Rotating Disk Electrode Measurements of the Electrochemical Reduction Reaction of Sm^{3+} and Eu^{3+} in LiCl-KCl Melt

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1. Introduction

Electrochemical behaviors of actinide and lanthanide ions have been widely studied to explain the fundamental electrochemical reactions in the pyrochemical processing [1]. In particular, electrochemical parameters, such as diffusion coefficient, exchange current density, were measured using cyclic voltammetry, chronoamperometry, etc. However, there is some disagreement between the values obtained by different groups.

The rotating disk electrode (RDE) is well-known, one of the effective electrochemical techniques, for determining various electrochemical parameters.

In the present work, we investigated various electrochemical parameters of Sm^{3+} and Eu^{3+} in LiCl-KCl melts by using the RDE technique.

2. Experimental

All the experiments were carried out in a glove box under Ar. The O_2 and H_2O level were maintained to be less than 1 ppm. LiCl-KCl eutectic salts and AgCl were obtained from Sigma Aldrich. $SmCl_3$ and $EuCl_3$ were purchased from Alfa Aesar (purity $\geq$ 99.998%).

Tungsten (Alfa Aesar, dia. 6.3mm) and glassy carbon (Alfa Aesar, dia. 2 mm) electrodes were used as the working and counter electrodes, respectively. The reference electrode was Ag wire that was immersed in 1 mol% AgCl in the LiCl-KCl eutectic melt.

The electrochemical experiments were performed using a Gamry Reference 3000. RDE data were obtained using a Pine Model MSRX rotator.

3. Results and Discussion

Fig. 1 shows the cyclic voltammograms (CVs) of Sm^{3+} and Eu^{3+} in the LiCl-KCl melt at 723 K and 783 K. Sm^{3+} and Eu^{3+} reduction peaks appear at -0.96 V and 0.25 V at 723 K, respectively. The temperature increase led to the anodic shift of the peak potential and the increaseof the peak current. We calculated the diffusion coefficients of Sm^{3+} and Eu^{3+} using the Randles-Sevick equation:

$$\frac{I_p}{\sqrt{v}} = 0.446 \frac{(nF)^{3/2}}{\sqrt{RT}} CS\sqrt{D} \quad (1)$$

where I_p is the reduction peak current, v is the scan rate, n is the number of electrons, F is the faraday constant, R is the gas constant, T is temperature, C is the concentration of bulk, S is area of electrode, and D is diffusion coefficient. The diffusion coefficients of Sm^{3+} and Eu^{3+} were estimated to be 5.6 x 10^{-6} and 5.4 x 10^{-6} cm^2/s at 723 K, respectively.

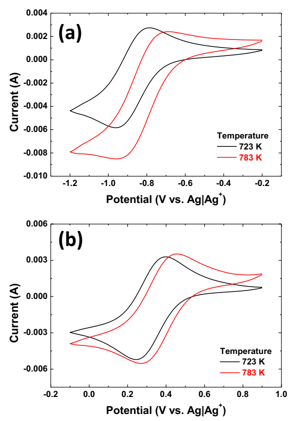

Fig. 1. CVs obtained in LiCl-KCl melt at 723 K and 783 K containing 1.5 wt.% (a) $SmCl_3$ and b) $EuCl_3$. Scan rate = 200 mV/s.

Fig. 2 shows linear sweep voltammograms (LSVs) of Sm^{3+} and Eu^{3+} at 723 K and 783 K in the LiCl-KCl melt using a W RDE. The Sm^{3+} and Eu^{3+} reduction currents show up at -0.6 V and 0.5 V at 723 K, respectively. The peak potentials shifted positively and the peak currents increased with increased temperature. We determined diffusion coefficient using the Levich equation:

$$i_L = 0.62nFAD_0^{2/3}\omega^{1/2}v^{-1/6}C \qquad (2)$$

where i_L is the limiting current, A is the electrode area, is the rotation speed, v is the kinematic viscosity, and C is the bulk concentration of the ion. The diffusion coefficients of Sm^{3+} and Eu^{3+} were estimated to be 5.4 x 10^{-6} and 6.1 x 10^{-6} cm^2/s at 723 K, respectively. These calculated values were close to the reported ones [2], [3].

We also built Tafel graphs for the reduction reactions and estimated Tafel slope, exchange current density, transfer coefficient, etc.

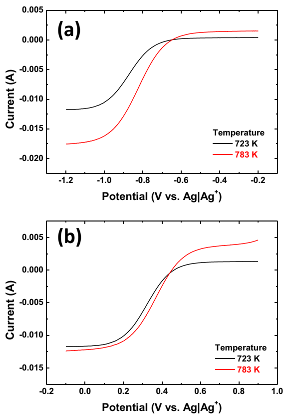

Fig. 2. LSVs obtained using W RDE in LiCl-KCl melt at 723 K and 783 K containing 1.5 wt.% (a) $SmCl_3$ and (b) $EuCl_3$. A rotation rate and scan rate are 1200 rpm and 5 mV/s, respectively.

4. Conclusion

Here, we studied the reduction of Sm^{3+} and Eu^{3+} at the various temperatures in the LiCl-KCl melt. The exchange current densities and transfer coefficients were determined for Sm^{3+} and Eu^{3+}.

REFERENCES

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