

Diffusivity and Absorptivity of EuCl_3 in a LiCl-KCl Molten Salt

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1. Introduction

Pyrochemical processing of nuclear fuels using molten salts has attracted much attention because of its potential to be applied for a future spent nuclear fuel management [1]. In the pyrochemical processing, there are a number of steps to electro-refine and electro-win each element of lanthanides and actinides, commonly called trans-uranic elements (TRU) [2,3]. In order to materialize the pyrochemical processing in the nuclear power plant environments, qualitatively and quantitatively monitoring of each elements is necessary. Thus, we have undertaken to develop an on-line observing system of the TRU in LiCl-KCl molten salt media by using electrochemical and spectroscopic methods. In this work, the electrochemical and spectroscopic behaviors of europium as a proxy material for TRU were investigated simultaneously in the LiCl-KCl molten salt.

2. Experimental

2.1 Chemicals

Lithium chloride (LiCl) / potassium chloride (KCl) eutectic salts (anhydrous beads) and europium chloride (anhydrous) were obtained from Aldrich Co. Ltd. (purity $\geq 99.999\%$). Silver chloride (AgCl) was purchased from Alfa Aesar (purity $\geq 99.998\%$). All the chemicals were used without further purification.

2.2 Electrodes

Tungsten and molybdenum wires were used as a working and counter electrode, respectively. These wires were encased in quartz tubes to prevent an electrical contact with other electrodes. One end of the wires was polished thoroughly by using sand paper prior to every use. The Ag/Ag⁺ reference electrode contains 1.00 mol% of AgCl in the LiCl-KCl eutectic melts and the Ag wire is inserted into the tube allowing the Ag wire being immersed in the molten salts. Finally, the top of the reference electrode was sealed with a Teflon tape to prevent an evaporation of the molten salts at high temperature.

2.3 Electrochemical measurements

The temperature of the molten salt was measured to $\pm 1^\circ\text{C}$ using a calibrated K type Chromel-Alumel thermocouple wire. Cyclic voltammograms were obtained using a voltametric analyzer (Gamry Instruments Reference 600 potentiostat/galvanostat) interfaced with a PC at various scan rates. Electrochemical potentials were measured by using a electrometer (Keithley Model 6514, input impedance = $2 \times 10^{14} \Omega$). All the performance and sample preparations were handled inside a glove box with argon atmosphere in which the oxygen content and moisture levels were less than 1 ppm.

An electrochemical cell of LiCl-KCl eutectic was heated and kept at desired temperature for 1 hour before each experiment. After acquiring a good featureless background of the working electrode, anhydrous EuCl_3 was added into the LiCl-KCl molten salt.

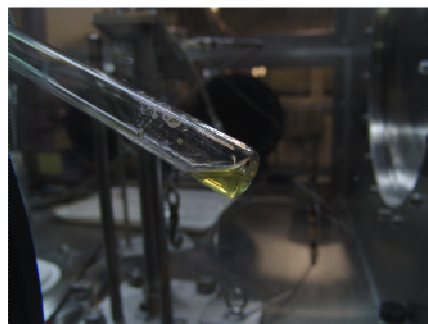


Fig. 1. Photograph of EuCl_3 dissolved in LiCl-KCl eutectic melt.

3. Results

Figure. 1 shows a photograph of EuCl_3 dissolved in a LiCl-KCl molten salt. The color of the mixture at 450°C was observed as pale greenish yellow.

Figure. 2 shows a cyclic voltammogram of EuCl_3 obtained from a tungsten wire in LiCl-KCl eutectic melt at 450°C . On a negative sweep direction, the cathodic peak starts to abruptly increase around -2.5 V and on a positive sweep direction a large anodic peak is found. These peaks are well known to be attributed to electrodeposition and oxidative dissolution of Li [4]. Around $+1.3\text{ V}$, an anodic current begins increasing on positive sweep direction. The positive current arises from an oxidation of chloride ions and evolution of chlorine gas. Except for about $+0.4\text{ V}$ between the

potential regions of the two reactions, Li electrodeposition and Cl_2 evolution, there is only double layer charging current in wide potential range which is called a potential window of LiCl-KCl eutectic melt. At +0.6 V, a cathodic current starts to increase and shows peak at +0.2 V on the negative potential sweep. In reverse scan, an anodic current is also increasing at +0.1 V and maximized at +0.4 V. This quasi reversible peaks may be associated with reactions europium ions below.

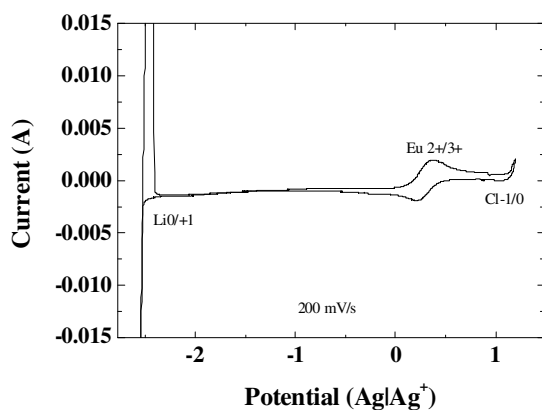
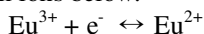


Fig. 2. Cyclic voltammogram of EuCl_3 obtained from W in LiCl-KCl eutectic melt at 450°C . Scan rate = 200 mV/s.

In order to obtain the diffusivity and more electrochemical information of the europium ions in a LiCl-KCl eutectic melt, the scan rate dependence of the peaks as well as other electrochemical procedures, such as a chronoamperometry and a chronopotentiometry have been used as well.

Europium ion is well known to absorb the UV-visible light of about 300 nm wavelength [5] so that it is pale yellow or greenish yellow in color as shown in Fig. 1. We have changed an applied potential on a working electrode in order to change oxidation state of europium ions in LiCl-KCl eutectic melt. Thus the absorptivity of each europium ion in the LiCl-KCl molten melt according to the oxidation state of the europium ions can be acquired easily. Additionally, we have observed the electrochemical and spectroscopic behaviors of europium ions simultaneously in the LiCl-KCl eutectic melt for an on-line observing system. The details of the results will be presented in a poster session.

4. Conclusions

Electrochemical and spectroscopic methods were employed to observe the behavior of europium ions in a LiCl-KCl eutectic melt. In the electrochemical data, the peak potentials of the europium ions were shown at +0.2 V and +0.4 V for the cathodic and anodic current, respectively. Diffusivity and absorptivity of the

europium ions were obtained in the LiCl-KCl eutectic melt. Additionally, the relationship between the oxidation state and the absorbance of the europium ions was observed by a simultaneous measurement of the electrochemical and spectroscopic behaviors of the europium ions.

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