Electrochemical Behavior of U(III) and U(IV) in Molten LiCl-KCl Eutectic

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The investigation of the reversibilities of the electrode reactions for the U(III)-U(IV) system in LiCl-KCl eutectic melt mainly based on the potential-time relationships by chronopotentiometry has been presented. A theoretical chronopotentiogram for a reversible redox system has been derived and U(III) and U(IV) have been confirmed to form a reversible redox system. Standard potentials for the couple of U(IV)/U(III) in LiCl-KCl eutectic melt have been determined against the Ag/AgCl reference electrode over the temperature range from 390 to 530°C, and to be 0.595 V at 450°C.

1 Introduction

For the development of electrochemical analysis of U(III) and U(IV) in LiCl-KCl eutectic salt, the chronopotentiometry of U(III) and U(IV) in LiCl-KCl has been investigated previously¹⁾. In this paper, the investigation of the reversibilities of the electrode reactions mainly based on the potential-time relationships by the chronopotentiometry is presented. The results of the measurements of emf of the couple of U(IV)/U(III) in LiCl-KCl at temperature ranging from 390 to 520°C with the same apparatus are reported also.

2 Experimental

Materials, purification methods and the apparatus used in this experiment are the same as those previously reported¹⁾. A pen-recorder was used to observe the potential change of the indicator electrodes against the Ag-AgCl reference electrode. When the potential reached a constant value at each temperature, it was determined with a digital-voltmeter. The AgCl content of the reference electrode was determined to be 1.29 mol%. The constant current

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Fig. 1 Constant current circuit for chronopotentiometry
circuit is illustrated in Fig. 1.

3 Results and Discussion

3.1 Potential-time curves

The potentials were measured by anode and cathode chronopotentiometries in LiCl-KCl eutectic at 450°C for the following electrode processes, respectively,

The potential of the test electrode for a reversible process can be calculated from the concentration of the reductant C_r and that of the oxidant C_o at the electrode surface by Nernst's equation. For a reversible process in which both oxidant and reductant are soluble species and the oxidant is the only solute initially, and

for cathode chronopotentiometry, C_r and C_o are expressed as follows²⁾,

$$C_r = 2it^{1/2}/nF\pi^{1/2}D_r^{1/2} \quad (3)$$

$$C_o = C_o^\circ - 2it^{1/2}/nF\pi^{1/2}D_o^{1/2} \quad (4)$$

where i : the current density, t : electrolytic time, n : the number of electrons involved in electrode process, F : Faraday constant, D_r : the diffusion constant of the reductant, C_o° : the bulk concentration of the oxidant, D_o : the diffusion constant of the oxidant. Then electrode potentials are obtained for cathode chronopotentiometry as follows,

$$E = E_{r/4} + \frac{RT}{nF} \ln \frac{\tau_c^{1/2} - t^{1/2}}{t^{1/2}} \quad (5)$$

$$E_{r/4} = E^\circ + \frac{RT}{nF} \ln \frac{f_o D_r^{1/2}}{f_r D_o^{1/2}} \quad (6)$$

where E : a potential of the electrode, R : gas constant, T : absolute temperature of the system, τ_c : transition time for cathode chronopotentiometry, E° : the standard potential for the couple of the oxidant and the reductant, f_o : activity coefficient of the oxidant, and f_r : activity coefficient of the reductant. The potential $E_{r/4}$ is approximately equal to the standard potential E° since the ratio $f_o D_r^{1/2}/f_r D_o^{1/2}$ in equation (6) is close to unity.

For anode chronopotentiometry of the oxidant species which is only the solute involved in the solution, the potential of the electrode is,

$$E = E_{r/4} - \frac{RT}{nF} \ln \frac{\tau_a^{1/2} - t^{1/2}}{t^{1/2}} \quad (7)$$

where τ_a is transition time for anode chronopotentiometry.

The potential-time curve for a reversible process in which both oxidant and reductant are soluble species is ordinarily expressed by equation (5) or (7). Plots of potential E against $\log \{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ of the cathode and anode chronopotentiometries in LiCl-KCl eutectic salt are shown in Figs. 2 and 3. The conditions of anode and cathode chronopotentiometry are shown in Figs. 2 and 3 where c is the concentration of UCl_3 or UCl_4 . Both plots are almost linear and the electrode reactions (1) and (2) have been confirmed to be reversible. The slopes of the straight lines in both Figures agree with the value $2.303 RT/F$, and give n values to be 0.91 and 0.89 respectively. Some deviations from the linearities are observed at both ends of the curves in

Fig. 2 Plot of E vs. $\log \{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ for anodic chronopotentiogram

T : 450°C, i : 6.07 mA/cm², C : 3.2×10^{-2} mol/l, τ : 1.20 sec

Fig. 3 Plot of E vs. $\log \{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ for cathodic chronopotentiogram

T : 400°C, i : 6.07 mA/cm², C : 3.1×10^{-2} mol/l, τ : 1.00 sec

Figs. 2 and 3. They may be attributed to double-layer effects. When t approaches zero or τ , the potential of the electrode changes rapidly so that the current consumed for charging the double-layer increases. Consequently, the real electrolytic current is reduced, and deviates from the relations of equations (5) and (7) which are valid under the condition of constant current.

For the case of a reversible system that a oxidant and a reductant coexist in the same solution, the concentration of the reductant at

the electrode surface C_r is not expressed by equation (3) correctly so that equation (5) does not hold. The correct expression for C_r for cathode chronopotentiometry is.

$$C_r = C_r^\circ + 2it^{1/2}/nF \pi^{1/2} D_r^{1/2} \quad (8)$$

where C_r° is the bulk concentration of the reductant, and expressed as,

$$C_r^\circ = 2\tau_a^{1/2} i/nF \pi^{1/2} D_r^{1/2} \quad (9)$$

By introducing equations (8) and (9) in place of equation (3) in Nernst's equation, one obtains for cathodic chronopotentiogram,

$$E = E^\circ + \frac{RT}{nF} \ln \frac{f_o D_o^{1/2}}{f_r D_r^{1/2}} \cdot \frac{\tau_c^{1/2} - t^{1/2}}{\tau_a^{1/2} + (D_o/D_r)t^{1/2}} \quad (10)$$

Similarly, for anodic chronopotentiogram, one obtains

$$E = E^\circ + \frac{RT}{nF} \ln \frac{f_o D_o^{1/2}}{f_r D_r^{1/2}} \cdot \frac{\tau_c^{1/2} + (D_r/D_o)t^{1/2}}{\tau_a^{1/2} - t^{1/2}} \quad (11)$$

A theoretical potential-time curve calculated from equation (10) is shown in Fig. 4 (a), together with the curve (b) calculated from equation (5).

Equation (10) has an asymptotic form when t approaches zero,

$$t \rightarrow 0, E \rightarrow E^\circ + \frac{RT}{nF} \cdot \left\{ \frac{1}{\tau_c^{1/2}} + \frac{1}{\tau_a^{1/2}} \left(\frac{D_o}{D_r} \right) \right\} t^{1/2} \quad (12)$$

The potential of the electrode varies, therefore, parabolically with time initially, as shown in Fig. 4 (a). It is noticeable that a potential-time

Fig. 4 Theoretical potential-time curves
(a): Calculated from eq. (10)
(b): Calculated from eq. (5)

Fig. 5 Plots of E vs. $\log x$
(a) Anodic chronopotentiogram
 $x = \frac{\tau_c^{1/2} + (D_r/D_o)t^{1/2}}{\tau_a^{1/2} - t^{1/2}}$, τ_a : 1.10 sec, τ_c : 3.62 sec
(b) Cathodic chronopotentiogram
 $x = \frac{\tau_c^{1/2} - t^{1/2}}{\tau_a^{1/2} + (D_o/D_r)t^{1/2}}$, τ_a, τ_c : same above
 UCl_3 : $2.73 \times 10^{-2} \text{ mol/l}$, UCl_4 : $4.21 \times 10^{-2} \text{ mol/l}$,
 T : 453°C i : 6.07 mA/cm²

curve starts with infinite slope even in a reversible redox system. Reilley *et al.*³⁾ have investigated chronopotentiometry of Fe(III)-Fe(II) system in aqueous solutions. They concluded that a measurable degree of irreversibility was present in Fe(III)-Fe(II) system from the observation that the cathodic and anodic chronopotentiograms started with infinite slopes. Such conclusion could not be derived from the above discussion.

The U(III)-U(IV) system forms a reversible redox system. Fig. 5 shows that equations (10) and (11) hold for the U(III)-U(IV) system. The anodic curve (a) and the cathodic curve (b) joint at the point of zero potential, and construct a straight line. The slope of the line agrees well with the value of $2.303 RT/F$ and give n value to be 1.00

3.2 Emf of the Couple of U(IV)/U(III) in LiCl-KCl

Emf of the couple of U(IV)/U(III) was measured in molten LiCl-KCl at a temperature ranging from 390 to 520°C. The results are shown in Fig. 6 where x is the mole ratio of

Fig. 6 Potentials of the couple U(IV)/U(III) against Ag-AgCl reference electrode
 $x = (\text{UCl}_4)/(\text{UCl}_3)$
 ● : Temperature increasing
 ○ : Temperature decreasing

Fig. 7 Relation between potentials and $\log (\text{UCl}_4)/(\text{UCl}_3)$

U(IV) to U(III). Fig. 7 shows plots of emf against $\log x$ at various temperatures. The main errors found in Fig. 7 may be attributed to difficulties of the determination of the initial concentrations of UCl_4 and UCl_3 . As the small amounts of UCl_4 and UCl_3 were used for the measurements, it was difficult to weigh

Table 1 Standard Potentials of the Couple U(IV)/U(III) in LiCl-KCl

Reference	Reference electrode	Temp. (°C)	E° experimental	E° vs. $\text{Cl}_2/2\text{Cl}^-$
This work	Ag/AgCl	400	0.610	1.535
		450	0.595	1.505
		500	0.578	1.474
Hill <i>et al.</i> ⁵⁾	$\text{Pt}/\text{Pt(II)}$	450	1.25	1.55
Kisza <i>et al.</i> ⁶⁾	C/ Cl_2	400		1.511
		459		1.468
		515		1.410
ibid.	Ag/AgCl	400	0.186	1.121
Kuroda <i>et al.</i> ⁷⁾	C/ Cl_2	550		2.419
Martinot <i>et al.</i> ⁴⁾	Ag/AgCl	400	0.633	1.568
		450	0.610	1.521
		500	0.589	1.485
		550	0.567	1.450

them accurately. The slope of the lines in Fig. 7 deviates slightly from the value calculated by Nernst's law. In the U(III)/U(O) system Martinot *et al.*⁴⁾ found the similar deviations relative to Nernst's law, and concluded that the deviations were attributed to the existence of negative chloro complexes of the type of UCl_{3+y}^{y-} and UCl_{4+y}^{y-} .

As AgCl behaves ideally in LiCl-KCl eutectic melt, and as the concentrations of UCl_3 , UCl_4 , and AgCl are low enough to neglect junction potentials in this measurement, the data of emf can be recalculated to the $\text{Cl}_2/2\text{Cl}^-$ reference electrode. The recalculated values are listed in Table 1 together with the literature values for the comparison. In these cases, the method of the measurement, the type of reference electrode, the uranium concentration, the temperature, and the type of junction between the two half cells must be considered. Hill *et al.*⁵⁾ measured the potentials by polarography. Kisza *et al.*⁶⁾ evaluated the standard emf using a special kinetic procedure. Other authors measured the potentials by the emf method. There are some discrepancies between the data listed in Table 1. The main source of the discrepancies may be the high sensitivity of U(III) and U(IV) to oxidation and hydrolysis. The large deviations observed in Kuroda *et al.* values⁷⁾ are probably due to oxidation of uranium ionic species.

The standard potentials of U(IV)/U(III), E°_{12}

in this work are summarized as follows,

$$E_{12}^{\circ} = 1.946 - 6.10 \cdot 10^{-4} T(V). \quad (13)$$

The standard potential of the couple U(IV)/U(O), E_2° can be calculated from the potentials of the couples U(IV)/U(III) and U(III)/U(O) as follows,

$$E_2^{\circ} = (E_{12}^{\circ} + 3E_1^{\circ})/4 \quad (14)$$

where E_1° is the standard potential of the couple U(III)/U(O). To achieve the calculation, the data of Kiszka *et al.*⁶⁾ for the potential of the couple U(III)/U(O) were used.

$$E_1^{\circ} = 2.8667 - 5.387 \cdot 10^{-4} T(V). \quad (15)$$

The standard potential of U(IV)/U(O) is, therefore,

$$E_2^{\circ} = 2.598 - 5.57 \cdot 10^{-4} T(V). \quad (16)$$

<E407> (Received Jan. 29, 1975)

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