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ELECTROCHEMISTRY OF PLUTONIUM(III) IN MOLTEN ALKALI CHLORIDES

D. A. NISSEN

NOVEMBER, 1965

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ELECTROCHEMISTRY OF PLUTONIUM(III)
IN MOLTEN ALKALI CHLORIDES

By

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Chemistry Department

November, 1965

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

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INTRODUCTION

Chronopotentiometric and cyclic voltametric techniques have been used to study the electrochemical reduction of Pu(III) to the metal in molten chloride solutions, in particular, the eutectic LiCl/KCl system. A postulated mechanism for the cathodic reduction of Pu(III) in this melt system as well as information on its diffusion properties are presented in this report.

Current interest in the use of molten salts as media for processing nuclear fuels, especially for the electrowinning⁽¹⁾ and electrorefining⁽²⁾ of plutonium metal, has demonstrated the need for a fundamental study of the electrochemistry of plutonium in molten salts.

With the exception of the work of Benz^(3,4) on thermodynamic values for the reaction

in molten LiCl and NaCl, very little is known about the electrochemistry of the Pu/Pu(III) couple in molten media. Of particular interest is the possibility that Pu(III) may undergo an initial reduction to a lower oxidation state before being reduced to the metal. The existence of a stable plutonium valence state lower than three would be of interest from a theoretical as well as a practical standpoint.

SUMMARY

The charge-transfer reaction apparently takes place in one step,

involving a three electron change. There is no evidence that the cathodic reduction of Pu(III) to the metal passes through a stable lower oxidation state in the LiCl/KCl melt system.

The results of chronopotentiometric experiments show that Pu(III) exhibits dissimilar behavior as the temperature of the melt is changed. At 400 °C a characteristic function, the $i_{\text{OT}}^{1/2}$ product, is invariant with current density. At higher temperatures this function changes as the current density changes. It would appear on this basis that at 400 °C plutonium, possibly in the form of a complex molecule, undergoes direct reduction to the metal. At temperatures in excess of 400 °C, an equilibrium apparently exists between two complex species of plutonium; and the rate of transformation from one form to another is the rate controlling step.

Except for the fact that Pu(III) undergoes a single three-electron reduction to the metal, the mechanism is uncertain. It is anticipated that electrochemical relaxation techniques coupled with proposed spectrophotometric studies will be helpful in defining the reduction mechanism more exactly.

EXPERIMENTALCell and Instruments

The melt was contained in a graphite crucible which in turn was enclosed in a quartz cell. The top

of the cell was flanged and ground flat to provide a seal with the lid which was fabricated from Pyrex and had standard taper joints fastened to it. Such things as electrodes, etc., which were to be put into the cell were equipped with standard taper joints; in this way a sealed system was provided, and a controlled atmosphere could be kept over the melt.

Electrodes for the chronopotentiometric experiments were cut from 7 mil tungsten sheet, spot welded to a 10 mil tungsten wire, and polished to a mirror finish. Electrodes for cyclic voltametric studies were made by sealing a 24 gage tungsten wire into Vycor tubing. These wires were then polished to try to produce as uniform a surface as possible.

A Ag/AgCl half-cell (0.1 molal AgCl in LiCl/KCl) served as the reference electrode for both the chronopotentiometric and cyclic voltametric studies. It was separated from the main body of the melt by a Pyrex membrane. In some cases, for the sake of convenience, a spectrographic grade graphite rod which dipped into the melt acted as a quasi-reference electrode. Although the graphite assumes a mixed potential of unknown magnitude, its value was constant (within ± 1 mV) over extended periods of time.

The melt temperature for these experiments was maintained within ± 2 °C by the use of a vertical, nichrome wire-wound resistance furnace controlled by a Wheelco indicating millivolt meter.

A chronopotentiometric circuit, previously described by Delahay,⁽⁵⁾ was

coupled with an oscillographic recorder which was used to record the potential of the tungsten indicating electrode as a function of time. Details of the instrument can be found in the paper by Stromatt.⁽⁶⁾ The cyclic voltameter was based on one described by Alden.⁽⁷⁾

Melt Preparation

To obtain reproducible and meaningful results, it was necessary to exercise the most extreme care in the preparation of the melt. The sequence of operations included prolonged treatment of the LiCl/KCl solvent, both unfused and molten, with HCl followed by a preelectrolysis of the melt at -1.9 versus the Ag/AgCl reference electrode. A blank melt of high purity could be produced by taking appropriate precautions (having a chronopotentiometric transition time of less than 0.01 sec at -1.9 V). After any additions to the melt were made it was treated with HCl for about 6 hr.

Helium, which had been purified by passing over zirconium turnings maintained at 750 °C and then through $\text{Mg}(\text{ClO}_4)_2$, was used to provide an inert atmosphere over the melt.

To insure that the graphite crucible which was used to contain the melt did not act as a source of contamination, it was boiled in concentrated hydrochloric acid, then in distilled water, and thoroughly dried before being used.

All preparative and experimental work was done in a glove box through which a flow of predried air was passed.

RESULTS

Among the several techniques available for studying electrode reaction mechanisms and diffusion properties, two were chosen for this study: cyclic voltammetry and chronopotentiometry. The first of these techniques, cyclic voltammetry, is simply a variation of a more classical electrode polarization technique, polarography. In cyclic voltammetry, the potential of the polarized electrode is made to vary periodically within set limits and the resulting current is recorded as a function of voltage.

Figure 1 shows a typical voltamogram for the reduction of Pu(III) to the metal, followed by oxidation of

FIGURE 1. VOLTAMAGRAM OF Pu(III) AT A TUNGSTEN MICROELECTRODE IN LiCl/KCl AT 400 °C. CONCENTRATION OF Pu(III) = 1.65×10^{-5} moles/cm³

the metallic deposit, at 400 °C in the eutectic LiCl/KCl system. Reduction of Pu(III) to the metal takes place at about -0.84 V and is followed by reduction of the solvent at about -2.1 versus the Ag/AgCl reference electrode. The subsequent oxidation step occurs as a single peak which has a form characteristic of the oxidation of a solid product. There appears to be no evidence that the reduction step passes through a stable subvalent state in this melt system. From the proximity of the reduction and oxidation potential, one can conclude that the reduction process, at 400 °C, is reversible.

Chronopotentiometry is simply an electrolysis technique in which a current pulse of predetermined magnitude and duration is applied to an electrochemical cell under conditions of linear diffusion while recording the potential of the test electrode as a function of time. An important experimental quantity in chronopotentiometry is the transition time, τ . This is the time interval after the onset of electrolysis when the surface concentration of the electroactive material diffusing the electrode reaches zero and a jump of the electrode potential occurs.

Figure 2 shows a typical chronopotentiogram for the same system and temperature as for Figure 1. In this case, as in the preceding one, there is no evidence for a stable subvalent state of plutonium; no intermediate reduction steps are apparent before the final one which is the reduction to the metal.

FIGURE 2. CURRENT-REVERSAL CHRONOPOTENTIOTAGRAM OF Pu(III) AT A TUNGSTEN ELECTRODE (ELECTRODE AREA 1.16 cm^2) AT 400°C IN LiCl/KCl. CONCENTRATION OF Pu(III) = $1.65 \times 10^{-5} \text{ moles/cm}^3$

Figure 3 presents the data from chronopotentiometric experiments as a plot of the product of the current density, i_o , and the square root of the transition time, $\tau^{1/2}$, versus the current density for various values of the temperature and concentration of PuCl_3 in the eutectic LiCl/KCl system.

The $i_o \tau^{1/2}$ product shows two different characteristics: at 400°C it is invariant with current density (for $i_o > 2 \times 10^{-2} \text{ A/cm}^2$); at 500 and 600°C the $i_o \tau^{1/2}$ - i_o relationship has a finite slope.

DISCUSSION

The relationship between the transition time and the current density for a reaction sequence of the type

FIGURE 3. THE $i_o \tau^{1/2}$ PRODUCT AS A FUNCTION OF i_o FOR Pu(III) AT A TUNGSTEN ELECTRODE (ELECTRODE AREA 1.16 cm^2) IN LiCl/KCl AT VARIOUS TEMPERATURES AND CONCENTRATIONS OF Pu(III)

is given by the equation⁽⁸⁾

$$i_o \tau^{1/2} = \frac{nFC(\pi D)^{1/2}}{2} - \frac{\pi i_o}{2K(k_f + k_b)^{1/2}} \cdot \text{erf} [(k_f + k_b)^{1/2} \tau^{1/2}] \quad (2)$$

where K = the equilibrium constant
 k_f and k_b = the formal rate constants for the chemical reaction which, in Equation (1), precedes the charge-transfer reaction

C = the concentration in moles/cm³

D = the diffusion coefficient in cm²/sec

i_o = the current density in A/cm²

τ = the transition time in seconds

n = the number of electrons involved in the charge-transfer reaction

F = the value of the Faraday (96,500 coulombs/equiv.).

In those cases where the argument of the error function is greater than 2, Equation (2) reduces to

$$i_o \tau^{1/2} = \frac{nFC(\pi D)^{1/2}}{2} - \frac{\pi i_o}{2K(k_f + k_b)^{1/2}} \quad \dots (3)$$

This equation predicts that the $i_o \tau^{1/2}$ - i_o relationship should be linear with a slope equal to

$$-\frac{\pi^{1/2}}{2K(k_f + k_b)^{1/2}} \quad (4)$$

and an intercept equal to

$$\frac{nFC(\pi D)^{1/2}}{2} \quad (5)$$

If the quantity $K(k_f + k_b)^{1/2}$ is sufficiently large ($<500 \text{ sec}^{-1/2}$), the slope becomes essentially equal to zero and Equation (3) reduces to

$$i_o \tau^{1/2} = \frac{nFC(\pi D)^{1/2}}{2}$$

which gives the relationship between the transition time and the current density for a simple diffusion-controlled process and predicts that the $i_o \tau^{1/2}$ product should be invariant with i_o .

Using the applicable equations, as discussed earlier, and the information given in Figure 3, values of the diffusion coefficient for Pu(III) have been calculated for various temperatures and plutonium concentrations. These values are given in Table I.

The values of the diffusion coefficient given in Table I for Pu(III) in molten LiCl/KCl are in reasonable agreement with those determined for Bi(III) in the same solvent system by Laitinen and Ferguson, 0.68×10^{-5} at 400 °C,⁽⁹⁾ and by Thalmayer et al, 0.63×10^{-5} at 400 °C and 1.0×10^{-5} at 450 °C.

TABLE I. DIFFUSION COEFFICIENTS FOR THE EUTECTIC LiCl/KCl SYSTEM AS A FUNCTION OF TEMPERATURE AND PLUTONIUM CONCENTRATION

Pu(III) Concentration		Temperature °C	$i_o \tau^{1/2}$ $(A/cm^2) \times 10^3$	Diffusion Coefficient $(cm^2/sec) \times 10^5$
$(moles/cm^3) \times 10^5$	Molality $\times 10^2$			
1.65	1.01	400	9.6	0.51
1.60	1.01	500	13.7	1.11
1.55	1.01	600	16.0	1.62
3.55	2.17	400	22.2	0.59
3.44	2.17	500	30.8	1.21

The temperature dependence of the diffusion coefficient is a measure of the activation energy for the diffusion of Pu(III). A plot of the logarithm of the diffusion coefficients shown in Table I versus the reciprocal of the absolute temperature is linear and yields an activation energy of 6.7 kcal/mole.

Figure 3 shows that the values of $i_0 \tau^{1/2}$ depart markedly from linearity at low current density for all values of the temperature. There are two possible explanations which might account for this.

If convection currents had been present in the melt, they would have caused an enhancement of the transition time by increasing the amount of electroactive material at the electrode over that which would have been available on the basis of diffusion alone. In no case, however, was the

transition time longer than about 3 sec. Measurement of the transition time for the reduction of Cd(II) in a similar experimental setup showed that there was no interference from convection for transition times up to 5 sec.⁽¹¹⁾

This same departure from linearity was noted by Gierst and Juliard⁽¹²⁾ and was attributed to an increase in the cathode area due to the formation of dendritic growths. If this was the case in these experiments, this phenomena should disappear at temperatures in excess of 640 °C, the melting point of plutonium metal; however, experimental difficulties prevented an examination of this system at temperatures in excess of 600 °C.

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