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Electrodeposition of uranium in stirred liquid cadmium cathode

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Abstract

The electrodeposition of U in a liquid Cd cathode was known to be hampered by the formation of dendritic U on the Cd surface. Electrotransports of uranium to the stirred liquid Cd cathode were carried out at 773 K for different cathode current densities and different Reynolds number of stirring. The maximum amount of U taken in the liquid Cd cathode without forming dendrites was found to increase with an increasing Reynolds number of stirring and decrease with increasing cathode current density. © 1997 Elsevier Science B.V.

1. Introduction

Pyrometallurgical processing has been developed for its advantages in economics and nuclear proliferation resistance [1]. The electrorefining process is a key step in the processing where the elements in the chopped spent fuels are anodically dissolved into chloride forms such as UCl_3 and $PuCl_3$, while U–Pu mixture and U alone are reduced at a liquid Cd cathode and a solid cathode, respectively [2,3].

The deposition of the mixture of Pu and U in the liquid Cd cathode was, however, known to be hampered by the tendency of the deposited U to form dendrites [3,4], which grew out of the Cd cathode crucible. Once the dendritic U is formed on the liquid Cd cathode, a current is concentrated on it and the cathode works as a solid cathode resulting in the interruption of the Pu deposition. Hence, it is necessary to avoid the formation of U dendrites for collecting Pu by the liquid Cd cathode. ANL has been developing 'pounder type liquid Cd cathode' which incorporates an axial and rotating motion agitator for pushing down the deposited U into Cd, however, only high Pu/U ratio products have been successfully recovered [5]. On the other hand, the authors have been developing the stirred liquid Cd cathode where the rotating flow of liquid Cd restrains the deposited U from forming dendrites to obtain a higher U/Pu ratio product [3]. We have reported the possibility of increasing the maximum amount of U taken into the Cd cathode with decreasing cathode current density for the cathode with constant stirring [6]. In this study, electrodeposition of U onto the liquid Cd cathode was carried out at various rotation speeds of stirring in order to clarify the dependence of the maximum amount of U taken into the Cd cathode on the Reynolds number of stirring.

2. Experimental

2.1. Sample and apparatus

A polarographic grade LiCl–KCl eutectic mixture (Li/K = 51/49 in mol) and $CdCl_2$ were purchased from APL Engineered Materials. They were delivered in sealed glass ampoules and contained < 50 ppm water. A cylindrical piece of $> 99.9\%$ pure metal U (6 mm diameter × 50 mm) obtained from BNFL was used after the surface oxide was filed away. The $> 99.99\%$ pure metal Cd shots obtained from Furnuchi Chem. Corp. were rinsed with dilute nitric acid and degreased with acetone. The low carbon steel electrorefining cell (180 mm internal diame-

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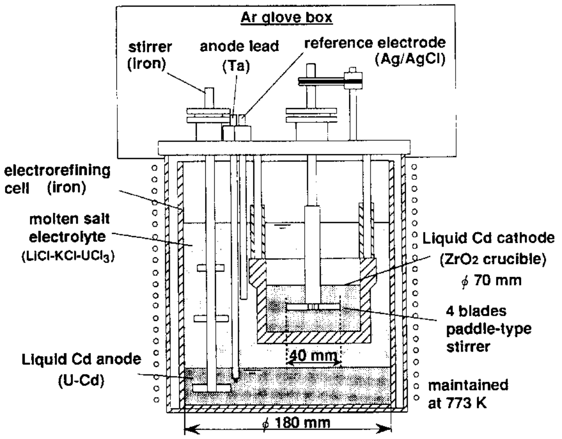


Fig. 1. Schematic view of the electrotransport cell with a liquid Cd cathode assembly.

ter, 200 mm depth) was contained in a glove box filled with pure argon of < 20 ppm O_2 and H_2O. As shown in Fig. 1, the cell contains a liquid Cd anode (8 kg) and a molten LiCl–KCl eutectic mixture (4.9 kg) where a liquid Cd cathode assembly is suspended. The cathode assembly consists of liquid Cd (1.21 kg) in the zirconia crucible (70 mm internal diameter, 60 mm depth) supported by a steel equipment insulated by a zirconia tube and a paddle-type stirrer made of four blades (20 × 5 mm). The cathode and anode potentials were measured by an Ag/0.1 wt% AgCl–LiCl–KCl reference electrode.

2.2. Procedure

After the Cd anode and electrolyte salt were melted at 773 K, U and $CdCl_2$ were charged as oxidant to form UCl_3 in the amount required for the electrolyte salt concentration to be about 4 wt%. The cathode assembly that contained Cd shots was submerged and melted in the salt phase and the current–potential curve was measured to determine the range of current density without polarization. The tests to electrodeposit U onto the liquid cadmium cathode stirred with a rotation of 50, 100 and 200 rpm were then carried out at cathode current densities of 0.2 and 0.25 A/cm^2, respectively. The experimental condition of each electrodeposition is summarized in Table 1, where the intensity of stirring is also shown by using the Reynolds number of stirring defined as $Re = (nd^2)/\nu$, where n, d and ν denote rotation rate (1/s), stirrer diameter (m) and kinematic viscosity (m^2/s), respectively.

During the transports, the U concentration in the cathode, anode and electrolyte salt was periodically sampled and analyzed by ICP-AES of Seiko EG&G SPS7000. The formation of dendrites was detected by the cathode potential and was confirmed by visual observation as described in Section 3.

3. Results and discussion

3.1. Current–potential curves

The current–potential curve of U was measured as in Fig. 2 where the line on the left hand and on the right hand show the cathode and anode, respectively. In the measurement, the current was increased and decreased stepwise to confirm the reproducibility. As seen in Fig. 2, the overpotential of reduction is not a logarithmic function of the current density but a linear function of it. Considering that the overvoltage includes an Ohmic solution resistance drop, the linearity of the curve suggests this reduction follows the Buttler–Volmer equation at a small overpotential. Hence, the reaction may not be rate determined by the

Table 1
Condition and results of U electrodeposition to liquid cadmium cathode

	Conditions of electrotransports					
	current–potential		stirring		Results of dendrite formation	
	cathode current density [a] (A/cm^2)	cell voltage [b] (V)	rotation rate (rpm)	Reynolds number	current passed before dendrite formation (Ah)	U in Cd before dendrite formation [a] (wt%)
RUN-20/200	0.20	~ 0.98	200	2.3×10^4	> 28	> 6.4
RUN-20/100	0.20	~ 0.95	100	1.1×10^4	34	7.7
RUN-20/050	0.20	~ 1.0	50	5.7×10^3	20	4.7
RUN-25/200	0.25	~ 1.2	200	2.3×10^4	28	6.4
RUN-25/100	0.25	~ 1.2	100	1.1×10^4	21	4.9
RUN-25/050	0.25	1.0–1.3	50	5.7×10^3	19	4.4

[a] Liquid Cd cathode: 1210 g Cd, 37.2 cm^2.

[b] Cell voltages before dendritic formations were almost stable with the exception of RUN-25/050.

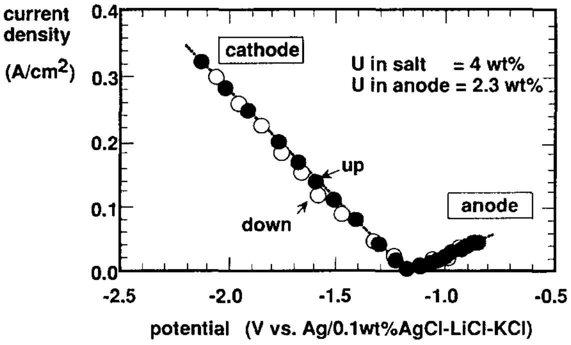


Fig. 2. Current–potential curve obtained before electrotransport.

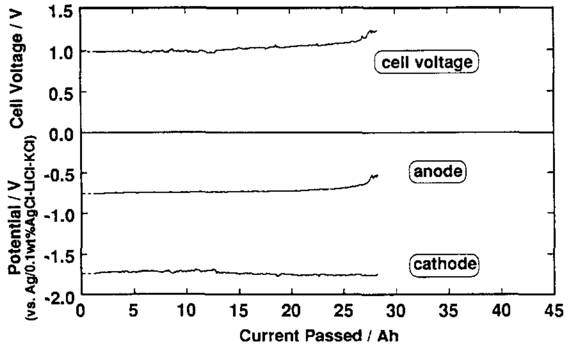
diffusion of the U ion in the salt electrolyte for the range of this electrotransports.

3.2. Concentration and potential profile during electrodeposition

The electrotransport of U from the Cd–U anode to 1210 g of liquid Cd cathode was first carried out at a constant cathode current density of 0.20 A/cm^2 with stirring at 200 rpm (RUN-20/200). About 83 g of U (6.9 wt% in Cd) was electrodeposited on the Cd cathode without forming dendrites, resulting in U depletion from the Cd anode. As shown in Fig. 3, U depletion detected by anode polarization agreed well with the concentration analysis of the anode Cd. From Fig. 3, U can be deposited without forming dendrites in more than its solubility limit (2.35 wt% [7]) while the U concentration in the cathode Cd appeared to stop increasing because the solid sample was hard to be sampled. The maximum amount of U taken in the liquid Cd cathode was, however, only determined as > 6.9 wt% in Cd for this transport. The initial amount of U in the anode Cd was, hence, increased to 188 g (2.35 wt% in anode Cd) to avoid U depletion before dendrite formation in the electrotransports afterwards.

In RUN-25/200, 38 Ah (112 g of U) was electrotransported at a constant cathode current density of 0.20 A/cm^2 with stirring at 50 rpm. As shown in Fig. 4, dendritic deposits grew on the top edge of the cathode crucible pulled out after electrotransport. The concentration and potential profiles during electrotransportation are shown in Fig. 5. The U concentration in the Cd anode shows that ideal electrotransport continued until the end of transport, while the cathode potential that exhibited a fluctuation at around 28 Ah followed a deviation as large as 500 mV. In order to clarify the relationship between potential deviation and dendrite formation, the cathode assembly was pulled out several times during electrotransportation of RUN-20/050. Fig. 6 shows the gradual growth of U dendrites as the positive deviation of the cathode potential is increased. The large positive deviation may be ascribed to the growth of large dendrites on the crucible edge, because it decreases cell resistance due to the increase in cathode area or shortening of the distance between the anode and cathode. On the analogy of the visualized experiment of Zn deposition in a liquid Ga cathode with aqueous solution [8], the appearance of a small fluctuation of cathode poten-

(a) Potential Profile



(b) Concentration Profile

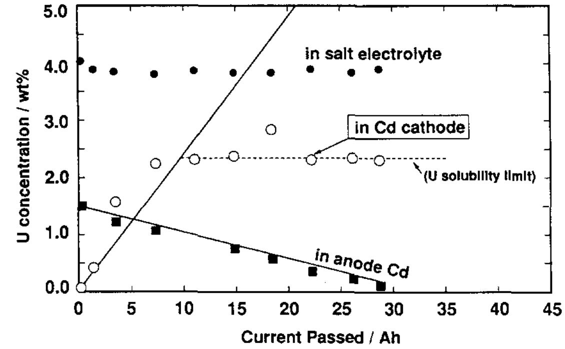
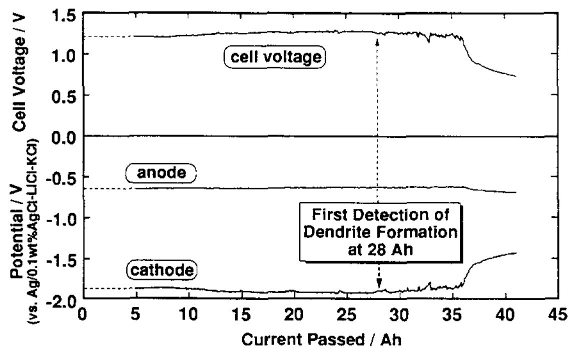


Fig. 3. Potential and concentration profile during RUN-20/200 (a) potential profile, (b) U concentration profile. The straight lines in (b) indicate the calculated behavior assuming 100% current density.

Fig. 4. Dendritic U formed cathode assembly pulled out after electrotransport of RUN-20/200.

(a) Potential Profile



(b) Concentration Profile

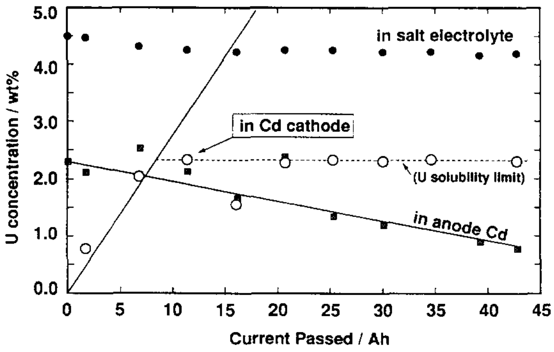


Fig. 5. Potential and concentration profile during RUN-25/200 (a) potential profile, (b) U concentration profile. The straight lines in (b) indicate the calculated behavior assuming 100% current density.

tial before a large positive deviation may be a sign of the formation of dendritic U, which grew and sunk repeatedly onto the Cd surface before the dendrite grew long enough to reach the top edge of the cathode crucible. The similar potential and concentration profiles as well as dendritic deposits on the cathodes were obtained for other electrotransports, RUN-20/100, RUN-25/100 and RUN-25/050.

3.3. Amount of U collected as a function of current density and Reynolds number

As described above, the maximum amount of U taken before dendrite formation can be calculated from the point where the cathode potential started fluctuating prior to a large positive deviation. The amount of U collected without forming dendrites in each electrotransport was derived and listed in Table 1. They are also plotted in Fig. 7 as a function of cathode current density and of Reynolds number of stirring. As shown in Fig. 7, the maximum amount of U taken in the Cd cathode increased with increasing Reynolds number of stirring from 5700 to 23 000 and decreased with increasing cathode current density from 2.0 to 2.5 A/cm^2.

This result seems straightforward, however, it is difficult to explain quantitatively because dendrite formation occurs at more than the solubility limit. If we assume that the deposited U diffuses into the bulk Cd at a flux of J_U (mol/cm^2 s), the formation of dendrite should depend on the competition between J_U and the flux of reduction

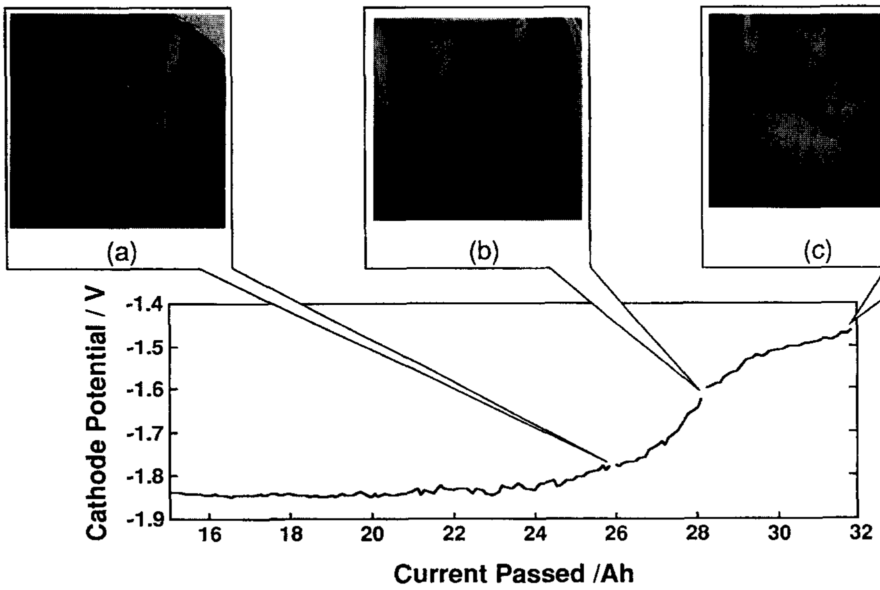


Fig. 6. Dendritic growth on liquid Cd cathode and cathode potential (RUN20/050).

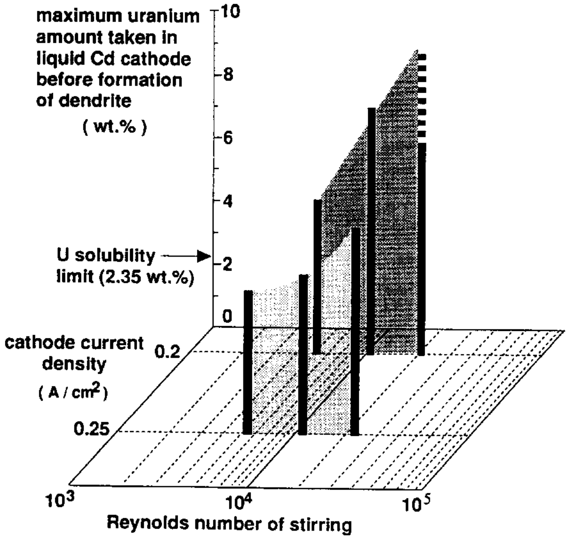


Fig. 7. Maximum U taken in liquid Cd cathode without formation of dendrite.

current, $i_c/3F$, where i_c is cathode current density and F is the Faraday constant, in the following way:

$$\frac{i_c}{3F} > J_U, \quad \text{deposited U forms dendrites,}$$

$$\frac{i_c}{3F} \le J_U, \quad \text{deposited U does not form dendrites.}$$

Hence, the derivation of J_U as a function of Reynolds number and of the U concentration in Cd is necessary. Dependency on the Reynolds number may be derived by calculating the fluid dynamics of liquid Cd, since J_U at a U concentration of more than the solubility limit is not dominated by chemical diffusion but by convection. On the other hand, dependency on the U concentration in liquid Cd is difficult to figure out because the dendrite formations of this study occurred at more than the solubility limit, where the chemical activity of U does not change with a change in concentration. Further study is needed to obtain a universal relationship between the maximum amount of U with the Reynolds number of stirring and with the current density.

4. Conclusion

The electrodeposition of U onto a liquid Cd cathode was carried out at different rates of stirring and different current densities. As much as 8 wt% of U was successfully collected in the Cd cathode without forming dendrites. The maximum amount of U taken on the Cd cathode was found to increase with increasing Reynolds number of stirring from 5700 to 23000 and decrease with increasing cathode current density from 2.0 to 2.5 A/cm^2.

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