An Electrochemical Impedance Spectroscopy Analysis Of Redox Behaviour Of Uranium In Liquid Cadmium In LiCI-KCI Eutectic

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Abstract:

Electrochemical studies on the redox mechanism of uranium in cadmium are carried out in the present work using LiCl-KCl-UCl_3 as electrolyte. DC polarization and electrochemical impedance spectroscopy methods were used to estimate exchange current density of uranium in cadmium and elucidate the diffusion and charge transfer characteristics in cadmium during anodic dissolution and cathodic deposition of uranium.

Keywords: Pyroprocessing, exchange current density, electrochemical impedance spectroscopy.

1. Introduction

Liquid cadmium is used for the recovery of uranium, plutonium and minor actinides in pyropartioning process using LiCl-KCl eutectic as electrolyte [1]. The present study aimed at investigating electrochemical behavior of uranium in liquid cadmium using DC polarization and impedance spectroscopy methods. DC polarization method has been earlier used by the authors to estimate exchange current density of various redox couples [2]. The work is extended in the present paper to liquid cadmium anode (containing uranium) and cathode systems. Uranium slices are added to liquid cadmium such that it is well beyond its saturation solubility in cadmium for anodic polarization measurements. Experiment in this regard is applicable to recovery of uranium from cadmium pool in electrorefiner where loosely adhered uranium dendrites can fall from cathode during electrorefining.The present paper is aimed at estimating exchange current density of uranium in cadmium in anodic and cathodic cases using polarization methods and investigating the difference in mechanism of anodic dissolution of uranium from cadmium and cathodic deposition of uranium in cadmium using electrochemical impedance spectroscopy.

2. Experimental

1.1 Preparation of electrolyte and electrodes

LiCl-KCl-UCl_3electrolyte was prepared by equilibrating anhydrous $CdCl_2$ with excess U metal in LiCl-KCl eutectic at 773 K for about 35-40 h. Preparation of liquid cadmium electrode is discussed elsewhere [2]. Uranium containing liquid cadmium electrode was prepared by adding uranium slices to cadmium pool. Fig. 1 shows liquid cadmium electrode used for polarization and impedance measurements. All experiments were carried out using a three-electrode assembly under inert atmosphere in the temperature range 698-798 K. DC polarization and impedance measurements were carried out using PGSTAT AUTOLAB 302N system equipped with IF030 interface and data processing was done using GPES and FRA software packages.

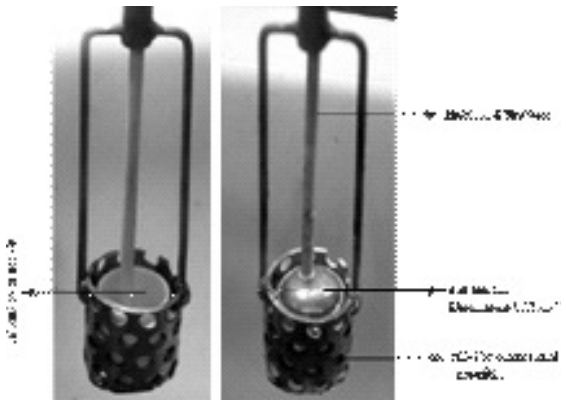


Figure 1: Liquid cadmium electrode used for electrochemical measurements. First figure shows the empty alumina crucible with insulated Mo wire. Second figure shows liquid cadmium pool in alumina crucible.

3. Results and discussion

3.1 Cyclic voltammetry

The cyclic voltammograms of liq. Cd (cathodic) and liq. Cd containing 3.03 wt. % uranium (anodic) as working electrode employing LiCl-KCl-UCl_3 electrolyte at 773 K are shown in Fig. 2a and 2b, respectively. The start potential, onset potentials for uranium dissolution and deposition, peak potentials and direction of sweep are labelled. In Fig. 2a, the point of inflection (potential at which current changes its sign) during the cathodic sweep appears at -1.01 V and peak potential at -1.37 V. The onset potential at -1.01 V is attributed to the deposition of uranium in cadmium forming uranium- cadmium alloy. The potential can also be referred to apparent equilibrium potential of uranium in cadmium. Application of higher cathodic overpotential beyond -1.01 V leads to an increase in the solubility of uranium in cadmium due to continued deposition of uranium with a limiting current density of 72 $mAcm^{-2}$ reaching at a peak potential of -1.37 V. In the anodic sweep, onset for uranium dissolution starts at -1.26 V with an anodic peak appearing at -1.15 V. Beyond -1.15 V, there is gradual decrease in anodic current suggesting partial dissolution of uranium from cadmium. In Fig 2b, onset for uranium dissolution from cadmium containing uranium appears at -1.38 V that can be referred to apparent equilibrium potential of uranium-cadmium alloy. The limiting current density of 58 $mA.cm^{-2}$ is reached at a peak potential of -1.14 V. In the cathodic sweep, onset for deposition of uranium appears at -0.96 V with a peak potential at -1.38 V. Both the voltammograms are similar in all respects except that in Fig. 2a, onset for uranium dissolution is at -1.26 V whereas in Fig. 2b, it is at -1.38 V.

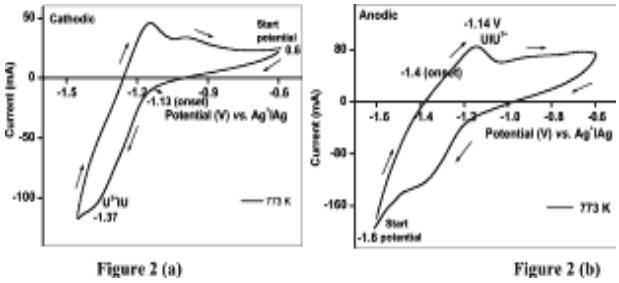


Figure 2 (a) Figure 2 (b)

Figure 2: Cyclic voltammogram of uranium in cadmium at 773 K, (a) at liquid cadmium (b) at liquid cadmium containing uranium (3.03 wt.%). Scan rate: 100 mV/s.

3.2 Polarization measurements

DC polarization technique is described previously by the authors [2]. Similar procedure was adopted in the present work where at each applied potential, current was recorded and subsequently logarithm of current density was plotted against overpotential calculated from equilibrium potential data. From the derived Tafel constants, exchange current density was estimated. A comparison of Tafel plots of cathodic polarization and anodic polarization of uranium in cadmium is shown in Fig. 3. Exchange current density estimated from Tafel constants is summarized in Table 1. Exchange current density in the anodic case is comparatively higher than that in the cathodic case for which reasons are not clearly known. The logarithm of exchange current density against the reciprocal of temperature was linearly fitted to derive the activation energy associated with the redox process (Fig. 4). The fitted equations are given by the following expressions:

$$\text{Anodic:} \quad \ln i = 3.85 + \frac{-5616.8}{T(K)}$$

$$\text{Cathodic:} \quad \ln |-i| = 1.15 + \frac{-3909.4}{T(K)}$$

System	i_o (mAcm^{-2})				
	698 K	723 K	748 K	773 K	798 K
Anodic (Sat'd cadmium pool with cadmium)	14.41 ± 1.02	20.29 ± 1.04	26.49 ± 1.03	33.89 ± 1.0	39.48 ± 1.05
Cathodic (Fresh liquid cadmium pool)	12.00 ± 1.05	13.68 ± 1.08	17.60 ± 1.04	20.19 ± 1.03	23.75 ± 1.05

The activation energy for anodic and cathodic cases was found to be 46.7 and 32.5 kJ/mol, respectively.

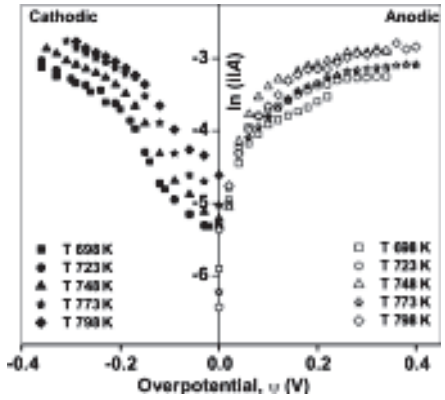


Figure 3: Tafel plots of uranium in cadmium for anodic and cathodic polarization cases.

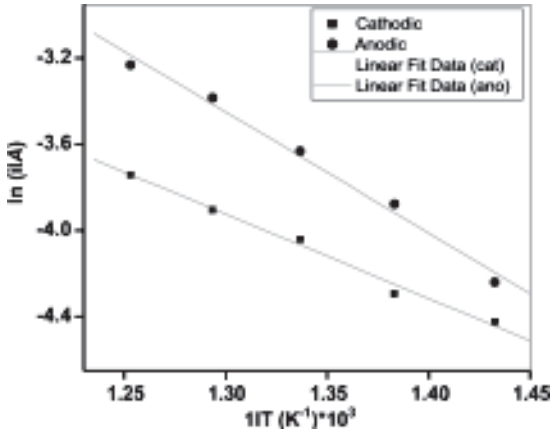


Figure 4: Plot of logarithm of the exchange current density vs. 1/T for cathodic and anodic polarization cases of uranium in cadmium.

3.2 Impedance spectroscopy

Electrochemical impedance spectra were performed over a frequency range 10-5000 Hz using a perturbation signal having amplitude of 10 mV. The potential region covered in the impedance scan was from -0.8 V to -1.4 V. Figure 5 shows the profile of real impedance vs. applied potential for liquid cadmium containing uranium (anodic case, Fig 5a) and liquid cadmium (cathodic case, Fig 5b). Impedance scans were also taken at specific applied potentials and they all had a common feature of a Warburg response at low frequencies and a small semi-circle at higher frequencies. The impedance scans are suggestive of a diffusion controlled reaction with a fast charge transfer reaction. In Fig. 5a, there are two minima appearing at ~-1.2 V and ~-0.8 V in real impedance plots whereas in Fig. 5b, there is a single minimum observed at ~-1.12 V. In Fig. 5a, the first minimum corresponds to the dissolution of unalloyed uranium from cadmium. It is known that activity coefficient of uranium is

~100 at the saturation solubility of uranium (2.36 wt. %). Since the composition of uranium is 3.03 wt. %, excess uranium will dissolve first during anodic polarization at ~-1.2 V. The second minimum corresponds to the dissolution of alloyed uranium in cadmium. In between -1.2 V and -0.8 V, uranium diffuses from cadmium bulk towards the cadmium-salt interface. In Fig. 5b, only one minimum is observed in the potential region -1.24 to -1.18 V corresponding to the diffusion of uranium from

salt bulk towards salt-cadmium interface followed by fast charge transfer to form uranium. This is followed by diffusion of uranium into cadmium bulk to form uranium-cadmium alloy. This difference in redox behavior is not captured in the cyclic voltammograms possibly because of very fast charge transfer kinetics at -0.80 V in Fig5a.

Practical implementation of this experimental data is to study the feasibility of recovering uranium from cadmium pool of electrorefiner that might have fallen into it from steel cathode during electrodeposition of uranium. Since the volume of cadmium pool is quite large, it is expected that uranium would not cross its saturation solubility in cadmium. From Fig 5a, alloyed

uranium dissolves at ~-0.80 V. So suitable experiments can de designed for achieving complete dissolution of uranium from cadmium into salt electrolyte.

differences in the variation of real impedance against applied potential between anodic and cathodic polarization cases. Appearance of a minimum in the plot of real impedance vs. applied potential was suggestive of fast charge transfer kinetics of uranium in cadmium and the process was considered to be diffusion controlled.

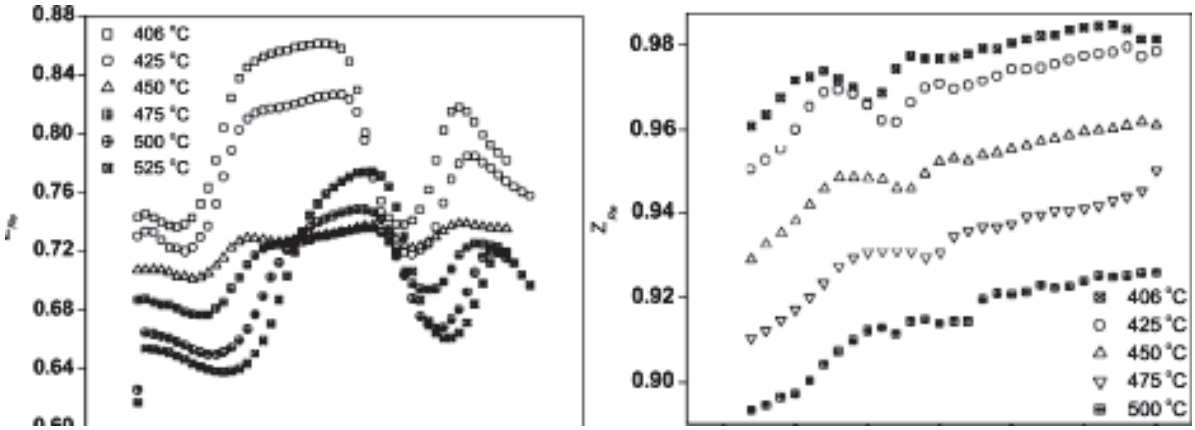


Fig. 5 (a) **Fig. 5 (b)**

Figure 5: Variation of real impedance vs. applied potential for(a) uranium-cadmium alloy pool (anodic) (b) at liquid cadmium (cathodic). Spectra were recorded at 1000 Hz.

4. Conclusions

Redox behavior of uranium in cadmium was investigated using LiCl-KCl-UCl_3 as electrolyte. Exchange current density of uranium at liquid cadmium was estimated for anodic and cathodic polarization cases and was found to be in the range of 12-40 $mAcm^{-2}$ in the temperature range 698-798 K. Electrochemical impedance spectroscopy performed at liquid cadmium electrode led to marked

References

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