Construction of a Rotating Disk Electrode System for Measuring Electrochemical Parameters of a Metal Ion in LiCl–KCl Melt: Electrochemical Properties of Sm³⁺

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Pyrochemical processing and molten-salt reactors have recently garnered significant attention as they are promising options for future nuclear technologies, such as those for recycling spent nuclear fuels and the next generation of nuclear reactors. Both of these technologies require the use of high-temperature molten salt. To implement these technologies, one must understand the electrochemical behavior of fission products in molten salts, lanthanides, and actinides. In this study, a rotating-disk-electrode (RDE) measurement system for high-temperature molten salts is constructed and tested by investigating the electrochemical reactions of Sm³⁺ in LiCl–KCl melts. The results show that the reduction of Sm³⁺ presents the Levich behavior in LiCl–KCl melts. Using the RDE system, not only is the diffusion-layer thickness of Sm³⁺ measured in high-temperature molten salts but also various electrochemical parameters for Sm³⁺ in LiCl–KCl melts, including the diffusion coefficient, Tafel slope, and exchange current density, are determined.

Keywords: Pyrochemical processing, LiCl−KCl, Rotating disk electrode, Samarium, Tafel slope, Exchange current density

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1. Introduction

The electrochemical behaviour of lanthanide and actinide elements at high temperatures has been extensively studied because pyrochemical processing and molten salt reactors using molten salts are considered promising options for future recycling spent nuclear fuel and next generation nuclear reactors, respectively [1-5]. To better understand the metal behaviours during their operations, accurate knowledge of the electrochemical properties is essential. In particular, electrochemical parameters are one of the most important factors when predicting reactions that occur in the molten salts, designing the operation of the process, and building facilities.

Many electrochemical parameters for the electrochemical reactions of actinides (An) and lanthanides (Ln) in various molten salts, such as the diffusion coefficient, apparent standard potential [3], rate constant, electron transfer coefficient, and exchange current [2], have been measured and reported [6]. However, the reported values do not show consistency between the publications. For example, Tafel slopes for electrochemical reactions of U^{3+} in LiCl−KCl melt are 0.098 V·dec^{-1} [7], 0.069 V·dec^{-1} [2], and 0.23 V·dec^{-1} [8] at 500°C. Pesic et al. raised difficulty to measure the exchange current density due to the lack of well-defined linear regions in the Tafel plots. Instead, they suggested a range of the exchange current densities for an electrodeposition of Ce in LiCl−KCl as the values between 0.01 and 0.1 A·cm^{-2} [9].

In general, wire-type electrodes have been used as working electrodes to measure the electrochemical properties in molten salts because of their simple configuration and several constraints derived from the harsh molten salt environment, difficulty of the confining electrode area, cell configuration in high temperature furnace, etc. Due to the advantages of the wire-type electrodes and confining problem of the electrode area, conventional planar electrodes have not yet been widely used in high-temperature molten salts.

Here we introduce a rotating disk electrode (RDE) measurement system for high temperature molten salts using a planar tungsten electrode. The RDE measurement system, one of the conventional electrochemical measurement techniques, is employed in molten salts in order to access more exact values of the diffusion coefficient, Tafel slope, exchange current density, etc. The RDE measurement system was tested in a LiCl−KCl melt containing lanthanide ions (Sm^{3+}), and used to determine various electrochemical parameters. Here, the Sm^{3+} ion was chosen among lanthanide elements because it is one of the most abundant lanthanide elements in the fission products and exhibits a neutron poisoning effect [10].

2. Experimental

LiCl−KCl eutectic salts were obtained from Aldrich Co. Ltd. (purity ≥ 99.99%). $SmCl_3$ and AgCl were purchased from Alfa Aesar (purity ≥ 99.998%). All chemicals were used without further purification.

The RDE measurements were carried out using a Pine model MSRX rotator equipped with a rod-type W planar electrode. The temperature of the molten salt was measured within ± 1°C using a calibrated K-type Chromel-Alumel thermocouple wire. RDE results were obtained using Gamry Reference 600 interfaced with a computer. The scan rate for the RDE measurements was 5 mV·s^{-1}. The W working electrode was polished to a mirror finish using sand paper and diamond slurries (1 and 0.3 μm dia.). An Ag|Ag$^+$ reference electrode contains 1.00mol% of AgCl in the LiCl–KCl eutectic melt. A silver wire was then inserted into a Pyrex glass, immersing the Ag wire into the molten salts. A 5 mm diameter glassy carbon rod was used as the counter electrode.

Fig. 1(a) depicts an RDE system which consists of a manual lifter, potentiostat, temperature controller, rotating speed controller, rotator, and furnace. The RDE system was placed in a glove box in which a rectangle space was made in the bottom part [11] . Each rotation of the wheel on the height translator adjusts the RDE position by 3 mm within the furnace cell. To ensure proper contact of the RDE
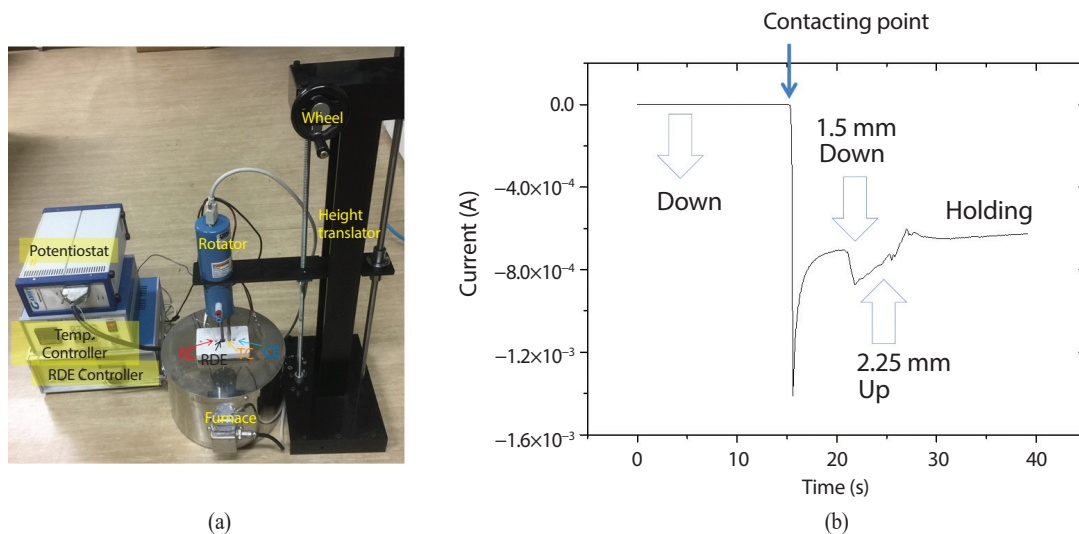
Fig. 1. (a) Picture of the RDE system which consists of a manual lifter, potentiostat, temperature controller, rotating speed controller, rotator, and furnace for high temperature. (b) Chronoamperometric curve at the open-circuit potential as a function of the height of contact of the RDE with the LiCl−KCl salt.

bottom with the LiCl−KCl, a procedure was conducted as described below. Initially, LiCl−KCl melt, equipped with reference and counter electrodes was prepared in the furnace. Next, rotating the wheel of the height translator moved the RDE down toward the LiCl−KCl surface while simultaneously monitoring the current in chronoamperometry at an open circuit potential region. When the RDE made contact with the LiCl−KCl, a sudden current increase was observed (Fig. 1(b)). The RDE was then further lowered by 1.5 mm and subsequently raised by 2.25 mm. Thus, the melt adhered to the bottom plane of the RDE at the height of 0.75 mm above the LiCl−KCl surface. This procedure established the meniscus of the LiCl−KCl to the base plane of the RDE, which was maintained throughout the RDE measurement [12]. Atop the furnace, a heat block with holes for electrodes and a thermocouple was covered to maintain a constant temperature.

3. Results and Discussion

Fig. 2(a) shows cyclic voltammograms (CVs) obtained using a planar W RDE in a LiCl–KCl melt containing SmCl$_3$ (7.7×10^{-4} mol·g^{-1}) at various scan rates, along with the scan rate dependence of the measured CV peak currents. The faradaic currents obviously increase with the increment of the scan rates [9]. The peak currents in the CVs exhibit a linear dependency on the square root of the scan rate (Fig. 2(b)), suggesting that the electrochemical reaction of Sm is diffusion-controlled. The diffusion coefficient can be calculated using the Randles–Sevcik equation:

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

where I_p is the peak current, v is the scan rate, n is the number of electrons exchanged in the reaction, F is the Faraday constant, C is the bulk concentration, S is the electrode area, D is the diffusion coefficient, R is the gas constant, and T is the temperature. The diffusion coefficient was estimated from the slope of the linear regression line in Fig. 2(b) as 2.47×10^{-5} cm^2·s^{-1} at 500°C. This value is somewhat larger than those obtained using a wire-type electrode in the literatures [13-15]. This discrepancy may arise from differences in the configurations of planar and wire-type electrodes.

Fig. 3(a) presents linear sweep voltammograms (LSVs) obtained using a W RDE immersed in a LiCl–KCl molten melt containing SmCl$_3$ (0.58×10^{-4} mol·g^{-1}). In curve a, the
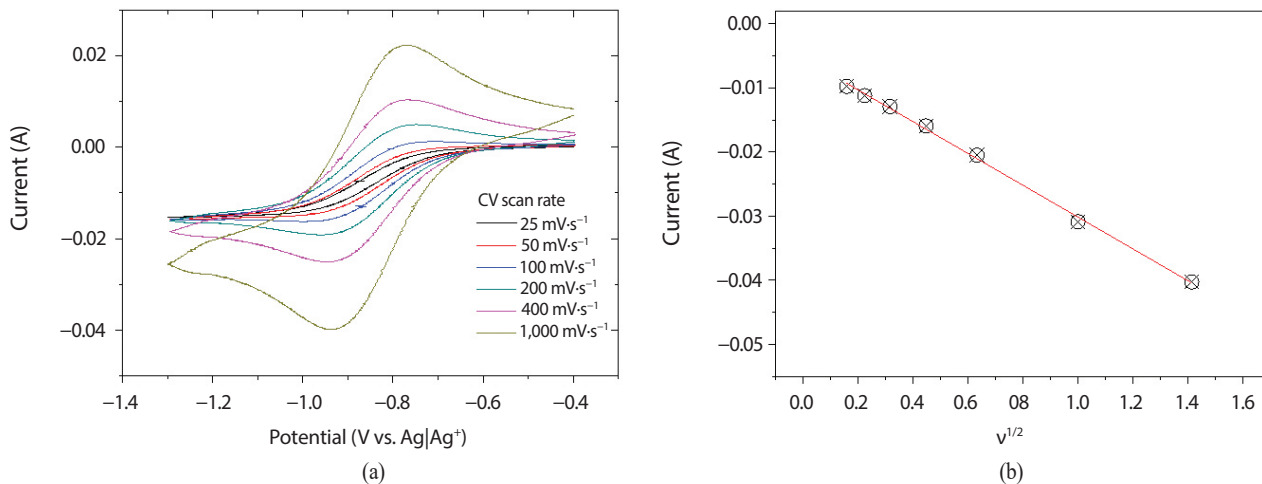
Fig. 2. (a) CVs obtained using a W rotating disk electrode in a LiCl–KCl melt containing SmCl$_3$ at 500°C and (b) scan rate dependence of the CV peak currents.
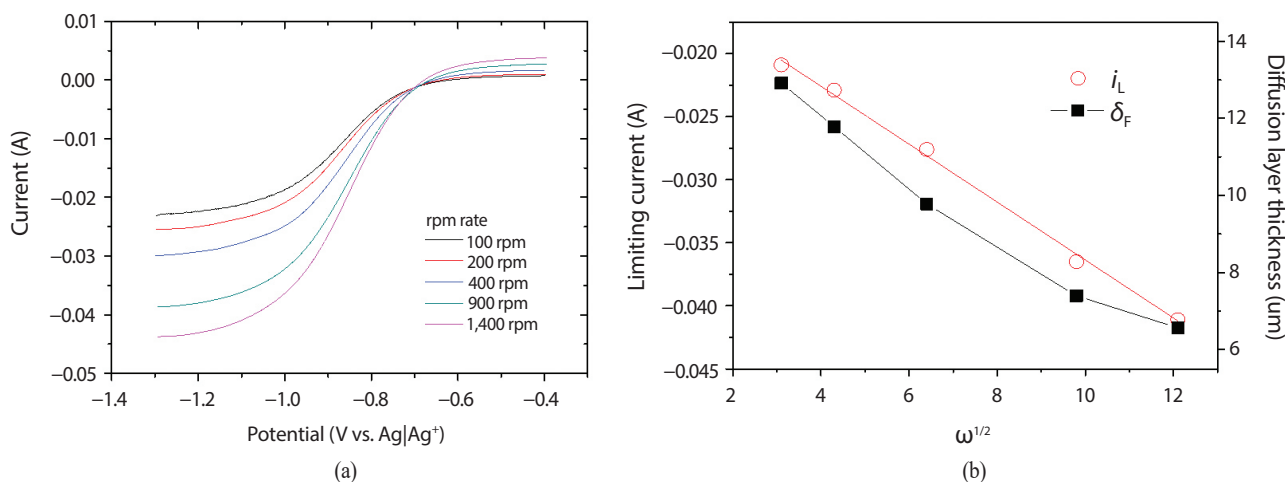

Fig. 3. (a) Linear sweep voltammograms (LSVs) obtained using a W rotating disk electrode with various rotating rates in a LiCl–KCl melt containing SmCl$_3$ at 500°C. (b) Levich plot and double layer thickness for the LSVs in (a). The scan rate was 5 mV·s⁻¹.

Sm³⁺ reduction current commences around −0.20 V. As the potential is swept negatively, the cathodic current rapidly increases to −1.05 V and then gradually increases further. At potentials more negative than −1.1 V, the current becomes nearly constant, indicating the limiting current. The limiting current exhibits a noticeable increase as the rotating speed of the RDE increases. The mass transport phenomenon at the RDE was developed and described by Benjamin Levich [16]. The movement of ions to the electrode surface is dominated by diffusion across a thin layer of electrolyte on the electrode, referred to as the diffusion layer in RDE measurement. The thickness of the diffusion layer on the electrode can be approximated as follows:

$$\delta_F = 1.61 D_0^{1/3} v^{1/6} \omega^{-1/2} \tag{2}$$

where δ_F is the diffusion layer thickness, D_0 is the diffusion coefficient of the ion, v is the kinematic viscosity (3.2

Table 1. Diffusion coefficients of Sm(III) in LiCl−KCl eutectic molten salts obtained by using a tungsten working electrode [13-15]

Temperature (K)	$D \times 10^5$ (cm²·s⁻¹)	Electrode system	Electrochemical technique	Ref.
773	2.47	Planar tungsten electrode	CV	This work
	1.71		RDE	
773	1.3	1 mm dia. tungsten wire	CV	[13]
723	1.02	L=100 µm microsquare tungsten electrode	CV	[14]
763	1.65	50 µm dia. microdisk tungsten electrode	LSV	[15]

mPa s), and ω is the rotation speed.

The limiting current at each rotation speed can be described using the Levich equation:

$$i_L = 0.62nFAD_0^{2/3}v^{-1/6}\omega^{1/2}C_0 \qquad (3)$$

where i_L is the limiting current, n is the number of electrons exchanged in the reaction, F is the Faraday constant, A is the electrode area, and C_0 is the bulk concentration of the ion. In this work, the kinematic viscosity was measured with a homemade viscosity measurement system [17]. Fig. 3(b) displays the Levich plot and the thickness of the diffusion layer obtained from the limiting currents of the LSVs in Fig. 3(a). The diffusion coefficient of the Sm³⁺ cation in the LiCl–KCl melt can be evaluated from the slope of the linear regression for the data in Fig. 3(b). The diffusion coefficient was calculated to be 1.71×10^{-5} cm²·s⁻¹, somewhat smaller than that obtained from the CV data in Fig. 2 and comparable to that in the literature as shown in Table 1 [13-15]. The larger diffusion coefficient obtained from the CV data may result from the convection and migration of Sm³⁺ cations to the planar electrode in the high-temperature molten salt. Rotating the electrode at a higher speed increases the speed at which the material reaches the electrode surface. The height of the limiting current is relevant depending on the rotating speed of the electrode. As the rotating speed increases, the limit current becomes more negative. The diffusion layer thickness obtained using the Levich equation is calculated by the limiting current,
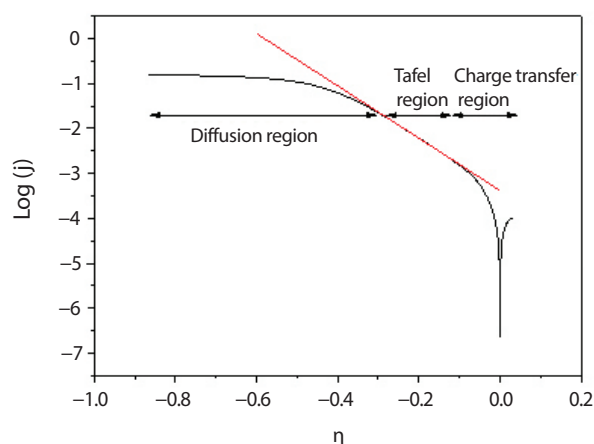

Fig. 4. Tafel plot obtained from the LSV data at 1,400 rpm in Fig. 2(a).

diffusion coefficient, and kinematic viscosity. The diffusion layer thickness of samarium ions depending on the rotating speed ranges from 6.5 µm to 13 µm as shown in Fig. 3(b). This value is comparable to the reported thickness of the diffusion layer in various systems [12].

It is also possible to construct a Tafel plot using data from the RDE measurements. The RDE technique has great merit for easily obtaining data under Tafel conditions because the rotation of the electrode supplies excess reactants to the electrode surface, mitigating the diffusion effect. The Tafel behaviour for the reduction of Sm³⁺ (Fig. 4) was estimated using the RDE data at 1,400 rpm, as reported above. The Tafel plot exhibits exemplary behavior with charge transfer, Tafel, and diffusion regions. These three regions were clearly observed in Fig. 4 as an abrupt decrease at low

overpotentials, a linear region at intermediate overpotentials, and a gradual increasing region. The Tafel region has rarely been reported in high-temperature molten salt environments under Tafel conditions. Here, the Tafel slope for Sm^{3+} reduction estimated from the linear regression of the Tafel region was 0.172 V·dec^{-1}. This slope corresponds to a transfer coefficient, α, of 0.89 at 500°C, somewhat higher than the value of 0.73 in our previous work [15]. It is also possible to obtain the exchange current density from the intercept of the linear regression when extrapolated to 0 V. The exchange current density was calculated as 4.15 A·m^{-2}. This value is almost same as the one in our previous results obtained from a microelectrode [15]. However, it is much bigger than that ($\sim10^{-2}$ A·m^{-2}) for simple electron exchange reactions, $Fe^{2+/3+}$ REDOX couple in aqueous solution [18]. These larger values of the transfer coefficient and exchange current density may be reasonable because the reactions occurred at high temperature and in a highly conductive electrolyte, LiCl−KCl melt [15].

4. Conclusions

In this work, an RDE measurement system was designed, constructed, and utilized to investigate the electrochemical properties of metal cations in a molten melt. It was observed that the reduction reaction of Sm^{3+} exhibited Levich behaviour. From the CV and the RDE results using a planar electrode, the diffusion coefficients of Sm^{3+} in LiCl−KCl melts were determined as 2.47×10^{-5} cm^2·s^{-1} and 1.71×10^{-5} cm^2·s^{-1} at 500°C, respectively. The reduction reaction of Sm^{3+} exhibited typical Tafel behaviour with three regions: charge transfer, Tafel, and diffusion. The transfer coefficients and exchange current densities were calculated to be 0.89 and 4.15 A·m^{-2}, respectively. The diffusion layer thickness of Sm^{3+} was measured to be approximately 10 μm in LiCl−KCl melts. RDE measurement system was constructed for high-temperature molten salts and successfully tested by measuring electrochemical parameters of Sm ions in LiCl−KCl melts. The constructed RDE system will be utilized to measure electrochemical parameters of various fission products in high-temperature molten salt media.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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