Exchange current density of uranium at liquid cadmiumin LiCl-KCl eutectic

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Abstract

Molten salt electrorefining is a key stepin pyroprocessing where the actinides from spent metallic fuel are separated from fission products using LiCl-KCl as electrolyte at 773 K. Liquid cadmium electrode plays an important role in the separation scheme where uranium, plutonium along with minor actinides are co-deposited. The present study is oriented towards the understanding electrode kinetics of U^{3+}|U couple at liquid cadmium using electrochemical techniques like cyclic voltammetry and DC amperommetry. Anodic stripping voltammetry was also carried out at cadmium containing uranium to measure the dissolution potential of uranium from cadmium. Exchange current density of U^{3+}|U couple in cadmium during anodic and cathodic polarization by Tafel plots at temperature 698-798 K is reported in the present work.

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1. Introduction

Molten salt electrorefining is a high temperature electrochemical separation process utilizing LiCl-KCl eutectic as electrolyte at 773 K for the recovery of uranium, plutonium and minor actinides. U is electrodeposited at the solid cathode and U, Pu along with minor actinides at the liquid Cd cathode [1]. The electrode processes during electrorefining are governed by three kinetic parameters; exchange current density, transfer coefficient and diffusion layer thickness. The evaluation of these kinetics parameters for various species is important for modelling the electrorefining process.The present paper discusses the estimation of exchange current density of U^{3+}|U couple at liquid cadmium in the temperature range 698-773 K.

Experimental

Preparation of electrolyte

The eutectic mixture of LiCl and KCl was vacuum dried for 120 h at 473 K prior to purifying it by bubbling chlorine gas at 773 K for 1h. The purified LiCl-KCl eutectic was stored in the glove box and it was used for preparation of electrolyte salt of LiCl-KCl-UCl_3. LiCl-KCl-UCl_3 was prepared by equilibrating $CdCl_2$ (99.9%, Alfa Aesar) with U metal in LiCl-KCl eutectic at 773 K for about 35-40 h. The concentration of U in the salt was estimated by Davies and Gray method [2].

Preparation of liq. Cd electrode

Liq. Cd was developed and fabricated in house which consisted of a SS 430 perforated basket connected to SS 304 tube and alumina crucible kept inside it for Cd shots loading. A 1.5 mm Mo wire insulated by alumina sleeve was kept inside the alumina crucible passing through SS 304 tube such that bottom end of Mo wire touched with Cd pool in alumina crucible and top end was used for electrical connection. The Cd metal shots was loaded into the alumina crucible of the electrode then immersed into LiCl-KCl eutectic at 773 K and the same repeated until shining surface of Cd was observed. About 20-22 g of Cd metal was loaded into alumina crucible. The pieces of uranium metal (0.37 g) were added into Cd pool and employed as working electrodes for the estimation of exchange current density of U^{3+}|U couple at liq. Cd during anodic polarization. A typical liq. Cd electrode is shown in Fig 3. The active electrode area for liq. Cd electrode was found to be 1.5 cm^2.

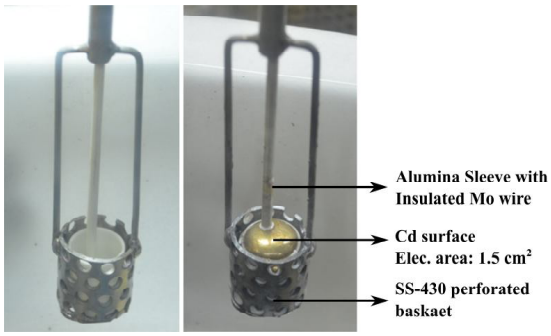


Fig.1 Liq. Cd cathode saturated with U metal in a SS-430 perforated basket

Procedure

A three electrode cell assembly consisting of SS 304 electrochemical vessel and top flange having provision for inserting the electrodes was used in present studies. A graphite rode of 8 mm dia. was used as a counter electrode and Ag|AgCl in LiCl-KCl used as reference electrode. The empty electrochemical cell with alumina crucible and graphite electrode was degassed at 698 K for 4-5 h. The electrochemical cell after assemble of electrodes and electrolyte salt was heated in a furnace slowly. The temperature of cell was controlled by a PID controller and measured by K-type thermocouple Argon gas was purged through the cell during the experiments. Electrochemical measurements were carried out using PGSTAT AUTOLAB302N with IF030 interface having GPES4.9 data processing software.

Results and discussion

Cyclic voltammetry

The cyclic voltammograms of U^{3+}at Mo electrode and liq. Cd cathodein LiCl-KCl at 773 K are shown in Fig.2a and 2b, respectively. Two cathodic peaks are observed in the voltammogramat inert Mo electrode; one corresponding to$U^{4+}|U^{3+}$couple at -0.35 V and other corresponding to $U^{3+}|U$ couple at -1.5 V. At liq. Cd cathode only one peak corresponding $U^{3+}|U$-Cd couple at -1.25 V is observed.As can be seen fromFig 2'a' and 'b' that there shift in the cathodic peak potentials for U at liq. Cd cathode compared to that at inert Mo electrode. This is attributed to the underpotential deposition at liq. Cd cathode due to the formation of U-Cd alloys.

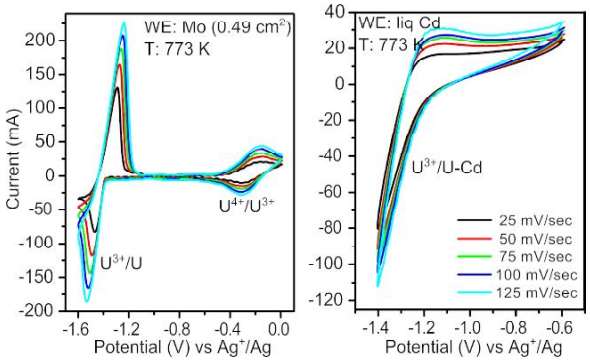


Fig. 2 (a) Fig. 2 (b)

Fig.2 Comparison of cyclic voltammograms of U^{3+}at inert electrode (a)and liq. Cd cathode (b) in LiCl-KCl eutectic at 773 K.

Polarization measurements

The *i-V* characteristics at liquid cadmium electrode were studied using DC amperometry and the results were analysed using Tafel plot analysis, which are estimated by using the following equations for cathodic and anodic polarization curves, respectively.

$$\ln[i_i] = \ln[i^{\circ}_{i,c}] - \frac{(z_i\alpha_i)F}{RT}\eta^{a}_{i,c} \qquad (1)$$

$$\ln[i_i] = \ln[i^{\circ}_{i,a}] + \frac{(1-\alpha_i)z_iF}{RT}\eta^{a}_{i,a} \qquad (2)$$

Transfer coefficient of $U^{3+}|U$couple at liq. Cdduring cathodic and anodic polarization was also estimated. A typical Tafel plot of U^{3+} at liq. Cd cathode is shown in Fig. 3. Exchange current densities and transfer coefficients of U^{3+} at liq. Cd during cathodic and anodic polarization are shown in table 1.

S. No.	Temp. (K)	Cathodic		Anodic	
		i_o (mA.cm^{-2})	Transfer coefficient ($\acute{a}$)	i_o(mA.cm^{-2})	Transfer coefficient ($\acute{a}$)
1	698	—-	—-	13.9 ± 1.1	0.89
2	723	—-	—-	19.2 ± 1.0	0.91
3	748	—-	—-	26.1 ± 1.1	0.91
4	773	19.3 ± 1.0	0.09	30.5 ± 1.1	0.92
5	798	—-	—-	33.9 ± 1.0	0.95

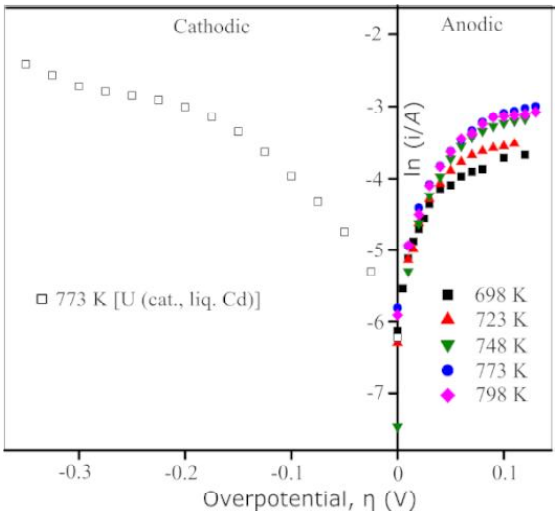


Fig.3 Tafel plots of U at liq. Cd at cathodic and anodic polarizationin molten LiCl-KCl eutectic

Conclusions

The exchange current density of $U^{3+}|U$ couple at liquid cadmium electrode in the temperature range 698-798 K employing LiCl-KCl eutectic have been determined for the first time.

Reference

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