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

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For the needs to kinetic studies of the transfer processes in liquid metal-molten salt system, a chronopotentiometric investigation for the quantitative analysis of U(III) and U(IV) in LiCl-KCl eutectic salt has been investigated. It was found that chronopotentiometry of U(III) and U(IV) obeyed Sand's equation, and U(III) and U(IV) have been determined with an accuracy of $\pm 3\%$ when there is no oxygen and water contamination at 450°C both in their individual solutions and mixed solutions.

According to Sand's equation, the product of current density i and $1/2$ power of transition time τ should be constant with different i 's. However, it was observed to hold within a limited range of current densities. Positive and negative deviations from the constancy were explained.

The diffusion coefficients of U(III) and U(IV) in LiCl-KCl eutectic salt at 400°C have been determined by chronopotentiometry as follows,

$$D_{U(III)} = 4.38 \cdot 10^{-4} \exp(-5,940/RT) \quad \text{cm}^2/\text{sec}$$

$$D_{U(IV)} = 1.73 \cdot 10^{-3} \exp(-7,430/RT) \quad \text{cm}^2/\text{sec}.$$

1 Introduction

Much of the interest has appeared in molten salt chemistry in the field of nuclear power technology, particularly from the needs of molten salt breeder reactor and pyrochemical reactor fuel reprocessing. The salt transport process for the spent nuclear fuel reprocessing has been thought to be one of the promising reprocessing methods for future fast breeder reactors.

While much information on the chemical equilibria with the process has been accumulated, relatively little work has been reported on the kinetics of the transfer process in liquid metal-molten salt systems. One reason may be the difficulties of experimental techniques particularly the chemical analysis of the system, since an "*in situ*" analytical method is necessary for a kinetic study.

Some electrochemical methods have been investigated for the determination of uranium

in molten salts. Hill et al.¹⁾ studied slow-scan voltammetry of U(III), U(IV), and UO₂(VI) in molten LiCl-KCl. Mamantov and Maning²⁾ investigated the reduction of U(IV) in molten fluorides by voltammetry, chronopotentiometry, and chronoamperometry. Their results provide the basis for an *in situ* electroanalytical method for the determination of uranium in molten salts.

In chloride melts, uranium exists as U(III) or U(IV). Melts rich in U(IV) may be highly corrosive towards structural materials. For practical use, melts rich in U(III) rather than U(IV) are therefore preferred, some U(IV) is however necessary to prevent the disproportionation of U(III) with deposition³⁾. The analyses of U(III) and U(IV) in their mixed solution are therefore very important. The application of chronopotentiometry to the analysis of molten salt system seems to be most convenient and an important method. Laitinen and Ferguson⁴⁾ reported the chronopotentiometric determination of Bi(III), Cd(III), Ag(I) and Cu(I) in molten LiCl-KCl eutectic salt and suggested the effects of electrode geometry and convection. Thalmayer et al.⁵⁾ determined the diffusion coefficient of U(IV) in LiCl-KCl by chronopotentiometry. Smir-

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nov et al.⁶⁾ determined the diffusion coefficients of U(III), U(IV), and $\text{UO}_2(\text{VI})$ by chronopotentiometry in NaCl-KCl melt. Caligara et al.⁷⁾ investigated the chronopotentiometric analyses of U(IV), U(III), and $\text{UO}_2(\text{VI})$ in molten LiCl-KCl, however, their method of determination of U(III) and U(IV) in the mixed solution seems to be too complicated. Owing to their method, first, the concentration of U(IV) was determined, followed by the reduction of U(IV) to U(III) with metallic uranium, then total amount of U(III) was determined, and the initial concentration of U(III) was obtained by subtracting the amount of U(IV) from the amount of total U(III). Initial amount of U(III) in the mixture might be determined directly by anode chronopotentiometry and the reduction process is not necessary. Therefore, a chronopotentiometric study to determine U(III) and U(IV) in molten LiCl-KCl eutectic solution at 450°C and the determination of diffusion coefficients of U(III) and U(IV) in LiCl-KCl in the temperature range from 400 to 500°C have been carried out.

2 Experimental

2.1 Materials

UCl_3 was prepared at 270°C by the reaction of HCl and UH_3 which was formed by uranium metal and H_2 gas reaction at 220°C. UCl_3 was purified from adsorbed HCl and by-product UCl_4 by heating in vacuum at 600°C for 3 hr. UCl_4 was prepared by chlorination of UCl_3 with Cl_2 gas at 280°C and purified by vacuum distillation at 600°C. LiCl, KCl and AgCl for salt solvent and reference electrode were obtained as reagent grade. LiCl-KCl and LiCl-KCl-AgCl melts were purified by almost the same method as that of D.L. Hill et al.¹⁾ The purified melt including AgCl was siphoned into 4 mm I.D. pyrex tubes and solidified. The sticks were taken out from the tubes, inserted in a bottle with a screw cap and a rubber gasket and stored in an Ar-filled glove box. The AgCl content of the reference electrode was determined to be 1.29 mole%.

2.2 Apparatus and procedures

The apparatus for chronopotentiometry is shown in Fig. 1. The constant current circuit is composed of a 7.5 V battery, two 2SC37 and two 2SA495 transistors and several resistances.

Fig. 1 Block diagram of the apparatus for chronopotentiometry

- a : Batteries
- b : Switch
- c : Constant current circuits
- d : Polar converter
- e : Cell
- f : Counter electrode
- g : Test electrode
- h : Reference electrode
- i : Cathode ray oscilloscope
- j : Polaroid camera

Fig. 2 Cell assembly

- 1 : Brass chain
- 2 : Glass cock
- 3 : Uranium chlorides
- 4 : O-ring seal
- 5 : Flange
- 6 : Water cooling coil
- 7 : To vacuum and Ar inlet
- 8 : Pyrex crucible
- 9 : Thermocouple
- 10 : Ag-AgCl reference electrode
- 11 : Pt test electrode
- 12 : Pt counter electrode
- 13 : Glass wool

The cell assembly of chronopotentiometry is shown in Fig. 2. The test electrode was constructed with a 5 mm square Pt foil and a Pt wire sealed in a pyrex tubing of 8 mm in diameter. The counter electrode consisted of a 20 mm square Pt foil which was large enough to avoid polarization. The reference electrode was constructed with a silver wire (1 mm ϕ) in equilibrium with a solution of Ag(I) (1.29 mole%) in the molten LiCl-KCl eutectic solvent. The reference electrode solution was separated from the testing molten salt by some small asbestos fibers sealed into the end of the pyrex tubing of the electrode.

UCl_3 and UCl_4 were weighed in a pyrex bucket in an Ar-filled dry-box. The bucket was hung down and immersed into the molten LiCl-KCl eutectic salt which had been melted previously in vacuum. The cell was filled with purified Ar and the electrodes and a thermocouple well were inserted into the melt. The cell was settled down for further 1 hr in order to complete the dissolution of UCl_3 and UCl_4 in the melt and to establish the equilibrium among the electrodes and the solutions, then the measurement was started. The potential change of the test electrode was measured by a cathode-ray oscilloscope and the resulting potential-time curves were recorded with a Polaroid camera. In order to obtain an accuracy in time measurement, intensity of the oscilloscope beam was modulated by rectangular pulses at interval of 20 msec. After every sweep, reversed current was passed through the cell just long enough to restore the potential of the test electrode.

3 Results and Discussion

3.1 Analysis of U(III) and U(IV) in each individual solution

UCl_3 was analysed by anode chronopotentiometry corresponding to the electrode reaction, $\text{U(III)} \rightarrow \text{U(IV)} + e^-$. In chronopotentiometry, the following Sand's equation holds,

$$\tau^{1/2} = \pi^{1/2} n F C^\circ D_o^{1/2} / 2 i \quad (1)$$

where, τ is transition time, C° is the bulk concentration of a reactant, D_o is the diffusion coefficient of the reactant, n is the valence of the reactant, F is the Faraday constant, and i is the current density. According to Sand's equation (1), the plots $\tau^{1/2}$ vs. $1/i$ and $\tau^{1/2}$ vs. concentra-

Fig. 3 Plots of $\tau^{1/2}$ vs. $1/i$ for the determination of UCl_3

Fig. 4 Relations between $\tau^{1/2}$ and UCl_3 concentration

tion must give straight lines. From the observation of the anode chronopotentiometry of U(III) in LiCl-KCl eutectic at 450°C, the relations between $\tau^{1/2}$ and $1/i$ are shown in Fig. 3, and the relations between $\tau^{1/2}$ and concentration of UCl_3 are shown in Fig. 4. These results show almost linear relations, though some scatters were appeared. One of the reasons of the scatters in Fig. 3 may be due to the deposition of ura-

mium metal on the electrode surface. Considerable scatters in Fig. 4 may be attributed to the contamination by oxygen and water.

According to equation (1), $i\tau^{1/2}$ vs. C^0 curve should give a straight line. This curve can be used as a calibration curve for chemical analysis. The results of anode chronopotentiometry for U(III) solutions at 450°C are shown by closed circles in Fig. 5. UCl_4 was analysed by cathode chronopotentiometry corresponding to the reaction, $\text{U(IV)} + e^- \rightarrow \text{U(III)}$. Sand's equation also holds for the cathodic chronopotentiometry of the U(IV) solutions, the relation between $i\tau^{1/2}$ and concentration at 450°C showed a straight line as illustrated by closed circles in Fig. 6.

Fig. 5 Relationship between $i\tau^{1/2}$ and UCl_4 concentration for anode chronopotentiometry

Fig. 6 Relationship between $i\tau^{1/2}$ and UCl_4 concentration for cathode chronopotentiometry

3.2 Analyses of U(III) and U(IV) together in the mixed solutions

U(III) and U(IV) in the mixed solutions might be determined directly by anode and cathode chronopotentiometries, respectively at 450°C. In this case, the procedure that Caligara et al.¹⁷ had proposed for the determination of U(III) in mixed solution was not necessary. The observed relationship between $i\tau^{1/2}$ and concentration of UCl_3 in mixed solutions for anode chronopotentiometry is shown by open circles in Fig. 5. The reproducibility of the measurement in each run was much more improved than the case of UCl_3 individual solutions as shown by the error ranges in Fig. 5. The same relationship between $i\tau^{1/2}$ and concentration of UCl_4 in mixed solution for cathode chronopotentiometry is shown by open circles in Fig. 6. The considerable scatters, however, still exist in these measurements, and extrapolations of the plots of Figs. 5 and 6 to zero $i\tau^{1/2}$ show that there is a "residual" concentration. This may be due to the contamination by oxygen and water.

The variation of the product $i\tau^{1/2}$ with the current density i for the oxidation of U(III) is shown in Fig. 7. From Sand's equation, the product $i\tau^{1/2}$ should be independent of the current density i , however, it holds only within a limited range of current densities. Positive and negative deviations from the constancy in $i\tau^{1/2}$ - i plots were observed by many investigators. Some explanations were given by Paunovic¹⁸.

(1) Surface roughness of the electrode

With decreasing thickness of the diffusion layer, unevenness of the surface becomes more important and the real diffusional area increases. One can

Fig. 7 Variation of $i\tau^{1/2}$ with i

thus expect positive deviations from constancy with increasing current density resulting from roughness of the electrode.

(2) Double-layer effect

The effect of charging of the double layer on $i\tau^{1/2}$ can be qualitatively estimated⁹⁾ by assuming that the charging of the double layer occurs constantly during time τ with the constant capacitive current $i_L = C_{DL}\Delta E/\tau$. With this assumption and from equation (1), the total current density is expressed as

$$i = nF\pi^{1/2}D^{1/2}C^0/2\tau^{1/2} + C_{DL}\Delta E/\tau \quad (2)$$

and $i\tau^{1/2}$ is expressed as

$$i\tau^{1/2} = nF\pi^{1/2}D^{1/2}C^0/2 + C_{DL}(\Delta E/\tau^{1/2}) \quad (3)$$

It follows from these equations that with decreasing τ , which corresponds to increasing i , the second term in equation (3) increases. Therefore, positive deviation is expected for large value of i .

(3) Non-linearity of the diffusion field

When the dimension of an electrode is large compared with the diffusion layer thickness, then the electrode surface referred to the diffusion layer approximates an infinite plane and the diffusion field is linear. As the thickness of the diffusion layer increases, the departure from linearity increases. Since the thickness of diffusion layer is given by $\sqrt{\pi D\tau}$, one would expect deviation due to non-linearity of diffusion for longer transition time, i.e., lower current densities. The thickness of the diffusion layer at the time when the deviation occurred was obtained to be 3.9×10^{-3} cm by the calculation from the value of τ at the inflection point in Fig. 7. This value is sufficiently small compared with the geometry of the test electrode, 0.5 cm square. The effect of non-linearity of the diffusion field is, therefore, not so significant in this measurement.

(4) Convection

A vertical Pt foil was used as the test electrode in this study, so that the effect of natural convection became serious. The diffusion layer induced by electrolysis extends with time, and it exceeds the Nernst boundary layer determined by hydrodynamic conditions, the influence of natural convection appears. The thickness of the diffusion layer at the time when the deviation from the constancy of $i\tau^{1/2}$ occurs gives the thickness of the Nernst boundary layer. The

value 3.9×10^{-3} cm calculated above agrees well with empirical magnitude of the order $10^{-2} \sim 10^{-3}$ cm⁹⁾.

From the results in Fig. 7, current densities must be chosen as transition times are in the range from 0.3 to 2.2 sec. Under these conditions, the transition time was determined with an accuracy of $\pm 6\%$ in each run. Since concentration is proportional to $\tau^{1/2}$, the concentration of U(III) and U(VI) were determined with an accuracy of $\pm 3\%$ respectively in each run.

3.3 Diffusion coefficients of U(III) and U(IV)

The diffusion coefficients of U(III) and U(IV) in LiCl-KCl eutectic salt were determined by chronopotentiometry in the U(III)-U(IV) system. Arrhenius plot of the diffusion coefficients of U

Fig. 8 Arrhenius plot of $D_{U(III)}$ in LiCl-KCl eutectic

a : This work
b : Caligara et al.⁷⁾

Fig. 9 Arrhenius plot of $D_{U(IV)}$ in LiCl-KCl eutectic

a : This work
b : Geldner et al.¹⁰⁾
c : Thalmayer et al.⁵⁾
d : Caligara et al.⁷⁾

Table 1 Comparison of D and ΔH_D at 400°C in LiCl-KCl eutectic

Ion	D 400°C (10^{-6} cm ² /sec)	ΔH_D 400°C (Kcal/mol)	Method	Reference
U(III)	5.6	5.94	Chrono. *	This work
	4.1	9.5	Chrono. *	Martinot et al. ¹¹⁾
U(IV)	7.3	7.43	Chrono. *	This work
	4.89	7.72	Chrono. *	Thalmayer et al. ⁹⁾
	4.5	11.1	Chrono. *	Martinot et al. ¹¹⁾
	10.3	6.3	Tracer	Geldner et al. ¹⁰⁾
	12.2	8.1	Viscous flow **	Geldner et al. ¹⁰⁾

* Chrono. : Chronopotentiometry

** Viscous flow : Viscous flow calculated from Stokes-Einstein equation

(III) obtained in this work, together with the plot of the literature values are illustrated in Fig. 8. Those of the diffusion coefficients of U(IV) are shown in Fig. 9. The plots gave straight lines, and the activation energies were calculated from those slopes. A summary of the results obtained in this work together with the values in literature is tabulated in Table 1.

The values obtained in this work for the diffusion coefficient of U(III) and U(IV) are not in good agreement with previous data, but are within a large spread of the literature value. The value obtained in this work for ΔH of U(IV) almost agrees with the values of Thalmayer et al.⁹⁾ and differs from the value of Caligara et al.⁷⁾ The difference between the values in this work and Caligara's is also noticed for ΔH of U(III). Thalmayer et al.⁹⁾ showed the viscous flow mechanism could not explain the observed diffusion behavior of U(IV) in LiCl-KCl. The results of this study support their conclusion. The comparison between ΔH for diffusion and ΔH for viscous flow is also given.

Caligara et al.⁷⁾ observed in their experiment that the activation energy for diffusion of both U(III) and U(IV) decreases with increasing temperature. They explained it by a vacancy mechanism.¹¹⁾ In this study, however, the temperature dependency of ΔH was not observed.

4 Conclusion

The main conclusions obtained in this experiments can be summarized as follows.

1) Chronopotentiometries of U(III) and U(IV) in LiCl-KCl eutectic salt have been investigated

and their behavior was found to obey Sand's equation.

2) Utilizing above chronopotentiometries, the concentration of U(III) and U(IV) both in LiCl-KCl eutectic individual solutions and mixed solutions could be determined at 450°C with an accuracy of $\pm 3\%$ when there is no contamination by oxygen and water.

3) The variation of the product of current density i and $1/2$ power of transition time τ with the current density i was studied. According to Sand's equation, the product $i\tau^{1/2}$ should be independent of the current density i , however, it held only within a limited range of current densities. Positive and negative deviations from the constancy in $i\tau^{1/2} \sim i$ plots were explained referring the explanation by Paunovic⁸⁾.

4) The diffusion coefficients of U(III) and U(IV) in LiCl-KCl eutectic salt at 400°C have been determined by chronopotentiometry as follows,

$$D_{U(III)} = 4.38 \cdot 10^{-4} \exp(-5,940/RT) \text{ cm}^2/\text{sec}$$

$$D_{U(IV)} = 1.73 \cdot 10^{-3} \exp(-7,430/RT) \text{ cm}^2/\text{sec}.$$

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