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Separation of plutonium from lanthanum by electrolysis in LiCl–KCl onto molten bismuth electrode

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Abstract

This work presents a study on the electroseparation of plutonium from lanthanum using molten bismuth electrodes in LiCl–KCl eutectic at 733 K. The reduction potentials of Pu^{3+} and La^{3+} ions were measured on a Bi thin film electrode using cyclic voltammetry (CV). A difference between the peak potentials for the formation of $PuBi_2$ and $LaBi_2$ of approximately 100 mV was found. Separation tests were then carried out using different current densities and salt phase compositions between a plutonium rod anode and an unstirred molten Bi cathode in order to evaluate the efficiency of an electrolytic separation process. At a current density of 12 mA/cm^2/wt% (Pu^{3+}), only Pu^{3+} ions are reduced into the molten Bi electrode, leaving La^{3+} ions in the salt melt. Similar results were found at two different Pu/La concentration ratios ([Pu]/[La] = 4 and 10). At a current density of 26 mA/cm^2/wt% (Pu^{3+}), co-reduction of Pu and La was observed as expected by the large negative potential of the Bi cathode during the separation test.

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1. Introduction

Pyrochemical separation processes for the recovery of uranium and to some extent for plutonium have been investigated since decades [1]. The integrated fast reactor (IFR) concept [2], originally developed by the Argonne National Laboratory (US) in the mid 1980s, is an integrated fuel recycling system where metallic fuel (U–Zr, U–Pu–Zr) from the EBR-II reactor is reprocessed by pyrometallurgical techniques. The main step of the process is the molten salt electrorefining [3,4], where the actinide elements (An) are separated and decontaminated from the fission products. Practically, the chopped metallic fuel is loaded in an anode basket and the actinides are separated from the bulk of fission products by electrotransport in a molten salt electrolyte, i.e. uranium onto a solid cathode and plutonium and minor actinides (MA) into a liquid Cd cathode [5]. The noble metal fission products can be left in the anode basket by controlling the anodic potential whereas alkali, alkaline earth and rare earth elements accumulate in the salt phase in the chloride form [6].

An additional system for the separation of Pu and MA that is being developed is molten metal/molten salt

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extraction [7]. This technique can be applied for the treatment and recovery of MA from high level liquid wastes (HLLW) generated in the PUREX reprocessing facility [8]. It requires that a calcination of the elements contained in HLLW followed by a chlorination of the corresponding oxides must be carried out before the reductive-extraction step by Cd–Li or Bi–Li metallic alloy [9]. The reduced actinides (An) are recovered as stable alloys (An–Bi, An–Cd) due to their low activity in the molten metal [6].

Electrotransport into different molten metal cathodes (for example Bi) and deposition or co-deposition of Pu and MA onto different solid cathodes [10] are currently also being investigated with the aim to develop improved pyrochemical methods for the separation of actinides from lanthanides by electrolysis. The main advantage using a molten metal as cathode is that corrosion reactions observed on solid inert electrodes (e.g. W and Mo), e.g. chemical reaction between Pu metal and U^{3+} or disproportionation reaction of Am metal in contact with its trichloride [11,12], can be avoided due to alloy formation. As shown by Sakamura et al. [13] the reduction potentials (M^{3+}/M^0) of actinides and lanthanides on molten electrodes are shifted positively compared to solid inert electrodes, such as W or Mo. In addition, the reduction potentials are compressed relative each other, which is a drawback in the view of an efficient An/Ln separation by electrolysis.

Cd has been selected as cathode material as actinides can easily be recovered by cadmium distillation of An–Cd ingots. According to thermodynamical data, however, the An/Ln separation is expected to be more efficient using Bi than Cd [14] or Zn [15]. In this work, we have measured the reduction potentials of Pu and La on Bi electrodes by cyclic voltammetry. Separation tests by electrolysis on a molten Bi pool were then carried out at different current densities and salt compositions in order to optimise the separation efficiency and to minimise the content of La in the cathode product.

2. Experimental

The electrochemical experiments, storage and handling of all chemicals were carried out in a glovebox in purified Ar atmosphere (1 ppm of water and oxygen). The experimental set-up and procedures for the preparation of $PuCl_3$ containing salt have been previously reported [16]. Addition of $LaCl_3$ salt was then done in order to obtain salt compositions of Pu^{3+} and La^{3+} in different ratios.

The cyclic voltammetry experiments were carried out in an electrochemical cell having a three-electrode set-up and a PAR 273 potentiostat with EG & G M270 electrochemical software. The reference electrode used was an Ag/LiCl–KCl–AgCl (1 wt%) prepared in a PYREX glass tube and the auxiliary electrode a 1 mm Mo wire bent into the shape of a spiral. Inert working electrodes were prepared using 1 mm metallic W wires and inserted approximately 5 mm into the bath.

3. Results and discussion

3.1. Cyclic voltammetry studies

Cyclic voltammetry of $PuCl_3$–LiCl–KCl and $PuCl_3$–$BiCl_3$–LiCl–KCl solutions recorded on a W working electrode are presented in Fig. 1. The rest potential of the W working electrode was about −0.45 V vs. Ag/AgCl (1 wt%) reference electrode in LiCl–KCl eutectic melts containing only $PuCl_3$ and about +0.20 V in melts in which both $PuCl_3$ and $BiCl_3$ were present. Without $BiCl_3$ dissolved in the eutectic salt, the Pu^{3+} reduction peak (Ic, see Fig. 1) is observed at −1.76 V and corresponds to the formation of Pu metal via a single three electron transfer [16]. This peak is associated with a typical metal reoxidation peak (Ia, see Fig. 1). When $BiCl_3$ and $PuCl_3$ are at the same time present in the solution, the electrochemical reduction of Bi^{3+} ions is observed around +0.13 V (peak IIc, bold curve, Fig. 1). During the scan between +0.13 mV and −1.10 V, Bi metal is continuously formed on the surface of the W electrode. Two reduction peaks (IIIc and IVc) then appear ($E_{\mathrm{pIIIc}} \sim -1.16$ V, $E_{\mathrm{pIVc}} \sim -1.34$ V), which both can be attributed to the reduction of Pu^{3+} ions on the W electrode modified by an electrolytic produced molten Bi thin film. According to the binary Pu–Bi phase diagram [17], peak IIIc and IVc could correspond to the formation of $PuBi_2$ and PuBi alloys, respectively. The reduction of Pu^{3+} on Bi is obtained at a more anodic potential than on W due to the low activity of Pu in the molten Bi [6]. Reoxidation peaks (IIIa) of Pu–Bi

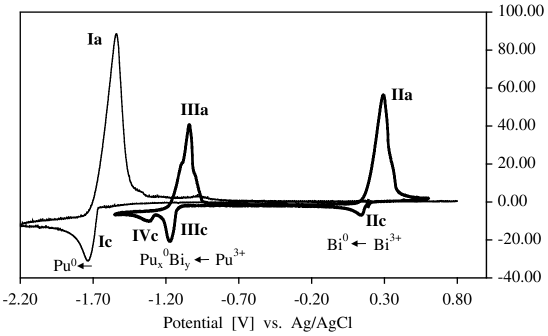

Fig. 1. Voltammograms of Pu^{3+} in LiCl–KCl on W and Bi film electrodes at 733 K. Working Electrode: W ($A \sim 0.2$ cm^2), $v = 200$ mV/s, [Pu] = 0.98 wt%. Curves: (—) LiCl–KCl + $PuCl_3$; (—) LiCl–KCl + $PuCl_3$ + $BiCl_3$.

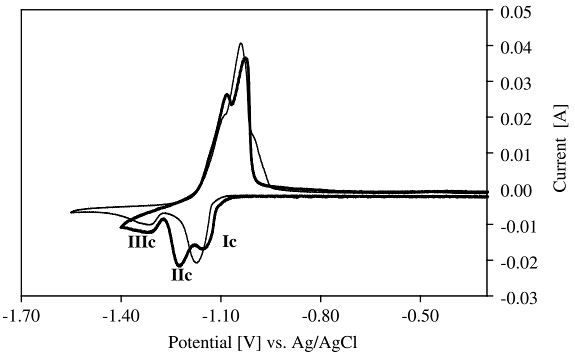

Fig. 2. Voltammograms of Pu^{3+} and Pu^{3+}/La^{3+} in LiCl–KCl on Bi film electrode at 733 K. Working Electrode: W ($A \sim 0.2\ cm^2$), $v = 200$ mV/s, [Pu] = 0.98 wt%. [La] = 0.96 wt%. Curves: (—) LiCl–KCl + $BiCl_3$ + $PuCl_3$; (—) LiCl–KCl + $BiCl_3$ + $PuCl_3$ + $LaCl_3$.

alloys formed during the cathodic scan occurs around −1 V.

Fig. 2 shows two voltammograms recorded on a thin film molten Bi electrode from salt mixtures of $PuCl_3$–$BiCl_3$–LiCl–KCl and $PuCl_3$–$LaCl_3$–$BiCl_3$–LiCl–KCl, at 733 K. The comparison between the two curves shows that the reduction peak of La^{3+} on Bi occurs at $E_{pIIc} = -1.23$ V. Peak Ic and IIIc correspond to the formation of Pu·Bi alloys. In the anodic scan, the reoxidation of La-Bi and Pu–Bi alloys results in a double peak around −1.05 V.

In Fig. 3, two cyclic voltammograms of Pu and La containing LiCl–KCl salt mixtures obtained using Bi thin film and W electrodes, respectively, at 733 K are shown. The voltammogram on W, shows the typical anodic and cathodic peaks corresponding to the one-step reduction of Pu^{3+} ($E_{pc} = -1.76$ V) and La^{3+} ($E_{pc} = -2.09$ V) with the formation of a metallic deposit of Pu^0 and La^0. The difference between the peak potentials of reduction of Pu^{3+} and La^{3+} is nearly 330 mV. In comparison, only 100 mV difference is observed between the reduction peaks of these two elements using a liquid Bi electrode.

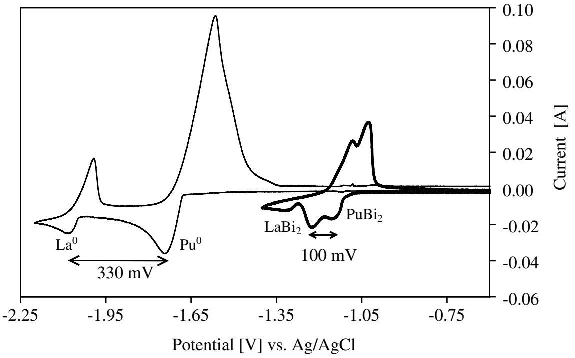

Fig. 3. Comparison between W and molten Bi film electrodes. Working Electrode: W ($A \sim 0.2\ cm^2$), $v = 200$ mV/s, $T = 733$ K. Curves: (—) on Bi, LiCl–KCl + $PuCl_3$ + $LaCl_3$ + $BiCl_3$. [Pu] = 0.98 wt%. [La] = 0.96 wt%, (—); on W, LiCl–KCl + $PuCl_3$ + $LaCl_3$. [Pu] = 0.87 wt%. [La] = 0.18 wt%.

3.2. Electro-separation tests

The separation of plutonium from lanthanum was performed by electrolysis on a molten bismuth pool starting with solutions of LiCl–KCl eutectic containing $PuCl_3$ and $LaCl_3$ salts. The molten Bi pool electrode ($A \sim 4.5\ cm^2$, height ~7–8 mm) was not continuously stirred during the electrolysis. The experiments were carried out under constant current and salt samples were taken to monitor the Pu and La concentrations. The dissolution of a metallic Pu rod was chosen as the anodic reaction and the following electrochemical reactions are thus expected during the electro-separation:

Anodic side $Pu^0 \rightarrow Pu^{3+} + 3e^-$

Cathodic side $M^{3+} + 3e^- \xrightarrow{Bi} M^0Bi_2$

where M can be Pu or La, depending on the applied current density.

Assuming that the anodic dissolution of the metallic Pu rod proceeds at 100% faradic yield and 100% of the reduction's current is used for the conversion of Pu^{3+} to Pu metal, then the concentration of Pu^{3+} in the salt phase is expected to remain constant during a separation test. Under such conditions, plutonium is therefore electro-transported from the anode to the molten Bi electrode.

The two first electro-separations involved a salt containing 0.87 wt% of Pu^{3+} and a Pu^{3+}/La^{3+} ratio of approximately 4. Two electrolyses of this solution were carried out at 12 mA/cm²/wt% (Pu^{3+}) and 35 mA/cm²/wt% (Pu^{3+}). Fig. 4 shows the Pu and La concentrations

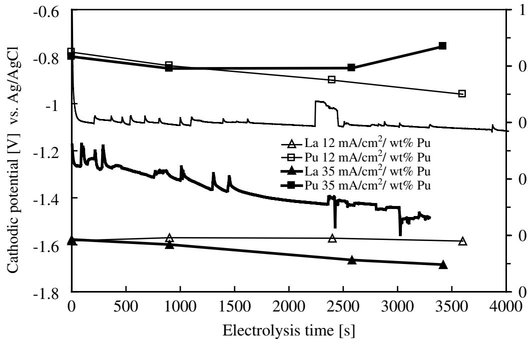

Fig. 4. Evolution of cathodic potentials and concentrations in electrolysis of Pu and La.

in the salt phase as well as the evolution of the cathodic potential as a function of the time of electrolysis. At low current density (12 mA/cm^2/Pu^{3+} wt%), the anodic ($E_a = -1.55$ V) and cathodic ($E_c \sim -1.10$ V) potentials are both stable. This cathodic potential corresponds to the reduction potential of Pu^{3+} obtained in the cyclic voltammograms shown in Fig. 2. Thus, at this current density, only Pu is reduced onto the Bi cathode which is also confirmed by the constant concentration of La^{3+} ions in the salt phase (see Table 1, Run 1). The concentration of Pu in the salt phase is, however, not constant and decreases somewhat during the electrolysis. This can be explained if the faradic yield of anodic oxidation of the Pu rod is less than 100%.

When the test was performed using the same melt composition but at higher current density, i.e. 35 mA/cm^2/wt% (Pu^{3+}), a stable anodic potential ($E_a \sim -1.37$ V) was obtained. The cathodic potential dropped from $E_c = -1.20$ V in the beginning of the electrolysis, to about -1.45 V in the end, which is a more negative potential compared to the previous experiment carried out at lower current density. In this potential range, reduction of La should occur according to the cyclic voltammograms obtained on the Bi film electrode (see Fig. 2). It is confirmed by the concentration of La^{3+} ions in the salt phase, which decreases from 0.19 wt% to about 0.10 wt% (see Table 1, Run 2). Consequently, half of the amount of La^{3+} ions originally present in the solution was reduced at this current density. In addition, the Pu^{3+} concentration in the salt phase showed an increasing trend (see Fig. 4). This is explained if a part of the cathodic current was used for the reduction of lanthanum (and maybe also of lithium) causing a decrease in the faradic yield of Pu^{3+} reduction.

The separation tests were repeated with a higher concentration of Pu^{3+} (1.84 wt%) in the LiCl–KCl eutectic giving a Pu^{3+}/La^{3+} ratio of around 10. Two different current densities, 11 and 26 mA/cm^2/wt% (Pu^{3+}), were applied starting with the same initial melt composition (see Run 3 and 4, Table 1). Fig. 5 shows the evolution of the La^{3+} and Pu^{3+} concentrations and the cathodic potential evolutions as a function of time during the two electrolyses. At low current density, 11 mA/cm^2/wt% (Pu^{3+}), the same result is found as in the experiment using the lower Pu^{3+} concentration (Run 1, Table 1), i.e. the cathodic potential ($E_c = -1.15$ V) corresponds to a selective reduction of Pu^{3+} into the molten Bi phase. This is confirmed by the constant La^{3+} concentration given in the Table 1 (Run 3).

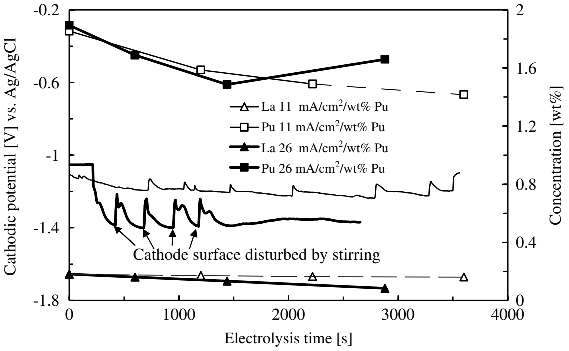

Fig. 5. Evolution of cathodic potentials and concentrations in electrolysis of Pu and La.

At 26 mA/cm^2/wt% (Pu^{3+}), the cathodic potential is more negative than in the previous test and La^{3+} ions are reduced together with Pu^{3+} ions (see Table 1, Run 4). This result is in good agreement with the result obtained with a lower Pu^{3+} concentration in the salt phase (see Fig. 4 and Table 1, Run 2). It can be noticed that the stirring of the Bi pool has a strong influence on the value of the cathodic potential. By electrolysing at a high current density, the result can be an interface not composed of pure Bi. If the diffusion of Pu into the Bi bulk phase is not fast enough the surface concentration of Pu might exceed the solubility limit. Accumulation of a solid intermetallic compound would then be expected, which could act as barrier preventing further formation of Pu–Bi alloy as the access of free Bi is blocked. In such a case, solid Pu or lithium would be deposited at more negative potential. A punctual and manual stirring of the Bi pool leads to a rapid increase of the cathode potential value (see Fig. 5) which must correspond to the dispersion of the PuBi$_2$ layer into the molten electrode leaving again a clean Bi surface. The cathodic potential dropped again

Table 1
Conditions for electrolysis of Pu and La

Run	Pu/La ratio	Charge (C)	Current		E_c (V) vs. Ag/AgCl	E_a (V) vs. Ag/AgCl	Pu^{3+} and La^{3+} in salt (wt%)			
							Before		After	
			(mA)	(mA/cm^2/wt% Pu)			Pu	La	Pu	La
1	4	210	50	12	−1.1	−1.55	0.85	0.18	0.70	0.18
2	4	515	150	35	−1.2 to −1.45	−1.37	0.83	0.19	0.87	0.10
3	10	365	100	11	−1.15	−1.41	1.85	0.18	1.42	0.17
4	10	695	250	26	−1.4	−1.20	1.89	0.18	1.66	0.08

LiCl–KCl + PuCl$_3$ + LaCl$_3$, $T = 733$ K, Bi pool surface area, $A = 4.5$ cm^2.

rapidly as soon as the stirring was stopped (see Fig. 5). It seems therefore that the electrochemical reduction, at 250 mA (Run 4, Table 1) for 5 cm^2 of molten Bi, is faster than the diffusion of Pu into the Bi phase leading to a bad collection of Pu into the molten Bi electrode. On the basis of the results obtained in the four different electrolyses described above, it appears that the efficient separation of Pu from La onto unstirred Bi pool can be obtained at 12 $mA/cm^2/wt\%$ (Pu^{3+}). Iizuka et al. [6] have optimised the electroplating conditions of Pu^{3+} onto unstirred molten Cd cathode in LiCl–KCl media. It was found that the maximum current density was proportional to the concentration of Pu^{3+} in the melt, which means that the reaction is controlled by the mass transfer in the salt phase. The optimal current density, avoiding the formation of solid deposit or lithium reduction, was found to be 22 $mA/cm^2/wt\%$ (Pu^{3+}). These results did not take into consideration separation from lanthanide fission products. For a melt containing 7 wt% of Pu^{3+} and for a Cd pool of 30 cm diameter, the speed of recovery of Pu was calculated to be 324 g per hour. According to the authors, this value is considered high enough as an initial condition for the design of an electrorefiner for a pyrometallurgical process. The speed of recovery is comparable with the 250 g of U per hour, obtained at the Argonne National laboratory [18] during a three-year feasibility campaign for the uranium recovery onto a solid cathode in LiCl–KCl media.

4. Conclusions

The plutonium separation from lanthanum was investigated onto an unstirred liquid Bi electrode in LiCl–KCl media at laboratory scale. Cyclic voltammetry was used in order to measure reduction potentials of Pu^{3+} and La^{3+} ions on Bi thin film electrodes. Only 100 mV difference was found between the potential peak for the formation of $PuBi_2$ and $LaBi_2$. Electro-separation tests on Bi pool electrodes were carried out under different constant current conditions and salt melt compositions. It was found that the applied current must be carefully chosen in order to get an efficient Pu/La separation. The current has to be smaller than the limiting current imposed by the diffusion of Pu^{3+} ions in the salt phase. In addition, using an unstirred molten electrode, the rate of reduction must be small enough to avoid a Pu concentration exceeding the solubility limit at the Bi–salt interface. A too high Pu surface concentration leads to the accumulation of a solid intermetallics layer that blocks the access of free Bi necessary for the Pu–Bi alloy formation. Mechanical stirring of the Bi pool can overcome this problem. It was also shown that a punctual stirring lead to a rapid increase of the cathodic potential. It was found that Pu could be efficiently deposited and separated from lanthanum at 12 $mA/cm^2/wt\%$ (Pu^{3+}). This value is in the same order of magnitude as the 22 $mA/cm^2/wt\%$ (Pu^{3+}) found by Iizuka et al. for an unstirred molten Cd electrode. Separation attempts carried out at higher current densities, i.e. >25 $mA/cm^2/wt\%$ (Pu^{3+}), failed as Pu and La were reduced at the same time leading to a poor separation.

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