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The influence of electrode material nature on the mechanism of cathodic reduction of ytterbium (III) ions in fused NaCl–KCl–CsCl eutectic

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ABSTRACT

This work presents the influence of electrode material nature on the mechanism of cathodic reduction of ytterbium (III) ions in fused NaCl–KCl–CsCl eutectic at the temperature range 723–1073 K. Transient electrochemical techniques such as linear sweep, cyclic, semi-integral and square wave voltammetry, and potentiometry at zero current have been used in order to investigate the reduction mechanism of ytterbium ions on inert and active working electrodes, transport parameters and thermodynamics properties of the ytterbium compounds. The influence of the material of working electrode on the mechanism of the cathode process was determined. The results obtained show that the reduction reaction $\mathrm{Yb(III)} + \bar{e} \Longleftrightarrow \mathrm{Yb(II)}$ on *W* electrode is reversible being controlled by the rate of the mass transfer. The diffusion coefficient of $[\mathrm{YbCl_6}]^{3-}$ complex ions was calculated at different temperatures and the apparent standard electrode potential of the soluble–soluble redox system $\mathrm{Yb^{3+}/Yb^{2+}}$ was obtained. The reduction reaction of ytterbium (III) ions on Al active electrode was investigated. $\mathrm{Al_2Yb}$ and $\mathrm{Al_3Yb}$ alloys are formed during the polarization on the surface of working electrode.

1. Introduction

Rare earth metals and alloys based on a rare earth and a light or transition metals are increasing in importance, particularly in the fields of magnetism, energy and high technology [1,2]. The use of molten salts, as a reaction media, provides a unique opportunity for the electrowinning and electrorefining of high purity rare earth metals, as well as for the electrochemical synthesis of their alloys.

Another important issue concerning rare earths and molten salts is pyrochemical reprocessing of nuclear fuel, which is presently considered a promising option for the proposed advanced fuel cycles [3–5]. The reason for this interest is mainly due to the potential advantages of dry processes in the assessment of new concepts for partitioning and transmutation (P&T). P&T concept is nowadays considered as one of the strategies to reduce the long-term radiotoxicity of the nuclear wastes. To achieve this, the efficient recovery and multi-recycling of actinides (An), especially TRU elements, in advanced dedicated reactors is essential [6,7]. Molten salts as a reaction media have two important advantageous properties as a solvent material in nuclear processing: (i) The radiation stability of molten salts allows the reprocessing of spent fuels of high radioactivity (i.e. spent fuel with short cooling time) without any increase of solvent waste, and (ii) since molten salt is not a neutron moderator such as water is a comparatively large amount of fissile material can be handed in the process equipment.

Special attention is devoted to rare earth fission products (REE) mainly due to its neutronic poison effect and the high content into the spend fuel. Also REE have similar chemical properties to those of actinides hence separation between these groups of elements is very difficult. For this reason, a good knowledge of the basic properties of An [8–10] and REE [11–15] in the proposed separation media is very important.

There is some information concerning the behavior of ytterbium compounds in molten chlorides. The electrochemistry of Yb(III) in molten NaCl–KCl, KCl and CsCl were determined by transient electrochemical techniques. The apparent redox potentials of the couple Yb(III)/Yb(II) and diffusion coefficients of Yb(III) and Yb(II) were calculated [16]. Using transient electrochemical techniques the electrochemistry of Yb(III) in molten 2LiCl–3KCl, NaCl–2CsCl and CsCl was determined. The influence of the nature of the solvent on the electrochemical and thermodynamic properties of ytterbium compounds was discussed [17,18].

An electrochemical behavior of Yb(III) ions on active Ni electrode in molten NaCl–KCl solution was investigated at 973 K. It was shown that the reaction occurs in two steps: electrochemical formation of Yb(II) ions and electrochemical process of alloy formation [19].

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The goal of this work is to determine the influence of electrode material nature on the mechanism of cathodic reduction of ytterbium(III) ions in fused NaCl–KCl–CsCl eutectic in the temperature range 723–1073 K using transient electrochemical techniques.

2. Experimental

The experiments were carried out under inert argon atmosphere using an electrochemical quartz sealed cell using three electrodes set up. Different transient electrochemical techniques were used such as linear sweep, cyclic, semi-integral and square wave voltammetry, as well as potentiometry at zero current. NaCl–KCl–CsCl salt eutectic was purified under vacuum in the temperatures range 293–773 K. Then it was fused in atmosphere of dry argon. Afterwards the solvent was purified by the operation of the direct crystallization [20]. Yb^{3+} ions was prepared by direct addition of anhydrous $YbCl_3$ to the electrolytic bath consisted of NaCl–KCl–CsCl eutectic.

The electrochemical measurements were carried out using an Autolab PGSTAT 30 potentiostat/galvanostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9).

The inert working electrode was prepared using a 1 mm metallic *W* wire (Goodfellow, 99.9%) and a 1 mm metallic Al wire (Goodfellow, 99.9%). It was immersed into the molten bath between 5 and 12 mm. The active surface area was determined after each experiment by measuring the immersion depth of the electrode. The counter electrode consisted of a 3 mm vitreous carbon rod (SU-2000). The Cl_2/Cl^- electrode was used as reference electrode. This electrode is the most important reference electrode because it can be used for the direct thermodynamic calculations. It standard construction is the following. The quartz tube with porous membrane in the bottom and molten standard solvent in it has the graphite tube for chlorine gas introduction into the system. The chlorine gas is bubbling through the standard melt during the experiment. The standard melt saturated with chlorine gas is separated from the investigated melt by porous membrane and is contacted only with graphite tube [21].

The ytterbium concentration was determined by taking samples from the melt which were dissolved in nitric acid solutions and then analysed by ICP-MS.

3. Results and discussion

3.1. Voltammetric studies on inert electrode

The electrochemical window obtained in fused NaCl–KCl–CsCl eutectic at 873 K on tungsten working electrode using cyclic voltammetry has been shown in Fig. 1 (1). Cathodic and anodic limits of the electrochemical window correspond to the reduction of the solvent alkali metal ions and to the oxidation of chloride ions into chlorine gas, respectively. After addition of $YbCl_3$ compound into the solvent one more single cathodic peak at a potential about -1.921 V vs. Cl_2/Cl^- and its corresponding anodic peak at -1.685 V vs. Cl_2/Cl^- at cyclic voltammograms was appeared at investigated scan rates, Fig. 1 (2).

Fig. 2 shows the linear sweep voltammograms for the reduction of Yb(III) ions in fused NaCl–KCl–CsCl eutectic at different sweep rates at 873 K on tungsten electrode. The voltammograms show a single cathodic peak at an approximately potential -1.919 V vs. Cl_2/Cl^-.

The reaction mechanism was investigated by analyzing the voltammetric curves obtained at several scan rates. The analysis shows on the one hand, that the cathodic and anodic peak potential (E_p) are almost constant and independent of the potential sweep rate. On the other hand, the cathodic and anodic peak current (I_p) are directly proportional to the square root of the polarization rate (υ). The waves are characteristic of a soluble–soluble system presumably related to the Yb(III)/Yb(II) redox couple [22].

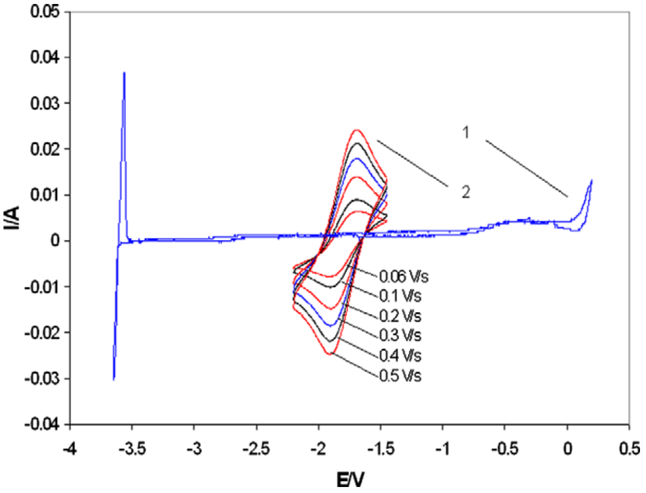

Fig. 1. Cyclic voltammograms of fused NaCl–KCl–CsCl eutectic at 0.1 V s^{-1} scan rate and NaCl–KCl–CsCl–$YbCl_3$ salt at different sweep rates at 873 K. $[Yb(III)] = 5.57 \times 10^{-2}$ mol kg^{-1}. Working electrode: *W* ($S = 0.31$ cm^2).

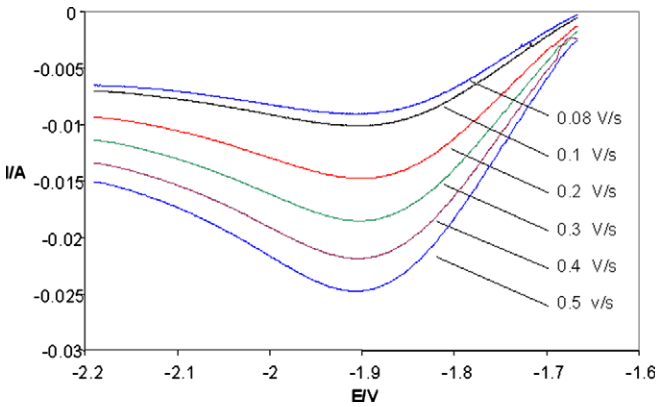

Fig. 2. Linear sweep voltammograms of fused NaCl–KCl–CsCl–$YbCl_3$ salt at different sweep rates at 873 K. $[Yb(III)] = 7.45 \times 10^{-2}$ mol kg^{-1}. Working electrode: *W* ($S = 0.36$ cm^2).

The number of electrons involved in the electrochemical reaction Yb(III)/Yb(II) has been determined by square wave voltammetry. The Gaussian-shaped symmetric cathodic wave was obtained at 873 K on inert *W* electrode, as shown in Fig. 3. The number of electrons exchanged is determined by measuring the width at half height of the reduction peak, $W_{1/2}$ (V), registered at different frequencies (6–80 Hz), using the Eq. (1), valid for reversible systems:

$$W_{1/2} = 3.52\frac{RT}{nF} \pm \Delta, \quad \text{V} \tag{1}$$

where T is the temperature (K), R is the ideal gas constant (J mol^{-1} K^{-1}), n is the number of electrons exchanged and F is the Faraday constant (96,500 C mol^{-1}), Δ is an experimental error (± 0.005 V).

At low frequencies, a linear relationship between the cathodic peak current and the square root of the frequency is found. Under these conditions the system can be considered as reversible being possible to apply Eq. (1). The number of electrons exchanged determined this way was close to one.