KINETICS OF ELECTRODE PROCESSES IN LiCl-KCl MELT

S. A. Kuznetsov, H. Hayashi†, K. Minato†, M. Gaune-Escard†

Institute of Chemistry, Kola Science Centre RAS
14 Fersman Street
Apatity, Russia, 184209

†Japan Atomic Energy Research Institute
2-4 Shirakata-Shirane Street
Tokai-mura, Japan, 319-1195

∗Ecole Polytechnique, IUSTI CNRS UMR 6595
5 Enrico Fermi Street
Marseille, France, 13453

ABSTRACT

The electrochemical behavior of UCl₄ and UCl₃ in LiCl-KCl eutectic melt was studied at 723-823 K by different electrochemical methods. Electroreduction of U(IV) in LiCl-KCl melt occurs via two successive steps involving transfer of one and three electrons. The diffusion coefficients of U(IV) and U(III) were determined by linear sweep voltammetry, chronopotentiometry and chronoamperometry. The values found by these methods are in a good agreement with each other. The standard rate constants for the redox reaction U(IV) + e⁻ → U(III) were calculated from cyclic voltammetry data and for the discharge process U(III) + 3e⁻ → U by using impedance spectroscopy method. The values of constants testify that redox process proceeds quasi-reversibly, mostly under diffusion control, while electrodeposition is mainly controlled by the rate of charge transfer.

INTRODUCTION

Molten salts electrorefining is a promising method for separation of uranium and plutonium from each other and from fission-product elements in a pyrometallurgical process for recycling of spent nuclear fuel. Thus knowledge of UCl₄ and UCl₃ electrochemistry dissolved in LiCl-KCl eutectic melt provide essential data for optimization of uranium electrorefining.

Electrochemical behavior of U(IV) was reported in several investigations (1-8). Electroreduction of UCl₄ in LiCl-KCl eutectic melt proceeds in two steps involving transfer of one and three electrons, respectively. The reversibility of the reduction of U(IV) to U(III) was evidenced by chronopotentiometry method (1) and confirmed by cyclic voltammetry measurements (2). At the same time in investigation (3) it was found that the slope of chronopotentiogram was smaller than the theoretical value corresponding to a single electron transfer. Tafel plots for the U(IV)/U(III) redox couple
have indicated that the redox process consisted of a complexation reaction followed by the electron transfer (4). The polarographic behavior of U(IV) and U(III) was observed during experiments (5) on a platinum microelectrode at 723 K. Only one wave corresponding to the reduction of U(III) to uranium metal was observed. Another investigation (6) showed that the U(III)/U couple in LiCl-KCl eutectic melt had significant deviations from Nerstian behavior. However the discharge process of U(III) to U was determined as reversible (7), but contradictory identified as quasi-reversible (2, 8). The above inconsistencies between different authors clearly show the uncertainty on the electroreduction mechanism.

Various investigations have been also carried out on the electrochemistry of the U(III)/U couple in molten LiCl-KCl eutectic. EMF measurements have been made in studies (9-15). A comparison of the obtained data is difficult due to the variety of experimental conditions such as: electrochemical cell construction, uranium concentrations, reference electrodes. These difficulties can be avoided by recalculation of the experimental values of the potentials at infinite dilution.

The diffusion coefficients of U(IV), U(III) in the LiCl-KCl eutectic were obtained by Martinot et al. by chronopotentiometry method (16, 17). They reported $D_{\text{U(IV)}}$ values of $4.5 \times 10^{-6}$ and $12.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ at the temperatures 673 K and 773 K, respectively. The diffusion coefficients of U(III) were less than those of U(IV) and they changed from $4.1 \times 10^{-6}$ up to $13.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ in the temperature range 673-823 K. In these studies it was found that the activation energy for the diffusion of U(IV) and U(III) decreases with increasing temperature. Leseur (1) also determined the diffusion coefficients of U(IV) and U(III) complexes. His data are a little bit smaller than those of Martinot and it should be noted that coefficients of diffusion obtained with graphite electrode were smaller than those with tungsten electrode (1). The values of diffusion coefficients and activation energies for diffusion of U(IV) and U(III) complexes are presented in Table 1.

These literature data in Table 1 are in disagreement with numerous data on the influence of oxidation state of central atoms on diffusion coefficients (18). These data are also incompatible with results of study (19), where U(III) coefficients of diffusion were larger than those of U(IV) in alkali chloride melts from NaCl to CsCl. For these reason re-investigation of $D_{\text{U(IV)}}$ and $D_{\text{U(III)}}$ in LiCl-KCl eutectic melt was necessary.

The present paper describes electrochemical behavior of U(IV) and U(III) in LiCl-KCl eutectic melt. The main aim is the determination of U(IV) and U(III) complexes electroreduction kinetic parameters such as: diffusion coefficients and standard rate constants of charge transfer.

**EXPERIMENTAL**

A general description of the electrochemical cell used for investigations was described previously (20). Most experiments were carried out in AlN or glassy carbon crucibles using tungsten electrode, and glassy carbon as quasi-reference and auxiliary electrodes. Therefore during experiments there was no contact between the melt and oxide materials. It was only at the final stage of experiments that a silver-silver chloride
reference electrode was immersed in the melt for a short time for the determination of potential peak, the melt being not used any longer after this measurements.

Electrochemical studies were performed employing linear sweep voltammetry (LSW), cyclic voltammetry (CV), steady-state voltammetry (SSV), chronopotentiometry (CP), chronoamperometry (CA) and impedance-spectroscopy (IS) using a PAR EG&G Model 273 potentiostat/galvanostat controlled by the PAR EG&G M270/250 4.40 software package and a Volta-Lab 40 potentiostat with software VoltaMaster 4. Experiments were carried out in the temperature range 723-823 K. Electrochemical curves were recorded on tungsten and molybdenum electrodes, 1 mm diameter with respect to a glassy carbon rod as a quasi-reference electrode and versus the silver-silver chloride reference electrode. The silver-silver chloride electrode consisted of a pyrex ampoule with very thin bottom in which LiCl-KCl eutectic mixture containing 0.00390 mole fraction AgCl was placed and a silver wire of 1mm diameter was immersed in the salt. The glassy carbon plate or ampoule (SU-2000) served as the counter electrode. Potentials versus silver reference electrode were converted to a Cl'/Cl reference electrode using the relation

\[ E/V = -1.0659 - 1.805 \times 10^{-4}T/K \]  

The temperature of molten salt was measured with \( \pm 1.0 \) K accuracy using a calibrated Chromel-Alumel thermocouple.

Polagraphic-grade LiCl-KCl eutectic and CdCl₂ salt were obtained from the Anderson Physics Laboratory. Tetrachloride of uranium was synthesized from \( \text{U}_3\text{O}_8 \) (Merck) by hydrogen reduction to \( \text{UO}_2 \) and then by chlorination with \( \text{CCl}_4 \) vapors (22). The product of synthesis had a green colour and chemical analysis of the prepared \( \text{UCl}_4 \) showed the ratio of \( \text{Cl}/\text{U}=4:1 \). Trichloride of uranium (dark purple colour) was prepared by the oxidation of \( \text{U} \) with \( \text{CdCl}_2 \) in LiCl-KCl melt at 773 K (23). Uranium salts were added to the LiCl-KCl eutectic melt placed in AlN or glassy carbon crucible (SU-2000). The total concentration of uranium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The preparation and electrochemical measurements were carried out in glovebox with a high quality argon gas atmosphere with moisture and oxygen concentration <2.0 ppm.

RESULTS AND DISCUSSION

The voltammetric curves of LiCl-KCl after \( \text{UCl}_4 \) addition to the melt are shown in Fig. 1. As seen from the figure the voltammogram is characterized by the presence of three electroreduction peaks, and three corresponding peaks of electrooxidation. According to published data (2, 8) we assumed that potentials of the \( R_1, OX_1 \) and \( R_2, OX_2 \) waves correspond to the electrode reactions

\[
\text{U(IV)} + e^- \rightarrow \text{U(III)} \]  

\[ \text{U(III)} + 3e^- \rightarrow \text{U} \]  

Electrochemical behavior of prepeak \( R_2^1 \) was discussed in papers (2, 24). In study (24) it was concluded that the prepeak \( R_2^1 \) is associated with reaction
U(III) + 2e'→U(I)  \[4\]

leading to the formation of a monovalent insoluble uranium compound adsorbed on the electrode. Probably, this wave is due to the surface alloy formation, since a prepeak was also observed during discharge of rare-earth metals at tungsten electrode (25). It is necessary to take into account the influence of this process on electrode reaction \[3\] especially at low UCl\textsubscript{4} concentration, because the height of waves R\textsubscript{21} and R\textsubscript{2} are comparable (Fig. 1). At the same time, in melts with relatively high uranium concentrations, the prepeak becomes negligible compared to that of process \[3\].

**Electrochemical behavior of redox couple U(IV)/U(III)**

**Cyclic voltammetry.** The cyclic voltammograms obtained in LiCl-KCl-UCl\textsubscript{4} melt on a tungsten working electrode at 723 K are presented in Fig. 2. Cathodic and anodic peaks are attributed to reduction of U(IV) to U(III) and oxidation of U(III) to U(IV) respectively. The cathodic and anodic peak currents are directly proportional to square root of potential scan rate up to \(v = 0.3 \text{ V s}^{-1}\) (Fig. 3a) and cathodic peak potential does not depend on the polarization rate in the same range of the sweep rate (Fig. 3b). The peak currents of electroreduction and electrooxidation processes are linearly dependent on the uranium concentration, while the peak potentials of redox couple do not depend on the concentration of uranium in the melt. The potentiostatic electrolysis at potentials of the cathodic peak does not lead to the formation of a solid phase at the electrode, and the electrode itself undergoes no visible transformation. This means that the product of this stage U(III) is soluble in the melt. According to the theory of linear sweep voltammetry (26), up to the polarization rate 0.3 V s\textsuperscript{-1} the electrode process is controlled by the rate of mass transfer. The number of electrons for this stage was calculated by means of the following equations (27)

\[
E_{cp/2}^C - E_{cp} = 2.2 \frac{RT}{nF} \quad [5]
\]

\[
E_{ap} - E_{cp} = 2.22 \frac{RT}{nF} \quad [6]
\]

where \(E_{cp}^C\) is the potential of the cathodic peak, \(E_{cp/2}^C\) is the potential of the half-peak, \(n\) is number of electrons, and \(E_{ap}\) is the potential of the anodic peak.

The calculation of the number of electrons (Table 2) reveals that one electron is transferred at the first stage.

The diffusion coefficient \((D)\) for the chloride complexes of U(IV) was determined from the slope of straight line in coordinates \(I_p \cdot v^{1/2}\) (Fig. 3a) using of the Randles-Shevchik equation (28)

\[
I_p^C = 0.4463F^{3/2}R^{-1/2}T^{-1/2}n^{3/2}ACD^{1/2} v^{1/2} \quad [7]
\]

where \(I_p^C\) is the peak cathodic current (A), \(A\) is the electrode area (cm\textsuperscript{2}), \(C\) is the bulk concentration of active species (mol cm\textsuperscript{-3}), \(D\) is the diffusion coefficient (cm\textsuperscript{2}s\textsuperscript{-1}), \(v\) is the potential sweep rate (V s\textsuperscript{-1}), and \(n\) is the number of electrons involved in the reaction.

The diffusion coefficient of U(IV) is estimated to be 0.68×10\textsuperscript{-5} cm\textsuperscript{2}s\textsuperscript{-1} at 723 K.
The same Eq. [7] was employed for calculation of $D_{U(III)}$ in the LiCl-KCl-UCl$_3$ melt on the basis of the peak current determined for the process

$$\text{U(III)} - e^- \rightarrow \text{U(IV)} \quad [8]$$

The diffusion coefficient of U(III) was found to be $1.02 \times 10^{-5}$ cm$^2$ s$^{-1}$.

**Steady-state voltammetry.** Analysis of semi-logarithmic dependencies $E$ vs. log$(I_d - I)$ and $E$ vs. log$[I_d - I]/I$ indicates that the relation between log$[I_d - I]/I$ and $E$ is linear (Fig. 6), thus confirming that process [2] is reversible and described by the Heyrovsky-Iklovich equation (27). From the $2.3RT/nF$ slope, the number of electrons involved in this step is essentially unity, the value obtained for the half-wave potential, relatively to silver-silver chloride reference electrode is $-0.309$ V or $-1.505$ V, when referred to Cl/Cl$_2$ reference electrode. The number of electrons was calculated from this value of half-wave potential using equations (27)

$$E^C_{p} = E_{1/2} - 1.11RT/nF$$

$$E^A_{p} = E_{1/2} + 1.11RT/nF$$

Results of calculation are presented also in Table 2. It was possible to determine the thickness of diffusion layer (δ) from the cathodic plateau of steady-state voltammetric curve which is described by (27)

$$I_d = nFACD/\delta$$

The limiting diffusion current $I_d$ was 0.336 mA at 723 K (Fig. 4), concentration was $2.03 \times 10^{-5}$ mol cm$^{-3}$, and hence $\delta = 1.6 \times 10^{-2}$ cm.

**Chronopotentiometry.** Further study of the electrochemical behavior of redox couple U(IV)/U(III) was carried out by means of chronopotentiometry. A chronopotentiogram for the U(IV) to U(III) electroreduction in the LiCl-KCl-UCl$_3$ melt at tungsten electrode is shown in Fig. 5. The transition time $\tau$ is determined by the duration of the potential plateau. Straight lines were obtained for the plots of $\tau^{-1/2}$ vs. $i$ for various concentration of U(IV) (Fig. 6). It was found that the square root of $\tau$ also increased linearly with increasing of added UCl$_3$ amounts, at various applied current densities. The chronopotentiometric curve did not shift towards of negative potentials when current density was increased. Thus, on the basis of chronopotentiometric data, it is possible to conclude that the electrochemical reduction of U(IV) to U(III) is a diffusion controlled process (27). The chronopotentiometric curve for the reversible electroreduction with a soluble substance formation is described by the following equation (27)

$$E = E^0_{E_u(E_u/E_x)} + RT/nF \ln(D_{ox}/D_{red})^{1/2} + RT/nF \ln(\gamma_{ox}/\gamma_{red})^{1/2} + RT/nF \ln((x^{1/2} - \tau^{1/2})/\tau^{1/2})$$

where: $D_{ox}, D_{red}$ and $\gamma_{ox}, \gamma_{red}$ are, respectively, the diffusion coefficients and the activity coefficients of the oxidized and reduced forms, and $\tau$ is the transition time.
It was determined that function $E$ vs. $\log \left(\left(\frac{x^{1/2}}{2} - \frac{t^{1/2}}{2}\right)/\frac{t^{1/2}}{2}\right)$ is a straight line with a slope which is very close to the value of 2.3 $RT/F$ corresponding to a one electron transfer. For reversible process Sand equation is valid (27)

$$It^{1/2} = \left(\frac{nFCD^{1/2}\pi^{1/2}A}{2}\right)/2$$  \[13\]

where $I$ is the current (A), $A$ is the area (cm$^2$) of the working electrode, $t$ is the transition time (s), $C$ is the bulk concentration of the reactant (mol cm$^{-3}$), and $D$ is the diffusion coefficient of the reactant (cm$^2$ s$^{-1}$).

Utilizing the Sand equation and the slope of the plot $x^{12}-i$ (Fig. 6), the diffusion coefficient of $U(IV)$ is estimated to be $0.74 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 723 K. The same procedure was used for the process [8] in the melt LiCl-KCl-UCl$_3$ and $D_{U(II)}$ equal to $0.97 \times 10^{-5}$ cm$^2$ s$^{-1}$ was obtained.

**Chronoamperometry.** Fig.7a shows a typical chronoamperogram for a tungsten electrode. The linear relationship between the current density and reciprocal square root of time is obtained (Fig. 7b). Accordingly the cathodic current density can be expressed by the Cottrell's equation (27)

$$I = nF\pi^{1/2}U(IV)AC/(\eta^{1/2}t^{1/2})$$  \[14\]

From the slope of the corresponding plot (Fig. 7b), the diffusion coefficient of $U(IV)$ was obtained as $0.84 \times 10^{-5}$ cm$^2$ s$^{-1}$. The diffusion coefficient of $U(III)$ determined by chronoamperometry was larger than for $U(IV)$ and has value $1.08 \times 10^{-5}$ cm$^2$ s$^{-1}$.

Steady-state diffusion conditions due to thermal convection are reached in 6.4 s (Fig. 7a), so the thickness of diffusion layer can be determined from the relation

$$\delta = (2Dt)^{1/2}$$  \[15\]

On the base of chronoamperometry method the thickness of diffusion layer is equal to $1 \times 10^{-2}$ cm.

**Diffusion coefficients.** As shown above, diffusion coefficients were obtained by different methods. These results are summarized in Table 3. As can be seen from Table 3, the diffusion coefficients of $U(IV)$ and $U(III)$ obtained by different methods are in a good agreement. Temperature dependencies of diffusion coefficients for $U(IV)$ and $U(III)$ were determined in the temperature range 723-823 K using linear sweep voltammetry at $v = 0.1$ V s$^{-1}$, because reproducibility of $D$ values obtained by voltammetry method was better than that in CP and CA methods. The diffusion coefficients are described by the following empirical equations

$$\log D_{U(IV)} = -2.46 - 1956/T \pm 0.03$$  \[16\]

$$\log D_{U(III)} = -2.64 - 1700/T \pm 0.02$$  \[17\]

The activation energies for diffusion ($\Delta H$) of $U(IV)$ and $U(III)$ were calculated from
\[-\Delta H/2.303 R = \partial \log D/\partial(1/T)\]  \[18\]

and are determined to be 37.45 kJ mol\(^{-1}\) and 32.55 kJ mol\(^{-1}\), respectively.

**Determination of the standard rate constants of the electrode reaction** \(U(IV) + e^- \rightarrow U(III)\) Analysis of plots in Fig. 5 shows that at \(v \geq 0.3\) V s\(^{-1}\), process [2] is quasi-reversible. A mixed diffusion and electron-transfer rate-controlled process [2] at \(v > 0.3\) V s\(^{-1}\) is indicated by the deviation of experimental points from linearity in the \(I_p^C v s. v^{1/2}\) plot (Fig. 3a), by the \(E_p^C v s. v\) dependence (Fig. 3b), and by the magnitude of the difference between \(E_p^A\) and \(E_p^C\), which is larger than it is required for a reversible process. For example, at a polarization rate of 1.0 V s\(^{-1}\), it is equal to 0.254 V (Table 2).

The problem of kinetic parameters determining on the basis of cyclic voltammetry was considered by Nicholson (29). The standard rate constant of the electrode process is related to the function \(\psi\) as follows

\[
\psi = \frac{k_s \left( \frac{D_{av}}{D_{red}} \right)^{\frac{1}{2}}}{\pi^{\frac{3}{4}} D_0 \alpha^{\frac{1}{2}} \left( \frac{nF}{RT} \right)^{\frac{1}{2}}^{\psi}}
\]

Here \(\psi\) is a function related to the difference between the peak potentials \(E_{p2}^C - E_{p1}^C\) (mV), \(k_s\) is the standard rate constant of the electrode process (cm s\(^{-1}\)), and \(\alpha = 0.5\) is the transfer coefficient.

The dependencies of \(E_{p2}^C - E_{p1}^C\) on the \(\psi\) function, reported in (29) for at the temperature 298 K, must be recalculated for the present working temperatures, and we used the following equations (30)

\[
(\Delta E_p)_{298} = (\Delta E_p)_{298/T}^{298}(T/298)^{1/2}
\]

[20]

\[
\psi_T = \psi_{298} (T/298)^{1/2}
\]

[21]

The values of the \(\psi_T\) function, obtained by means of equations [20] and [21] and used in conjunction with expression [19], made it possible to calculate the standard rate constants for charge transfer. The influence of temperature on the standard rate constants of electrode reaction [2] is presented in Table 4.

**Study of uranium electrodeposition**

**Cyclic voltammetry.** The electroreduction of U(III) to U(0) has been studied in the melt LiCl-KCl-UCl\(_3\) at metallic electrodes of tungsten and molybdenum. We investigated the current and the peak potentials dependencies on the polarization rate of the electrodeposited stage (Fig. 8). It was found that at 0.01 < \(v < 0.5\) V s\(^{-1}\) the discharge process is quasi-reversible. The quasi-reversible nature of the process in this range is indicated by the deviation of the experimental points from straight line in the \(I_p\) vs. \(v^{1/2}\) coordinates, by non-linear dependence of \(E_p\) on polarization rate, and by the magnitude of the \(E_{p2}^C - E_{p1}^C\) difference, which is larger than it is required for reversible process.
Increasing the sweep polarization rate from 0.5 to 2.0 V s\(^{-1}\) results in irreversible electroreduction, because the peak current is directly proportional to \(v^{1/2}\) and the peak potentials shift to the cathodic region with increasing scan rate (Fig. 8). Estimation of the \(\alpha n_a\) value (where \(\alpha\) is the charge transfer coefficient and \(n_a\) is the number of electrons transferred) is possible by applying the equation (27)

\[
\Delta E_p/\Delta \log v = \frac{2.303 RT}{2\alpha n_a F}
\]  

[22]

In the \(E_p-log v\) coordinates (Fig. 9) the slope 0.049 V (decade\(^{-1}\)) was determined at the temperature 723 K, resulting in the value 1.46 for \(\alpha n_a\). The \(\alpha n_a\) value can also be obtained also from expression (31)

\[
E_p-E_p/2 = -1.857RT/\alpha n_a F
\]  

[23]

and the value \(\alpha n_a = 1.49\) was found at the polarization rate \(v = 1.0\) V s\(^{-1}\). These results clearly show that the electroreduction of uranium is a quasi-reversible process in a certain interval of polarization rate. It should be noted that some authors in this case used the Berzins-Delahay equation for a diffusion controlled process with formation of insoluble product (28)

\[
I_p^C = 0.611F^{3/2}RT^{-1/2}n^{3/2}ACD^{1/2}v^{1/2}
\]  

[24]

which is not valid. This conclusion is well supported by the comparison of the diffusion coefficients of U(III) calculated from equation [24], which differ considerably from those obtained from Eq. [17]. In our opinion, it would be far better to use polarization rates where process [3] is irreversible and the Delahay’s equation is valid for determination of diffusion coefficients (28)

\[
I_p = 0.496nFCAD^{1/2}(\alpha n_a Fv/RT)^{1/2}
\]  

[25]

The diffusion coefficients \(D_{U(III)}\) obtained in the temperature range 723-823 K, at the polarization rate \(v = 1.0\) V s\(^{-1}\) (at this rate the double layer charging current was virtually insignificant relatively to the Faradaic current) are described by the following empirical dependence

\[
\log D_{U(III)} = -2.52-1796/T \pm 0.02
\]  

[26]

The \(D_{U(III)}\) values from empirical equations [17] and [26] are in a very good agreement.

**Steady-state voltammetry.** A steady-state voltammogram of electroreduction of U(III) complexes to U(0) was obtained in the melt LiCl-KCl-UCl\(_3\). An analysis of the semi-logarithmic dependencies \(E \) vs. \(\log(I_c-I)\) and \(E \) vs. \(\log[(I_c-I)/I]\) indicates that these functions are nonlinear. Thus the equation of Kolthoff-Lingane for reversible process with formation of insoluble product and Frumkin-Bagotskii equation for irreversible process (27) are not valid. Probably, because at steady-state conditions the process [3] is quasi-reversible. Reproducibility of steady-state voltammograms was good in spite of uranium deposition at the cathode surface, leading to a change in the electrode surface.
Impedance spectroscopy. The typical complex impedance diagram (Nyquist plot) at tungsten electrode is presented in Fig. 10. It is evident that the complex impedance diagram consists of two parts: one capacity loop on the higher frequency side is due to kinetic control by an electrochemical charge transfer stage at the electrode-electrolyte interface and the straight line with the slope of about 45° on the lower frequency is attributed to diffusion of U(III) species. The following equation can be used for the charge transfer resistance ($R_{CT}$) at the rest potentials (32)

\[
R_{CT} = \frac{RT}{nF}i_0 = \frac{RT}{n^2F^2k_sC^{1-\alpha}}u_{U(III)}
\]  

[27]

where $i_0$ is the exchange current density. This expression allows us to calculate standard rate constants of charge transfer. As can be seen from the Fig. 10 the charge transfer resistance ($R_{CT}$) at temperature 723 K is equal to 0.32 Ω. The calculation showed that $k_s = 1.8 \times 10^{-4}$ cm s$^{-1}$.

The standard rate constants of charge transfer at different temperatures are presented in Table 5. As can be seen from Tables 4 and 5 the standard rate constants of charge transfer for electrodeposition process [3] are two order of magnitude less than for redox process [2]. According to Matsuda and Ayabe (31), the electrochemical process is quasi-reversible if

\[
10^{2(1+\alpha)} < k_D/(D\nu F/RT)^{1/2} < 15
\]  

[28]

In our case at $\nu = 1.0$ V s$^{-1}$ and 723 K

\[
1.8 \times 10^{-5} < k_s < 0.27 \text{ cm s}^{-1} \quad \text{for couple U(IV)/U(III)}
\]
\[
2.2 \times 10^{-5} < k_s < 0.33 \text{ cm s}^{-1} \quad \text{for couple U(III)/U}
\]

Thus intervalence charge transfer of the couple U(IV)/U(III) proceeds quasi-reversibly mostly under diffusion control, but the process of electrodeposition mainly controlled by the rate of charge transfer.

CONCLUSIONS

Our study confirms that U(IV) electrochemical reduction in LiCl-KCl melt occurs via two successive stages involving the transfer of one and three electrons. It was determined that at sweep rate $\nu \leq 0.3$ Vs$^{-1}$ the electroreduction of U(IV) to U(III) is reversible, but at $\nu > 0.3$ V s$^{-1}$ a mixed diffusion and electron transfer control is observed. The discharge reaction of U(III) to U is complicated by the surface alloy formation process and for determination of kinetic parameters it is necessary to use a relatively high concentration of uranium in the melt. The process of electrodeposition is quasi-reversible at low sweep rates, but at $\nu > 0.5$ V s$^{-1}$ it becomes irreversible. The diffusion coefficients of U(IV) and U(III) were determined by linear sweep voltammetry, chronopotentiometry and chronoamperometry methods. The values of diffusion coefficients found by these
methods are in a good agreement. The charge transfer standard rate constants for the redox reaction were calculated on the basis of cyclic voltammetry data and for electrodeposition process using impedance spectroscopy method. The values of constants testify that the redox process proceeds quasi-reversibly, mostly under diffusion control, but the process of electrodeposition is mainly controlled by the rate of charge transfer.

ACKNOWLEDGMENT

The authors express their thanks to Dr. T. Ogawa for helpful discussions. SAK is grateful for support of this study under a JAERI grant and also acknowledges support from University of Provence.

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Table 1. Values of diffusion coefficients \((D)\) and activation energies for diffusion \((\Delta H)\) of U(IV) and U(III) complexes in molten LiCl-KCl eutectic at 723 K

| Complexes | \(D \times 10^{-6}\), cm\(^2\) s\(^{-1}\) | \(\Delta H, \text{kJ mol}\(^{-1}\) | Reference |
|-----------|-------------------------------|-----------------|-----------|
| U(IV)     | 6.6                           | 41              | 1         |
| U(IV)     | 8.0                           | 46              | 16-17     |
| U(III)    | 4.8                           | 36              | 1         |
| U(III)    | 6.8                           | 39              | 16-17     |

Table 2. Experimental and calculated data on the number of electrons transferred during redox process. Melt LiCl-KCl-UCl\(_4\) \((2.03\times10^{-5} \text{ mol cm}^{-3})\), T=723 K. Potentials relatively silver-silver chloride reference electrode

| \(\nu\) (V s\(^{-1}\)) | \(E_{p}\) (V) | \(E_{p/2}\) (V) | \(E_{p/4}\) (V) | \(E_{1/2}\) (V) | Eq. [5] | Eq. [6] | Eq. [9] | Eq. [10] |
|-------------------------|-------------|---------------|-------------|--------------|--------|--------|--------|--------|
| 0.05                    | -0.400      | -0.237        | -0.245      | -0.309       | 0.84   | 0.89   | 0.76   | 1.08   |
| 0.1                     | -0.400      | -0.232        | -0.241      | -0.309       | 0.81   | 0.87   | 0.76   | 0.99   |
| 0.2                     | -0.400      | -0.233        | -0.245      | -0.309       | 0.82   | 0.91   | 0.76   | 1.08   |
| 0.3                     | -0.400      | -0.223        | -0.232      | -0.309       | 0.78   | 0.82   | 0.76   | 0.90   |
| 0.5                     | -0.427      | -0.214        | -0.200      | -0.309       | 0.65   | 0.61   | 0.58   | 0.63   |
| 1.0                     | -0.436      | -0.227        | -0.182      | -0.309       | 0.65   | 0.54   | 0.54   | 0.54   |
Table 3. Diffusion coefficients of U(IV) and U(III) \((D \cdot 10^{-5}\text{ cm}^2\text{ s}^{-1})\) at 723 K obtained by various methods

| Experimental method          | \(D_{\text{U(IV)}}\) | \(D_{\text{U(III)}}\) |
|------------------------------|------------------------|-----------------------|
| Voltammetry                  | 0.68                   | 1.02                  |
| Chronopotentiometry          | 0.74                   | 0.97                  |
| Chronoamperometry            | 0.84                   | 1.08                  |

Table 4. Influence of the temperature on the standard rate constants for the redox reaction \(\text{U(IV)} + e^- \rightarrow \text{U(III)}\) in LiCl-KCl eutectic melt

| Temperature, \(T/\text{K}\) | 723            | 773            | 823            |
|------------------------------|-----------------|-----------------|-----------------|
| \(k_s\ \text{cm s}^{-1}\)    | \(1.60 \cdot 10^{-2}\) | \(2.85 \cdot 10^{-2}\) | \(4.79 \cdot 10^{-2}\) |

Table 5. Influence of the temperature on the standard rate constants for the electrodeposition process \(\text{U(III)} + 3e^- \rightarrow \text{U}\) in LiCl-KCl eutectic melt

| Temperature, \(T/\text{K}\) | 723            | 773            | 823            |
|------------------------------|-----------------|-----------------|-----------------|
| \(k_s\ \text{cm s}^{-1}\)    | \(1.8 \cdot 10^{-4}\) | \(2.6 \cdot 10^{-4}\) | \(3.4 \cdot 10^{-4}\) |
Figure 1. Cyclic voltammetric curve at a tungsten electrode in LiCl-KCl-UCl₄ melt. Area: 0.407 cm². Sweep rate: 0.1 V s⁻¹. Temperature: 723 K. Concentration of UCl₄: 2.23×10⁻⁵ mol cm⁻³. Reference electrode: silver-silver chloride.

Figure 2. Cyclic voltammograms for redox process at a tungsten electrode. Area: 0.407 cm²; Sweep rates: 0.1; 0.2; 0.25 V s⁻¹. Temperature: 723 K. Concentration of UCl₄: 2.03×10⁻⁵ mol cm⁻³. Reference electrode: silver-silver chloride.
Figure 3. The dependencies of peak current (a) and of peak potential (b) of the recharge process on the polarization rate. Area: 0.407 cm². Temperature: 723 K. Concentration of UCl₄: 2.03·10⁻³ mol cm⁻³. Reference electrode: silver-silver chloride.
Figure 4. Steady-state voltammogram for electroreduction of U(IV) to U(III) and semi-logarithmic dependencies. 1: E-lg (Id-I); 2: E-lg[(Id-I)/I]. Area: 0.407 cm². Sweep rate: 0.002 V s⁻¹. Temperature: 723 K. Concentration of UCl₄: 2.03×10⁻⁵ mol cm⁻³. Reference electrode: silver-silver chloride.

Figure 5. Chronopotentiogram of the recharge process at a tungsten electrode. Current density: 4.2 mA cm⁻². Temperature: 723 K. Concentration of UCl₄: 2.82×10⁻⁵ mol cm⁻³. Quasi-reference electrode: glassy carbon.

Figure 6. The relation between i and t⁻¹/² for the process U(IV) + e⁻ → U(III). Temperature: 723 K. Concentration of UCl₄: 2.82×10⁻⁵ mol cm⁻³.
Figure 7. (a) Chronoamperogram for electroreduction of U(IV) to U(III) at a tungsten electrode. (b) relation between I and t^-1/2. Area: 0.407 cm². Potential step: -0.410 V vs. silver-silver chloride electrode. Temperature: 723 K. Concentration of UCl₄: 2.03·10⁻⁵ mol cm⁻³.
Figure 8. Cyclic voltammetric curves at a tungsten electrode in LiCl-KCl-UCl₃ melt. Area: 0.322 cm². Sweep rates: 0.1; 0.2; 0.25 V s⁻¹. Temperature: 723 K. Concentration of UCl₃: 6.26·10⁻⁵ mol cm⁻³. Reference electrode: silver-silver chloride.

Figure 9. The dependencies of peak potential of the process U(III) + e⁻ → U on the polarization rate. V≥0.5 Vs⁻¹.
Figure 10. Nyquist plot in LiCl-KCl-UCl₃ melt at rest potential -0.6 V vs. silver-silver chloride electrode. Area: 0.165 cm². Temperature: 723 K. Concentration of UCl₃: $5.68 \times 10^{-5}$ mol cm⁻³. The frequency range 100 mHz ≤ ω ≤ 100 KHz.