

Short communication

The electrochemical behaviour of the Pr(III)/Pr redox system at Bi and Cd liquid electrodes in molten eutectic LiCl–KCl

Y. Castrillejo ^{a,*}, M.R. Bermejo ^a, P. Díaz Arocas ^b, A.M. Martínez ^{a,1}, E. Barrado ^a

^a Dpto de Química Analítica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena s/n, 47005 Valladolid, Spain

^b CIEMAT, Dpto de Fisión Nuclear, Avda Complutense 22, Madrid 28040, Spain

Received 15 November 2004; received in revised form 24 February 2005; accepted 6 March 2005

Available online 13 April 2005

Abstract

The electrode reactions of LiCl–KCl–PrCl₃ solutions at the surface of liquid electrodes, i.e. Cd and Bi, were investigated by electrochemical techniques. The redox potential of the Pr(III)/Pr couple at the liquid electrodes were observed at more positive potential values than those at one inert electrode. This potential shift was thermodynamically analysed by a lowering of activity of Pr in the metal phase. Cyclic voltammetry, using Cd and Bi pools as working electrodes, was conducted in order to study the reaction mechanism. The results suggest a quasi-reversible behaviour of the Pr(III)/Pr electrochemical system at the liquid electrodes, and the values of the kinetic parameters, k^0 and α as well as the reversible half wave potential, $E_{1/2}^r$, have been obtained. The interdiffusion coefficients of Pr in the metal phases seem to be similar to the diffusion coefficient of Pr(III) in solution. From comparison between the equilibrium potential adopted by a praseodymium electrode immersed in a solution containing Pr(III) ions, and the calculated $E_{1/2}^r$ of the system Pr(III)/Pr–M (being M = Cd or Bi) it has been possible to estimate the activity coefficients of Pr in the Cd and Bi phases. Open circuit chronopotentiometry using Cd or Bi film electrodes was also conducted. Electromotive force, *emf*, measurements for various intermetallic compounds in two-phase coexisting states were carried out in the temperature range of 673–823 K. The activities and relative partial molar Gibbs energies of Pr were obtained from the measured *emf* for various Pr–Cd and Pr–Bi intermetallic compounds, PrCd₁₁, PrCd₆, PrCd_{4.46}, PrBi₂ and PrBi. The relative partial molar entropies and enthalpies of Pr were also calculated from the temperature dependence of the *emf*. The standard Gibbs energies of formation for the Pr–Cd and Pr–Bi intermetallic compounds were calculated.

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Keywords: Molten chlorides; LiCl–KCl; Praseodymium; Liquid electrodes; Pr–Cd and Pr–Bi alloy formation

1. Introduction

Pyrochemical reprocessing of nuclear fuels using molten salts as solvent is considered nowadays a promising option for the proposed advanced fuel cycles [1–3]. It is mainly due to the potential advantages of dry processes

in the assessment of new concepts for partitioning and transmutation (P&T) [4], strategies with the aim to achieve the highest possible reduction of the radiotoxicity and volume of the nuclear waste in the back-end of the fuel cycle.

Several processes have been developed for the recovery of minor actinides, MAs, from irradiated nuclear fuel, i.e. metallic, nitride and oxide fuels, and high level radioactive liquid wastes [5–8]. Pyrometallurgical reprocessing of metallic fuel includes electrorefining and reductive extraction for recovering actinides in molten chloride/liquid metal systems as the major

* Corresponding author. Tel.: +34 9 83423000x4245; fax: +34 9 83423013.

E-mail address: ycastril@qa.uva.es (Y. Castrillejo).

¹ Present address: Department of Materials Technology and Electrochemistry, Sem Sælands vei 6, 7491 Trondheim, Norway.

steps. In this process, irradiated metal fuel is anodically dissolved into molten chlorides, the U is selectively collected on a solid Fe cathode due to the difference in the formation energies of chlorides, whereas Pu and MAs are collected into a liquid metal, usually Cd or Bi, with some amounts of lanthanide fission products [7,8].

The liquid–liquid reductive extraction between molten chlorides and liquid metals, as well as electrolysis using liquid metal cathodes, deserve an examination as possible techniques for the separation of actinides, An, from lanthanides, Ln, the most difficult fission products to separate due to their similar chemical properties [7–13]. In these separation systems, the solute cations in the molten salt phase are recovered into the liquid metal phase, directly by electrolysis or, in the case of reductive extraction, using metallic Li as a reductive agent. In the liquid metal phase, the solute metals are thermodynamically stabilized by forming chemical complexes with the solvent metals, by which the electrodeposition of the elements proceeds at sensible more anodic potentials than those in the elemental forms. The separation performance of lanthanides and actinides depends on the standard Gibbs energy of formation of their chlorides, and it is significantly influenced by their activity coefficients in both phases [14,15]. The stabilization of the solute metals by the interaction with the liquid solvent metals, Cd or Bi, results in deeply negative excess partial molar Gibbs energies of elements in these liquid metals. This is responsible for the low activity coefficients of Ln and An in these metals, by which the extraction of elements to the metal phase is promoted [15].

Since the operation of the liquid Cd or Bi metals significantly influences the feasibility of pyrometallurgical reprocessing, it is of crucial importance the knowledge of the electrochemical behaviour of actinides and lanthanides at the liquid cathodes for the design of the separation cell. However, there is sparse or even null information about the electrode reaction of these elements at the liquid electrodes. Shirai et al. [12,13,16] have studied the electrochemical behaviour of Pu(III)/Pu and Np(III)/Np couples at the interface between the LiCl–KCl and liquid Cd [12,16] and Bi [13,16], but to our knowledge the electrochemical behaviour of lanthanide ions at liquid metal cathodes have not yet been reported in the literature.

In the present paper, the electrode reactions of the Pr(III)/Pr couple on liquid Cd and Bi pool electrodes were investigated and compared with the use of an inert electrode. The differences between the equilibrium potential adopted by a Pr electrode and the half-wave potential $E_{1/2}$ observed by cyclic voltammetry at the liquid electrodes were used for estimating the activity coefficient of Pr in the liquid Cd and Bi metal phases. In addition, the Gibbs energies of intermetallic com-

pounds such as PrCd₁₁, PrCd₆, PrCd_{4.46}, PrBi₂ and PrBi, were evaluated by the analysis of the open circuit chronopotentiograms obtained with a film electrode, i.e. Cd or Bi coated W electrode, in the temperature range of 673–823 K.

2. Experimental

2.1. Preparation and purification of the melt

The appropriate amounts of the chloride mixture (eutectic LiCl–KCl, analytical grade) were melted in a 100 cm³ alumina crucible placed in a quartz cell inside a Taner tubular furnace. A West 3300 programmable device controlled the temperature of the furnace to ± 2 K. The working temperature was measured with a thermocouple nickel-chromium protected by an alumina tube inserted into the melt. All handling of the salts was carried out in a glove box mBraun Labstar 50 under an argon atmosphere.

The mixture was fused under vacuum, then raised to atmospheric pressure using dry argon; afterwards it was purified by bubbling HCl through the melt for 30 min, and then kept under an argon atmosphere which removed the residual HCl and maintained an inert atmosphere during experiments [17,18].

Solutions of Pr(III) were prepared by direct additions of PrCl₃ (Sigma–Aldrich 99.99%).

2.2. Electrochemical apparatus and electrodes

A PAR EG&G Model 273A potentiostat/galvanostat controlled with the PAR EG&G M270 software package, and a multimeter Fluke 45, were used to obtain electrochemical data. Simulated voltammograms were recorded with M271 COOL kinetic analysis software.

The reference electrode consisted of a silver wire (1 mm diameter) dipped into a silver chloride solution (0.75 mol kg⁻¹) in the LiCl–KCl molten mixture, contained in a Pyrex tube. Different working electrodes have been used: (i) Cd and Bi pool electrodes, (ii) Cd and Bi film electrodes, “CdFE” “BiFE” and (iii) tungsten wires of 1.0 mm in diameter in order to compare the results with the liquid electrodes.

Along the experiments with Cd and Bi pool electrodes, a graphite rod of 6.0 mm in diameter was used as counter electrode to ensure uniform current line distribution. For the other experiments a tungsten wire of 1.0 mm in diameter was used.

The liquid Cd and Bi pool electrodes were prepared in the following manner: some granules of Cd (99.999%; Sigma–Aldrich) or Bi (99.999% Sigma–Aldrich) were placed in a J shaped Pyrex tube, which

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