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SHORT COMMUNICATION

Electrochemical reduction of praseodymium chloride in LiCl–KCl melt

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1. Introduction

The mechanism of the electrochemical reduction of praseodymium ions in chlorides or fluorides is of great importance to the production of praseodymium metal by molten salt electrolysis. However, very little has been published about this subject. Picard, Mottot and Trémillon [1, 2] have studied the redox properties of praseodymium chloride. In their paper they show a cyclic voltammogram for molten LiCl–KCl eutectic, using a tungsten cathode, which indicates that praseodymium reduction occurs by a one-step process, i.e. $Pr^{3+} + 3e \longrightarrow Pr(s)$ at $E(Pr^{3+}/Pr(s)) = -3.15$ V (vs Cl_2).

In order to obtain a better understanding of the mechanism of the electrochemical reduction of praseodymium ions, we have studied the cathodic reduction of praseodymium in the molten eutectic LiCl–KCl at 450° C using cyclic voltammetry, chronoamperometry and the EDS analysis of the cathode surface.

2. Experimental details

2.1. *Chemicals*

LiCl (anhydrous, Grade Superior) and KCl (Analar) were purchased from BDH Chemicals Ltd.

$PrCl_3 \cdot 6H_2O$ was prepared by reacting pure Pr_6O_{11} with HCl. Anhydrous $PrCl_3$ was obtained under a dry HCl atmosphere (pressure lower than 1 atm) by slow heating to the following temperatures with a hold at each temperature of 4 h: 95° C, 125° C, 145° C, 220° C, 340° C [3].

2.2. *Electrochemical cell and electrodes*

The electrolysis cell, which was similar to that used for chromium deposition, is described in [4]. A vacuum or argon atmosphere could be maintained in the cell.

The working electrodes were tungsten rods with diameters of 1.5 or 2 mm and a pure iron strip. Before use, the tungsten cathode was polished and washed with distilled water and acetone and then dried. The iron cathode was polished by electrolysis in an H_3PO_4–H_2SO_4–CrO_3–H_2O solution and washed in distilled water and acetone and then dried.

The counter electrode was a pure graphite or a vitreous carbon rod. Both were prepared by boiling in dilute HCl solution for 1.5 h, then washed in distilled water and baked overnight in an oven at 150° C.

The Ag/AgCl (1 wt %)–LiCl–KCl/glass reference electrode was used. All potentials measured with this reference electrode are listed in this paper with respect to the chlorine reference electrode.

2.3. *Molten salt purification*

The whole apparatus containing the LiCl–KCl eutectic solvent was slowly evacuated until a pressure of 10^{-1} torr was achieved, whilst heating to 120° C, 200° C and 300° C, respectively, and then maintained at 300° C for at least 24 h. The cell was then let down to atmospheric pressure using argon and a bubbling tube lowered into the LiCl–KCl eutectic mixture. HCl was bubbled through the melt whilst heating to 450° C and bubbled for a further hour after this. Residual HCl was removed from the melt by sparging with argon for at least 3 h. The purity of the melt was checked using cyclic voltammetry before the addition of Pr^{3+} ions.

2.4. *Instrumentation*

A Wenking model PCA 72M controlled potential amplifier, sweep generator (model 175) and *X–Y/t* recorder were used for cyclic voltammetry and chronoamperometry.

EDS analysis was made with a JOEL JSM-35CF scanning electron microscope.

3. Results and discussion

After the purification of the LiCl–KCl melt, the residual current density was from 2.5 to 4 mA cm^{-2} at 450° C. Using graphite anode the electrochemical window of the melt was 3.6 V, extending from + 1.03 V (chlorine evolution) to − 2.59 V (lithium deposition) with respect to the Ag/Ag^+ reference electrode.

3.1. *Electrochemical reduction of Pr on the W cathode*

A typical cyclic voltammogram for the molten $PrCl_3$–LiCl–KCl at 450° C on a tungsten electrode is shown in Fig. 1. The metal deposition $Pr^{3+} \longrightarrow Pr^0$ is indicated by the sharp reduction wave occurring at $E_p = -3.10$ V. The sharp anodic stripping wave is typical of that expected for a metal deposition process. The

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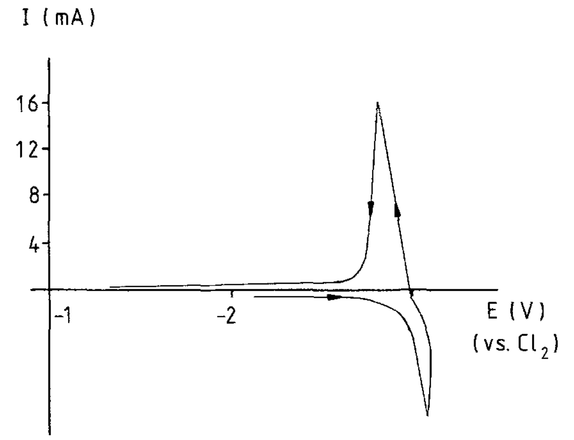

Fig. 1. Typical cyclic voltammogram for Pr^{3+} ions in the LiCl-KCl eutectic melt at 450° C on a tungsten cathode ($Pr^{3+} = 3 \times 10^{-2}\,mol\,kg^{-1}$, $A = 0.018\,cm^2$, $V = 0.05\,V\,s^{-1}$, counter electrode: graphite, reference electrode: Ag/Ag^+).

peak potential of the reduction wave is independent of the potential sweep rate. As shown in Fig. 2, the cathodic current peak height is linear with the square root of the sweep rate. It is thus clear that the reduction step at $E_p = -3.10\,V$ is a simple diffusion-controlled charge transfer process. The electron number involved for the reduction process at $E_p = -3.10\,V$ can be approximately estimated using the following equation [5]:

$$E_{p/2} - E_p = 2.2RT/nF \qquad (1)$$

Thus at 450° C

$$n = 0.1368/(E_{p/2} - E_p) \qquad (2)$$

In this experiment the difference between the half-peak potential $E_{p/2}$ and the peak potential E_p is about 0.05 V. The electron number, n, is thus calculated to be 2.75. This agrees with the conclusion of Picard *et al.* [1].

A further study of the electrochemical reduction of Pr^{3+} on the tungsten electrode was made using chronoamperometry. Several current-time curves obtained with increasing applied potential are shown in Fig. 3. At a potential of $-2.85\,V$ typical diffusion-controlled behaviour (I vs $t^{-1/2}$ linear) was observed. However, at a potential of $-3.10\,V$ and beyond, the I-t transients show the general form attributed to the presence of nucleation and growth phenomena [6]. The EDS analysis of the tungsten cathode surface in the case of electrolyses at -2.85 and $-3.10\,V$ showed that praseodymium deposition on the tungsten substrate only occurred at a potential of $-3.10\,V$. Thus, the mechanism of the electrochemical reduction on the tungsten cathode mentioned above has also been confirmed by chronoamperometry and EDS analysis of the cathodic product at constant potential.

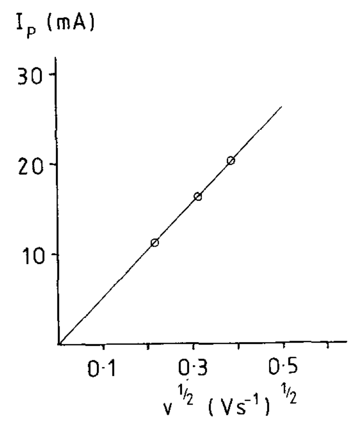

Fig. 2. A variation of the cathodic current peak height with the square root of the sweep rate at 450° C ($Pr^{3+} = 3 \times 10^{-2}\,mol\,kg^{-1}$, $A = 0.018\,cm^2$, working electrode: W, counter electrode: graphite, reference electrode: Ag/Ag^+).

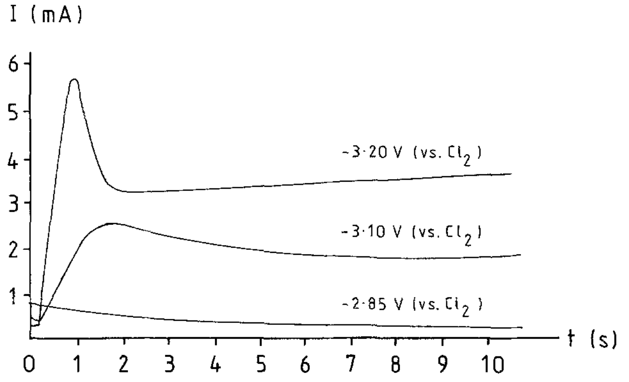

Fig. 3. Chronoamperometric reduction of Pr^{3+} in the LiCl-KCl eutectic melt at 450° C ($Pr^{3+} = 3.6 \times 10^{-2}\,mol\,kg^{-1}$, $A = 0.031\,cm^2$, working electrode: W, counter electrode: graphite, reference electrode: Ag/Ag^+).

3.2. *Electrochemical reduction of Pr^{3+} on the Fe cathode*

Figure 4 shows a typical cyclic voltammogram of the molten $PrCl_3$-LiCl-KCl at 450° C on an iron electrode. There is only one clear reduction wave at $E_{p_c} = -3.10\,V$ which corresponds to the oxidation wave at $E_{p_a} = -2.70\,V$. The EDS analysis of the cathode surface in the case of electrolysis at potential $-3.10\,V$ also evinced the praseodymium deposition on the iron substrate. But, probably owing to the formation of an Fe-Pr solid solution, the reduction wave at $-3.10\,V$ is much more rounded than that obtained for a tungsten cathode at the same potential. If the product of a reversible electrode reaction is soluble, either in the molten salt or a liquid substrate, then, according to the equation $\Delta E_p = E_{p_c} - E_{p_a} = 2.22RT/nF$ [4], the value for the anodic to cathodic peak potential separation (ΔE_p) should be 0.046 V if n equals 3. The experimental value 0.4 V is much larger than this. Further work will be necessary to test the applicability of this equation or otherwise to this solid solution case.

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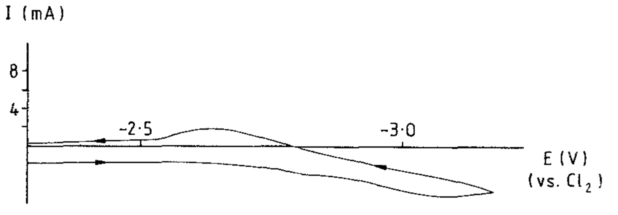

Fig. 4. Typical cyclic voltammogram of Pr^{3+} ions in the LiCl–KCl eutectic melt at 450° C on an iron cathode ($Pr^{3+} = 3.6 \times 10^{-2}\,mol\,kg^{-1}$, $A = 0.015\,cm^2$, $V = 0.15\,V\,s^{-1}$, counter electrode: graphite, reference electrode: Ag/Ag^+).

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