Cathodic behaviour of samarium (III) in LiCl-KCl melts on molybdenum and aluminium electrodes

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Abstract

The electrochemical behavior of samarium ions was investigated in LiCl-KCl melt at molybdenum and aluminium electrodes using different electrochemical techniques such as cyclic voltammetry, square wave voltammetries, chronopotentiometry and open circuit chronopotentiometry. On Mo electrode the electroreduction process of Sm(III) to Sm(II) is reversible within the electroactive window. The reduction of Sm(II) is not observed in cyclic voltammogram, but it can be reduced on Al electrode by forming Al-Sm alloy. It is an effective approach to extract Sm from spent nuclear fuel.

1. Introduction

Currently, spent fuel management is a key to sustainable development of nuclear energy. Advanced nuclear fuel cycles are under development worldwide in order to minimise the amount of high radiotoxic waste generated by nuclear power plants operation \cite{1}. Pyroprocessing has been developed for the separation of long-lived elements due to its advantages of a compactness, nuclear proliferation resistance,
and reduction of a secondary waste generation [2,3]. The chemical characteristics of lanthanides (Ln) in chloride melts merit further investigation for enhancing the chemical basis for Ln in molten salts and for developing techniques for Ln refining in pyro-electrochemical reprocessing process of spent nuclear fuels [4–6]. Samarium (Sm) is one of the Ln that has variant state and its chemical behavior on inert electrode has been investigated [7,8]. The electrolytic extraction of samarium at inert electrodes is impossible for molten salt recycling, because the reduction of Sm(II) is in a more negative potential than the solvent cations. Sm(II) can be reduced on reactive electrodes by forming alloys. It is an effective approach to extract Sm from spent nuclear fuel. The present work is devoted to study the reduction mechanism of Sm(III) in LiCl-KCl on inert molybdenum and reactive aluminium electrodes.

2. Experimental

Electrochemical experiments were carried out in a quartz cell under pure Ar atmosphere. The mixture of 50 wt.% LiCl-50 wt.% KCl was first dried for 24 h at 200 °C, afterwards, the temperature was raised up to 450 °C. Electrochemical techniques such as cyclic voltammetry, square wave voltammetry, chronopotentiometry and open circuit chronopotentiometry were carried out in an electrochemical cell having a three-electrode system. The measurements were carried out using an IM6eX electrochemical work station. The working electrodes were Mo wire (d=1mm) or aluminium wire (d=1mm). The surface area was determined after each experiment by measuring the immersion depth of the electrode. Before its use the surface was polished thoroughly with sand-paper and then washed with ethanol. Counter electrode was a 6 mm graphite rod. The reference electrode was a silver wire (1mm) dipped into a solution of AgCl (1 wt.%)–LiCl–KCl contained in a Pyrex glass tube.

3. Results and discussion

3.1. The electrochemical reduction of Sm(III) in LiCl-KCl melt on a molybdenum electrode

Cyclic voltammetry was carried out on a Mo electrode in the LiCl-KCl-SmCl₃ melt at 803 K. Fig. 1a shows a typical voltammogram obtained for LiCl-KCl-SmCl₃ (1.27 × 10⁻⁴ mol·cm⁻³) system. This voltammogram exhibits a single cathode peak A at -0.91 V, corresponding to the reduction of Sm(III) to Sm(II). In the positive potential scan direction a peak A’ is observed. The shape of the anode peak A’ suggests a soluble-soluble system. The reduction of Sm(II) is not observed in this cyclic voltammogram under our experimental conditions because it is more negative in potential than the Li(I)/Li(0) couple. This is in agreement with the data in the literatures [7]. In the cathodic limit, one couple of cathodic/anodic signals (D/D’) is observed which corresponds to the deposition/dissolution of lithium.

The number of exchanged electrons in the electroreduction process was determined by means of the square voltammetry technique, measuring the width of the half peak. Fig. 1b exhibits a typical of soluble-soluble system on the Mo electrode at 803 K, bell-shaped and symmetrical about the half-wave potential. The width of the half peak (W₁/₂) depends on the number of electrons exchanged and temperature as follows:

\[ W_{1/2} = 3.52 \frac{RT}{nF} \]

where \( n \) is the number of exchanged electrons, \( F \) is the Faraday’s constant, \( R \) is the gas constant and \( T \) is the absolute temperature in K. According to the equation 1, the exchanged electrons number is 0.95, a value close to one for electrochemical reduction of Sm(III) to Sm(II).
Fig. 1. (a) Cyclic voltammogram obtained for Sm^{3+} in LiCl-KCl melt on a Mo electrode \((A=0.332 \, \text{cm}^2)\) at 803 K, \([\text{Sm}^{3+}] = 1.27 \times 10^{-4} \, \text{mol} \cdot \text{cm}^{-3}\), scan rate: 200mV s^{-1}. (b) Square wave voltammogram for the reduction of Sm(III) in the LiCl-KCl on the Mo electrode at 803 K, \([\text{Sm}^{3+}] = 1.27 \times 10^{-4} \, \text{mol} \cdot \text{cm}^{-3}\), frequency: 15Hz.

Fig. 2a shows cyclic voltammograms obtained for \(1.27 \times 10^{-4} \, \text{mol} \cdot \text{cm}^{-3}\) SmCl\(_3\) in LiCl-KCl melts on a Mo electrode at various scan rates at 803 K. The value of the potential \(E_p\) of peak \(I_c\) is not shifted in the negative direction when the scan rate increase up to 800mV s^{-1}, indicating a reversible reaction. As can be seen in Fig. 2b, plots of the peak current of the peak \(I_c\) versus the square root of the scan rate, \(v\) (V·s^{-1}), are linear which indicates that the reduction process is controlled by diffusion of Sm(III) in the solution. For a soluble-soluble system, the diffusion coefficient of Sm(III) could be calculated by the Randles Sevcik equation:

\[
I_p = -0.4463AC_0(nF)^{3/2}(Dv/RT)^{1/2}
\]

Where \(I_p\) is the peak cathodic current (A), \(F\) is the Faraday’s constant, \(R\) is the gas constant, \(T\) is the absolute temperature (K), \(A\) is the electrode area (cm\(^2\)), \(C_0\) is the bulk concentration of the electroactive species (mol·cm\(^{-3}\)), \(D\) is the diffusion coefficient (cm\(^2\)·s\(^{-1}\)), \(v\) is the potential sweep rate (V·s\(^{-1}\)), and \(n\) is...
the number of electrons involved in the reaction. According to equation 2, the diffusion coefficient of Sm(III) at 803K is 2.33×10⁻⁵ cm²·s⁻¹.

3.2. The electrochemical reduction of Sm(III) in LiCl-KCl melt on an aluminium electrode

Fig. 3 shows the cyclic voltammograms obtained at 773 K on an aluminium electrode. The signals corresponding to the electrochemical exchange Sm(III)/Sm(II) are not noticed at the Al electrode, since the apparent standard potential of Al(III)/Al(0) is more negative than that of Sm(III)/Sm(II). A high anodic current B' corresponding to the anodic dissolution of the Al electrode material is observed at the beginning of the scan. As the potential grows more negative, peak B at around -1.06 V is caused by the reduction of Al(III), which originates from the anodic dissolution of the Al electrode. The electrochemical window of the Al electrode is limited cathodically by Li(0) reduction forming a Al-Li alloy. The peaks C/C' between Al and Al-Li alloy reduction/oxidation should be attributed to the formation/reoxidation of an Al-Sm alloy.

![Figure 3](image-url)

Fig. 3. Cyclic voltammograms obtained at an aluminium electrode (S=0.322 cm²) in LiCl–KCl system containing SmCl₃ at different cathodic limits at 773 K, [Sm³⁺]=1.02×10⁻⁴ mol·cm⁻³, Sweep rate: 100 mV·s⁻¹.

Fig. 4 presents a group of chronopotentiograms measured on an aluminium electrode (S=0.322 cm²) in the LiCl–KCl–SmCl₃ melts at different current intensities. At a cathodic current more positive than -5 mA, only a potential plateau 1 belonging to the deposition of aluminium occurs. When the cathodic current reach -7.5 mA to -12.5 mA, the curves exhibit a new potential plateau (plateau 2), which are associated with the underpotential deposition of Sm on Al electrode to form a Al–Sm intermetallic. Up to the current of -17.5 mA, a third plateau 3 associated to the formation of Al-Li alloy is observed. It is obvious that the potential ranges for deposition of Li, Sm and Al are the same as those observed in the cyclic voltammograms.

The open circuit chronopotentiometry (OCP) technique was used to study the Al–Sm intermetallic compounds using solid aluminium electrodes. A short electrodeposition of pure Sm metal was carried out on an Al wire, followed by measurements of its open circuit potential vs. time. As the deposited Sm metal reacts with aluminium forming intermetallic compounds, the relaxation E-t curve displays potential plateaus. Several series of OCP measurements were carried out at 733, 813, and 873 K using Al electrodes (see Fig. 5). All plateaus were detected for both surface types, which might indicate a higher stability of more Sm-rich alloy at lower temperatures and/or faster diffusion of Sm and Al through Al-Sm alloy layer at higher temperatures. Two plateaus can be clearly seen. The first plateau (plateau a), is related to the formation of Al-Sm alloy on an Al electrode. The plateau b is associated with the rest.
potential of the Al electrode. The potential plateaus corresponding to Al-Sm alloy formation and rest potential of Al electrode shift to a more positive potential with increasing the temperature. This phenomenon can be explained by Nernst equation.

4. Conclusions

The electrochemical behavior of Sm(III) ion on molybdenum and aluminium electrodes in molten LiCl–KCl was investigated by various electrochemical techniques. The results of cyclic voltammograms indicate that the electroreduction process of Sm(III) to Sm(II) is reversible, and the reduction of Sm(II) is not observed since its reduction potential is more negative than solvent. The diffusion coefficient of the reduction of Sm(III) to Sm(II) at 803 K is $2.33 \times 10^{-2} \text{cm}^2 \cdot \text{s}^{-1}$. The reduction of Sm(II) on Al electrode...
forms Al-Sm alloy. The potential plateaus of Al-Sm alloy formation and rest potential of Al electrode shift to a more positive potential with increasing the temperature.

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References