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Electrochemical and thermodynamic properties of ytterbium trichloride in molten caesium chloride

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ABSTRACT

This work presents the electrochemical study of $YbCl_3$ in molten CsCl in the temperature range 973–1073 K. Transient electrochemical techniques have been used in order to investigate the reduction mechanism, transport parameters and thermodynamics properties of the reaction $YbCl_2 + 1/2Cl_2 = YbCl_3$. The results obtained show that the reduction reaction $Yb(III) + \bar{e} \Longleftrightarrow Yb(II)$ is reversible being controlled by the rate of the mass transfer. The diffusion coefficient of $[YbCl_6]^{3-}$ complex ions was determined. The apparent standard electrode potential of the soluble–soluble redox system Yb^{3+}/Yb^{2+} was obtained by cyclic voltammetry.

1. Introduction

Partitioning and transmutation (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. Fuels proposed to transmute the actinides into short-lived or even stable radionuclides will contain significant amounts of Pu and minor actinides (MA) (Np, Am, Cm), possibly dissolved in inert matrices (U free), and will reach high burn-ups. Pyrochemical separation techniques offer some potential advantages compared to the hydrometallurgical processes to separate actinides from fission products (FP) contained in the irradiated fuel. The high radiation stability of the salt and metallic solvents used, resulting in shorter fuel cooling times stands out [1].

The aim of the separation techniques which are currently being investigated, both hydrometallurgical and pyrometallurgical ones, is to optimize the recovery efficiency of MA minimizing at the same time the FP content in the final product. Special attention is devoted to rare earth fission products (REE) mainly due to the neutronic poison effect and the high content into the spend fuel. In addition, REE have similar chemical properties to those of An hence separation between these groups of elements is very difficult. For this reason, a good knowledge of the basic properties of An and REE in the proposed separation media is very important [2].

This work presents the electrochemical study of $YbCl_3$ in molten CsCl at the temperature range 973–1079 K.

2. Experimental

Anhydrous $YbCl_3$ and CsCl were used in the experiments which were carried out under inert argon atmosphere using an electrochemical quartz sealed cell with a three electrodes setup. The inert working electrode was prepared using metallic *W* wire. The counter electrode consisted of a vitreous carbon rod. The reference electrode used was the $2Cl^-/Cl_2$ system.

The electrochemical measurements were carried out using an Autolab PGSTAT30 potentiostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9).

3. Results and discussion

Fig. 1 plots the cyclic voltammograms with a single cathodic peak at a potential of -1.941 V vs. $2Cl^-/Cl_2$ and its corresponding anodic peak at -1.707 V vs. $2Cl^-/Cl_2$. 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 square wave voltammetry technique was used to determine the number of electrons exchanged in the reduction of Yb(III) ions. Fig. 2 shows the Gaussian-shaped symmetric cathodic wave

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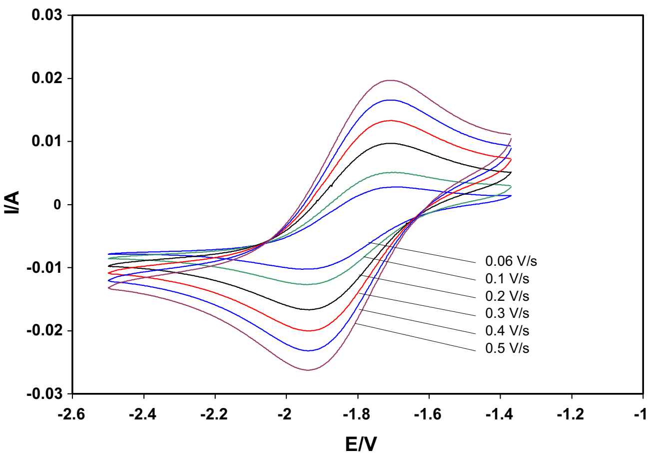

Fig. 1. Cyclic voltammograms of CsCl–$YbCl_3$ (3.70×10^{-2} mol/kg) melt corresponding to the reduction reaction $Yb(III) + e^- \Longleftrightarrow Yb(II)$ at 973 K. Working electrode: *W* (surface area = 0.25 cm^2). Scan rate = 0.1 V s^{-1}.

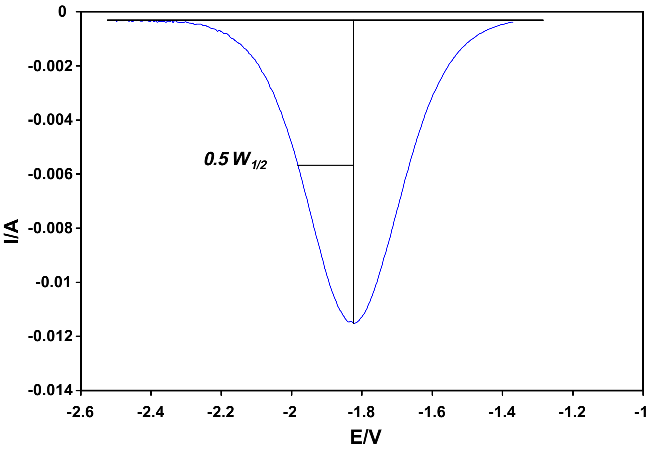

Fig. 2. Square wave voltammogram of CsCl–$YbCl_3$ ($3.70\ 10^{-2}$ mol/kg) at 12 Hz at 973 K. Working electrode: *W* (surface area = 0.25 cm^2).

obtained in the CsCl–$YbCl_3$ at 723 K. The number of electrons exchanged determined this way was close to one [3].

Open circuit potentiometry curves performed at potentials corresponding to values in the range of the cathodic peaks have not shown any plateau that could indicate the formation of solid phases on the tungsten surface. The working electrode did not show any visual change and the X-ray analysis the working electrode surface after experiments do not indicate the formation of a solid phase. All these results allow concluding that the reduction waves observed at around −1.941 V vs. Cl^-/Cl_2, corresponds to the reduction of Yb(III) ions into Yb(II), not being possible to observe the corresponding reduction of Yb(II)/Yb(0).

$$\mathrm{Yb(III)} + \bar{e} \Longleftrightarrow \mathrm{Yb(II)}. \qquad (1)$$

Based on these results, and according to the theory of the linear sweep voltammetry technique it is concluded that the redox system Yb(III)/Yb(II) is reversible and the reaction rate of the reduction is controlled by the rate of the mass transfer [4].

The diffusion coefficient of $[YbCl]_6^{3-}$ ions in molten chloride media was determined using the cyclic voltammetry technique and applying the Randles–Sevčik equation, valid for reversible soluble–soluble system [4]:

$$I_p = 0.446(nF)^{3/2} C_0 S \left(\frac{Dv}{RT}\right)^{1/2}, \qquad (2)$$

where *S* is the electrode surface area (cm^2), C_0 is the solute concentration (mol cm^{-3}), *D* is the diffusion coefficient ($cm^2\ s^{-1}$), *F* is the Faraday constant (96500 C mol^{-1}), *R* is the ideal gas constant (kJ K^{-1} mol^{-1}), *n* is the number of exchanged electrons, *v* is the potential sweep rate (V s^{-1}) and *T* is the absolute temperature (K).

The dependence of log (D) versus the reverse of the absolute temperature obeys by the Arhenius's law and is the following:

$$\lg D_{[YbCl_6]^{3-}} = -2.13 - \frac{2848}{T} \pm 0.02. \qquad (3)$$

The apparent standard potential of the Yb(III)/Yb(II) was determined from the cyclic voltammograms registered in $YbCl_3$ solutions tested at several temperatures.

According to the theory of linear sweep voltammetry the following expression, including the anodic and cathodic peak potentials can be applied in the case of a soluble–soluble reversible system [5]:

$$E^*_{\mathrm{Yb(III)/Yb(II)}} = \frac{(E_p^c + E_p^a)}{2}. \qquad (4)$$

From the peak potential values measured in the cyclic voltammograms, the following empirical equation for the apparent standard potential of the Yb(III)/Yb(II) versus the $2Cl^-/Cl_2$ reference electrode was obtained:

$$E^*_{\mathrm{Yb(III)/Yb(II)}} = -(2.262 \pm 0.004) + (4.2 \pm 0.2) \times 10^{-4} T, V. \qquad (5)$$

The apparent standard free-energy of the $YbCl_3$ formation reaction:

$$YbCl_{2(l)} + 1/2Cl_{2(g)} \Longleftrightarrow YbCl_{3(l)}, \qquad (6)$$

was calculated according to following expression:

$$\Delta G^*_{YbCl_3} = -nFE^*_{\mathrm{Yb(III)/Yb(II)}}. \qquad (7)$$

Its temperature dependence allows calculating the enthalpy and entropy of the $YbCl_3$ formation by means of the relation:

$$\Delta G^*_{YbCl_3} = \Delta H^*_{YbCl_3} - T\Delta S^*_{YbCl_3}. \qquad (8)$$

The apparent standard Gibbs energy of formation of $YbCl_3$ ($\Delta G^*_{YbCl_3}$) in the solvent tested can be expressed as:

$$\Delta G^*_{YbCl_3} = -218.25 + 0.041 \cdot T \pm 2.46, \mathrm{kJ/mol}. \qquad (9)$$

4. Conclusions

The electrochemical behaviour of $YbCl_3$ in fused CsCl was investigated. Reduction of Yb(III) into metal occurs in two steps, first, Yb(III) is reduced into Yb(II) being controlled by the rate of the mass transfer. The diffusion coefficients of $[YbCl_6]^{3-}$ ions were determined at different temperatures. The apparent standard electrode potential of the redox couple Yb^{3+}/Yb^{2+} was calculated from the analysis of the cyclic voltammograms registered at different temperatures and the thermodynamic properties of ytterbium compounds were assessed.

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