) and W (≥99.95%) were supplied by Soekawa Chemicals Co. Ltd. Actinide trichlorides were prepared by the oxidation of U and Pu metals with $CdCl_2$ in Cd–LiCl–KCl at 773 K. The products were colored dark purple and light green salts, which indicates the formation of UCl_3 and $PuCl_3$, respectively. These salts were added to the LiCl–KCl eutectic melt in order to obtain adequate concentrations of UCl_3 and $PuCl_3$. The concentrations of UCl_3 and $PuCl_3$ in the LiCl–KCl eutectic salts were determined by ICP-AES after the voltammetric measurements.

The preparation and voltammetric measurements were carried out in a glovebox with a high quality argon gas atmosphere with moisture and oxygen concentrations <1.0 ppm.

3. Results and discussion

There was no significant current peak in the potential range of +0.4 to −2.1 V vs. the Ag/AgCl reference electrode with W and Mo working electrodes in the molten LiCl–KCl electrolyte alone.

Fig. 2 shows the cyclic voltammograms obtained with 0.454 wt% UCl_3 in LiCl–KCl eutectic salt at the W working electrode at 773 K in the potential range of −0.3 to −1.8 V vs. the Ag/AgCl reference electrode. Two cathodic (a1, a2) and two anodic (b1, b2) peaks were observed in the voltammograms.

It is considered, by comparison of the apparent potentials with the published data [6,7], that the cathodic and the anodic peaks, a1 and b1, correspond to the redox couple given by

$$U^{3+} + 3e^{-} \rightarrow U \tag{1}$$

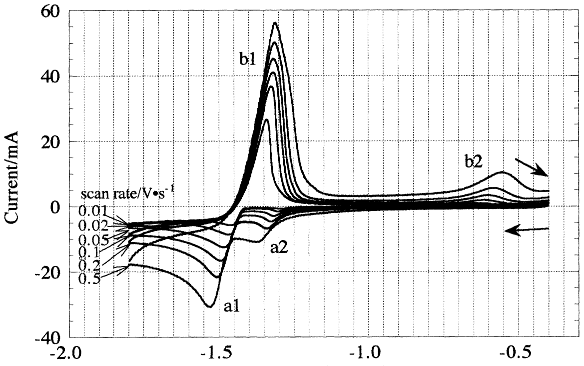

Fig. 2. Cyclic voltammograms of UCl_3 in molten LiCl–KCl at 773 K. UCl_3 concentration: 0.454 wt%. Working electrode: W. Apparent electrode area: 0.479 cm^2.

There is an approximately linear relationship between the cathodic peak currents a1 and the square root of the potential scan rates, except for 0.5 V s^{-1}. This indicates that the redox reaction may be nearly diffusion-controlled. On the other hand, it was found that the cathodic current at 0.5 V s^{-1} deviates from linearity. The potential differences between the cathodic and anodic peaks, a1 and b1, were twice or three times larger than the theoretical values [14], and increased with increase of the scan rate. These characteristics suggest that the redox reaction of U^{3+}/U may be quasi-reversible [14].

No dependence of the cathodic peak current on working electrode material and the temperature of the LiCl–KCl electrolyte was observed in the present work. It was also found that the peak potential showed no significant shift with the change of UCl_3 concentration; the potentials where the cathodic currents ascended in the voltammograms with 0.454 wt% UCl_3 were −1.430, −1.420 and −1.410 V at 723, 773 and 823 K, respectively, while those with 0.957 wt% UCl_3 were −1.425, −1.415 and −1.400 V, regardless of the scan rate. The peak heights were approximately proportional to the concentration of UCl_3. These effects of temperature and solute concentration observed in the present study can be represented by the Nernstian system considering the variations of the formation energy and activity of UCl_3 [14].

The cathodic current peaks at 823 K were about 1.3 times larger than those at 723 K for both working electrodes. This temperature dependence might be compatible with the fact that the redox reaction is controlled by diffusion, because the diffusion coefficient of U^{3+} in LiCl–KCl eutectic at 823 K is 2.0 times larger than that at 723 K and the peak current is proportional to the square root of the diffusion coefficient [5,14].

Poa et al. applied cyclic voltammetry to molten LiCl–KCl–$CaCl_2$–$BaCl_2$ containing 1.8 to 5.9 mol% UCl_3 with Mo and steel working electrodes, and pointed out that the redox reaction of U^{3+}/U was reversible. They noted simultaneously that the cathodic peak currents depended on the working electrode materials and both of the electrodes showed a different temperature dependence, which were about 1.5 and 2.3 times larger at 801 K for Mo and steel working electrodes, respectively, compared with those at 709 K [8,9]. Furthermore, they observed that the anodic and cathodic peak potentials for the reaction of U^{3+}/U shifted from −1.50 to −1.07 V vs. the Ag/AgCl reference electrode with increase of UCl_3 concentration from 1.8 to 5.9 mol% [8,9].

With regard to reversibility, the difference between the results of the present authors and those of Poa et al. is not considered to be so significant and could be explained by the difference in the experimental conditions. In particular, they carried out experiments with high concentrations of UCl_3. Generally, cathodic peak currents do not depend on the working electrode material in the case of diffusion-controlled reactions [14]. The large shift of the cathodic potential with change in the concentration of UCl_3 pointed out by Poa et al. [8,9] might be inconsistent with the reversibility of the reaction. It is necessary to carry out further investigations under various conditions in order to explain the difference between the results of the present authors and those of Poa et al.

The anodic peak current b1 did not increase in proportion to the square root of the scan rate and the half peak width became broad with increase of the scan rate. This behavior may be caused by the formation of an alloy between U and the working electrode material.

The cathodic and anodic peak currents, a2 and b2, were proportional to the scan rate and were independent of the concentration of UCl_3. The potential differences between b1 and b2 with the Mo working electrode, which were independent of the scan rate of the applied potential, were 0.720, 0.690 and 0.660 V, and those with the W working electrode 0.725, 0.695 and 0.660 V at 723, 773 and 823 K, respectively. These peaks may be attributable to monolayer adsorption and desorption of U on the working electrode. This behavior is generally called underpotential deposition. The potential can be correlated with the work functions of the working electrode material and the depositing metal [15]. It is considered that the potential differences between b1 and b2 with the W and Mo working electrodes were similar since the work function of W is approximately equal to that of Mo [16].

Cyclic voltammograms obtained with 0.454 wt% UCl_3 in LiCl–KCl eutectic salt with the W working electrode at 773 K in the potential range of +0.4 to −0.8 V are shown in Fig. 3. Cathodic and anodic peaks appear in the voltammograms. It is considered from the observed potentials that the anodic and cathodic peaks are attributable to oxidation of U^{3+} in the electrolyte to U^{4+} and reduction of the U^{4+} to U^{3+}, respectively, as represented by

$$U^{4+} + e^- \rightarrow U^{3+} \qquad (2)$$

The cathodic and anodic peak currents increased in proportion to the square root of the potential scan rate. This redox reaction is considered to be reversible because the potential difference between the two peaks is approximately identical to the theoretical value at any scan rate. The peak heights of the cathodic and anodic currents in the case of 0.957 wt% UCl_3 were about twice those of 0.454 wt% UCl_3. The standard redox potentials are estimated to be −0.299, −0.282 and −0.263 V vs. the Ag/AgCl reference electrode at 723, 773 and 823 K, respectively. These characteristics are independent of the working electrode materials and in agreement with those reported previously by other researchers [4,5,10].

Cyclic voltammograms for 0.544 wt% $PuCl_3$ in LiCl–KCl eutectic salt at 773 K in the potential range of −0.3 to −2.1 V vs. the Ag/AgCl reference electrode are shown in Fig. 4. Two cathodic (a1, a2) and two anodic (b1, b2) peaks are observed in the voltammograms. The cathodic and anodic peaks, a1 and b1, are a redox couple represented by [11]

$$Pu^{3+} + 3e^- \rightarrow Pu \qquad (3)$$

The cathodic peak current a1 varied linearly with the square root of the potential scan rate, except for 0.5 V s^{-1}. This indicates that the reduction of Pu^{3+} is nearly diffusion-controlled [14]. Since the potential differences between a1 and b1 are larger than the theoretical values, and the peak current at 0.5 V s^{-1} deviates from a linear relationship, the reaction is quasi-reversible as for the UCl_3–LiCl–KCl system. Irrespective of the scan rate and the temperature, the potential where the cathodic current began to rise for 0.544 wt% $PuCl_3$ in LiCl–KCl was more negative by 0.01 V than that for 1.00 wt% $PuCl_3$ as represented by the Nernstian system [14]. The cathodic peaks with 0.544 wt% $PuCl_3$ in the LiCl–KCl eutectic salts are about half of those with 1.00 wt% $PuCl_3$. The potentials where the cathodic currents ascended in the case of 0.544 and 1.00 wt% $PuCl_3$ in LiCl–KCl shifted by 0.02

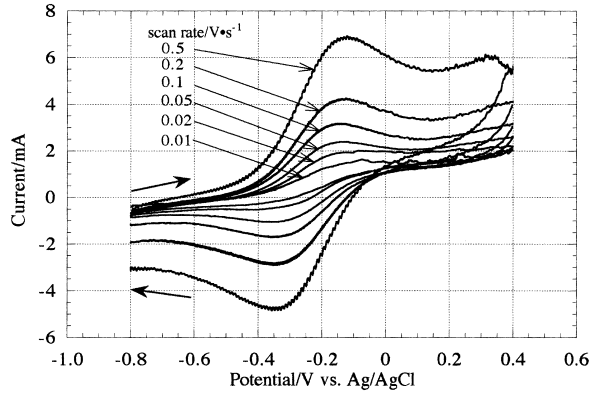

Fig. 3. Cyclic voltammograms of UCl_3 in molten LiCl–KCl at 773 K. UCl_3 concentration: 0.454 wt%. Working electrode: W. Apparent electrode area: 0.479 cm^2.

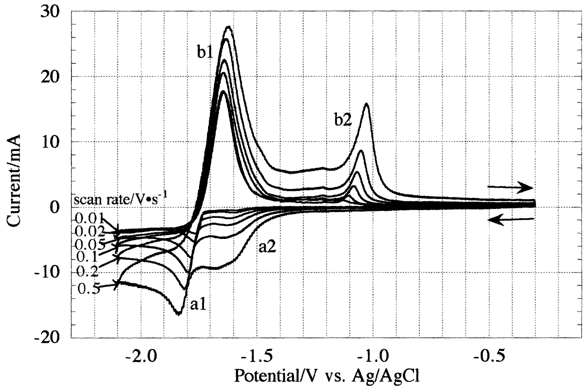

Fig. 4. Cyclic voltammograms of $PuCl_3$ in molten LiCl–KCl at 773 K. $PuCl_3$ concentration: 0.543 wt%. Working electrode: W. Apparent electrode area: 0.479 cm^2.

to 0.03 V for each 50 K rise. The cathodic current peaks at 823 K were about 1.6 times larger than those at 723 K. This can be explained on the basis of a diffusion-controlled reaction since the diffusion coefficient of Pu^{3+} in LiCl–KCl eutectic at 823 K is 2.2 times larger than that at 723 K [11]. Difference in the working electrode materials was not observed, but the cathodic current peak depended on the concentration of $PuCl_3$ and the temperature of the electrolyte as for the UCl_3–LiCl–KCl system.

Burris et al. obtained cyclic voltammograms for Pu in LiCl–KCl at a scan rate from 0.02 to 0.1 V s^{-1} and reported that this electrochemical reaction is controlled by diffusion mass transfer and is reversible [13]. However, Martinot and Duyckaerts determined the redox reaction by chlonopotentiometry and reported that the reduction of Pu^{3+} was slow because Pu^{3+} was solvated by coordination to chloride ion in the electrolyte and that the reduction was irreversible [11]. As for the reversibility of the redox reaction, the results obtained by Burris et al. might not be consistent with those obtain here because they measured the voltammograms only at a scan rate below 0.1 V s^{-1}. The present results for the redox reaction of Pu^{3+}/Pu are compatible with the results reported by Martinot and Duyckaerts.

The anodic peak current b1 is not proportional to the square root of the scan rate and the half peak width increases with increase of the rate, analogously to the UCl_3–LiCl–KCl system. Consequently, an alloy may also be formed in the case of Pu. The dissolution features of Pu at 723 K varied from those at 773 and 823 K as follows. The anodic peak b1 was split into two peaks, and the positive peak increased and shifted more positively with increase of the potential scan rate. This phenomenon could not be explained, but it may be possible that it was caused by a phase transition of the deposited metal or the formation of an alloy between the Pu and the cathodic electrode material.

The cathodic and anodic peak currents, a2 and b2, increased in proportion as the potential scan rate increased. These peaks were not dependent on the concentration of $PuCl_3$. The potential differences between b1 and b2 at 723, 773 and 823 K, which were independent of the potential scan rate, were 0.610, 0.420 and 0.420 V at the Mo working electrode and 0.600, 0.420 and 0.425 V, respectively, at the W working electrode. These depositions could also be correlated with the work functions of the electrode material and the depositing metal as well as the underpotential deposition of U [15]. The potential differences at 723 K were different from those at 773 and 823 K. This indicates that the energies for the desorption of Pu at 723 K were larger than those at 773 and 823 K, which may be caused by a phase transition of the deposited metal or alloy formation, as for the redox reaction of Pu^{3+}/Pu at 723 K. These characteristics suggest that the electrode reaction of Pu^{3+}/Pu is complicated by underpotential deposition, alloy formation between Pu and the working electrode material, a phase transition of Pu and some other complex formation [17].

Anodic and cathodic currents corresponding to the redox reaction of Pu^{3+}/Pu^{4+} were not observed in the potential region from -2.1 to 0.4 V vs. the Ag/AgCl reference electrode.

4. Summary

It was found from voltammetric analysis that the electrodeposition and dissolution of U and Pu may be quasi-reversible, although the redox reaction of U^{4+}/U^{3+} is reversible. The electrode reactions of U and Pu were complicated by underpotential deposition, alloy formation, phase transition and some other complex process. This means that it is necessary to take into account these effects on the electrode reactions of U and Pu.

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