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Short Communication

Understanding of Electrochemical Reduction of Sm^{3+} in a LiCl-KCl Molten Salt Solution at 773 K

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The electrochemical reduction of Sm^{3+} to Sm^{2+} in a LiCl-KCl eutectic melt has been investigated using chronoamperometry and cyclic voltammetry (CV). In this work, for the first time, the formal potential and standard rate constant of a Sm^{3+}/Sm^{2+} redox system have been measured at the same time through a curve fitting analysis for experimental CV curves which were obtained in a wide scan rate range of 0.5 to 10 V/s. The regression analysis results showed an excellent fit to all experimental CV data simultaneously, even though the curve fittings were performed within a wide range of initial transfer coefficient values, formal potentials, and standard rate constants. Finally, a proper formal potential, transfer coefficient, and standard rate constant for the Sm^{3+}/Sm^{2+} redox reaction were successfully extracted by the simultaneous CV curve fitting method.

Keywords: Sm^{3+}/Sm^{2+}**,** LiCl-KCl, Molten Salt, Formal Potential, Standard Rate Constant

1. INTRODUCTION

The pyrochemical separation technique which is considered as a promising route for the advanced fuel cycle has received much attention since it offers some potential advantages such as proliferation resistance and radioactive waste reduction, compared to the conventional aqueous processes[1,2]. Especially, it is thought that a nuclear fuel of sodium-cooled fast reactors (SFR) can be efficiently made by the pyrochemical process that consists of three kinds of steps which sequentially proceed. In the electrowinning that is the third step of the pyrochemical process, the uranium and transuranium species remaining in a molten salt are recovered by forming cadmium alloy at a liquid cadmium cathode. The quality of a SFR fuel is dependent significantly on process control of the electrowinning step because rare earth elements (REEs) that exist in a molten salt with a large content can be deposited to make a cadmium alloy contaminated with REEs.

To get optimal nuclear fuels for SFR, the deposition of REEs with neutronic poison effect should be minimized so that the total content of REEs within SFR fuels can be controlled less than 2%[3,4]. For this reason, special attention has been devoted to studies on the electrochemical properties of the REEs.

Recently, thermodynamic properties such as the standard potential for redox reactions of REE have been intensively investigated by many researchers[5-8]. So far, however, few research groups have addressed the kinetic properties of REEs in a molten salt media. Bermejo at al. calculated the standard rate constant (k^o), the transfer coefficient (α) and the half-wave potential ($E_{1/2}$) for Eu^{3+}/Eu^{2+} through analysis of a single CV curve[9]. It is well known, however, that the simultaneous determination of the characteristic parameters for an electrode reaction is not appropriate because there can be multiple interpretation for a CV curve. To overcome a limit of the previous work, we have recently presented the determination of the standard rate constant, standard potential and transfer coefficient for the Eu^{3+}/Eu^{2+} by non-linear curve fittings of six CV curves[10].

In this study, we have applied the new approach to elucidate electrode reaction of Sm which is one of abundant fission products. Very interestingly, the Sm species exist in a mixture of divalent and trivalent ions like Eu, but redox potentials of both Sm^{3+}/Sm^{2+} and Eu^{3+}/Eu^{2+} redox couples are quite different from each other. The standard electrode potential of Eu^{3+}/Eu^{2+} is so much higher than that of Sm^{3+}/Sm^{2+}[6,10]. The thermodynamic and kinetic parameters for the Sm^{3+}/Sm^{2+} redox system in LiCl-KCl eutectic melts were simultaneously estimated from the CV curve fittings by DigiSim software developed by Bioanalytical Systems, Inc.

2. EXPERIMENTAL SECTION

Fig. 1 shows a high-temperature electrochemical system used in this work, which is installed on the bottom side of an Ar-filled glove box. A three-electrode quartz cell was placed inside the furnace part. The temperature of molten salt systems was controlled by a furnace surrounding the quartz cell. A thermocouple was inserted into the cell to monitor the temperature. The temperature of a molten salt media was maintained at 773±2 K. On the other hand, the temperature of the glove box was maintained constant at 25°C by a cooling system located between the glove box and the furnace.

The concentration of the water and oxygen was maintained below 3 ppm while performing electrochemical experiments. Anhydrous LiCl (assay = 99.9%), KCl(assay = 99.9%), $SmCl_3$ (assay = 99.99%) were purchased from Aldrich-APL LLC and purified inside a glove box. The concentration of Sm^{3+} in LiCl-KCl eutectic melt was 0.010 M.

Mo rods (1 mm in diameter, Alfa Aesar Co.) were used as the working electrodes, and glassy carbon rods (3 mm in diameter, Alfa Aesar Co.) used as the counter electrode. The active surface area of working electrodes was determined by measuring the immersion depth of the electrode after experiments. Ag/Ag^+ electrode systems served as a reference electrode, the detail of which was described elsewhere[8].

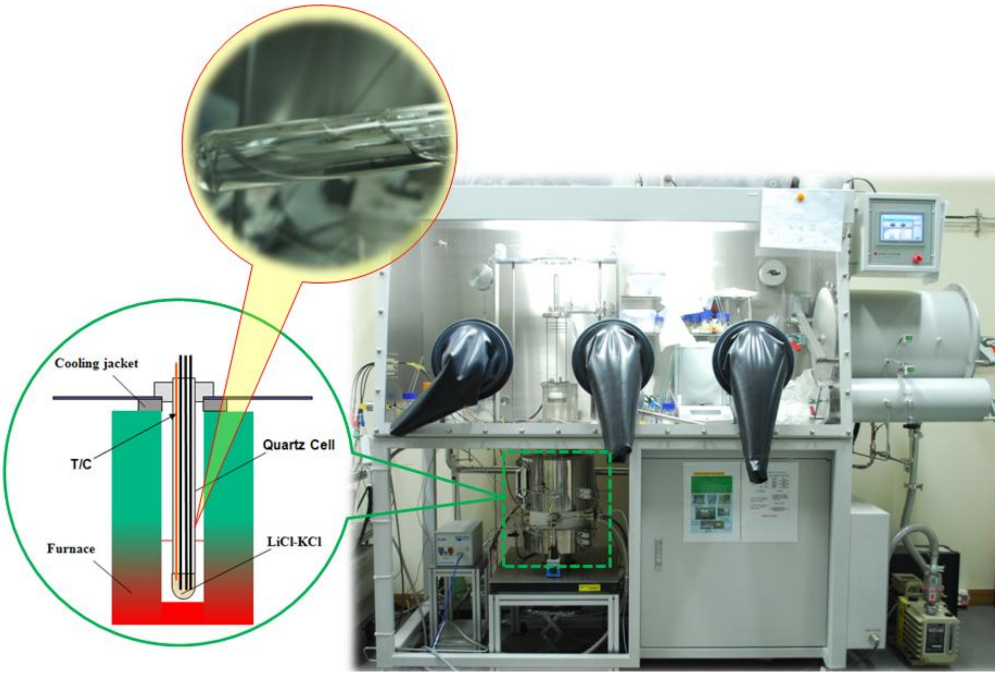

Figure 1. A high-temperature electrochemical system installed at the bottom part of an Ar-filled glove box.

To determine the characteristic parameters ($E^{o'}$, k^{o}, α) for the Sm(III)/Sm(II) redox systems, cyclic voltammograms were taken at various scan rates in the potential range of -0.4 to -1.2 V vs. Ag/Ag^{+}. Simultaneous CV curve fittings for six CV curves were carried out with DigiSim software (ver. 3.03b, Bioanalytical Systems, Inc.), which has been used to extract the characteristic parameters for the electrochemical reduction of sulfur[10-12]. The scan rate for the cyclic voltammetry was chosen between 0.5 V/s and 10 V/s. To get a pure faradaic response, the *iR* drop compensation was performed.

To avoid divergence in CV curve analysis, the diffusion coefficient of Sm^{3+} was determined from the slope of chronamperometric current prior to CV experiments. For the measurement of chronoamperometric current (total current) for the LiCl-KCl eutectic melt containing electroactive species, step potential of -0.4 to -1.2 V was applied to the working electrode. Non-faradaic chronoamperometric response (charging current) was measured in the LiCl-KCl eutectic melt without Sm species. Pure faradaic currents used to extract the diffusion coefficients of Sm^{3+} were obtained by subtracting the charging current from the total current. For the electrochemical measurements, Autolab PGSTAT302 potentiostat (Eco-Chimie) was used.

3. RESULTS AND DISCUSSION

The pure chronoamperometric response for faradaic reaction of Sm^{3+} was obtained from the total current subtracted by charging current which was measured in the blank solution without Sm^{3+} ions. Data obtained at short times less than 20 msec were not used for the regression analysis because of potentiostatic limitations.

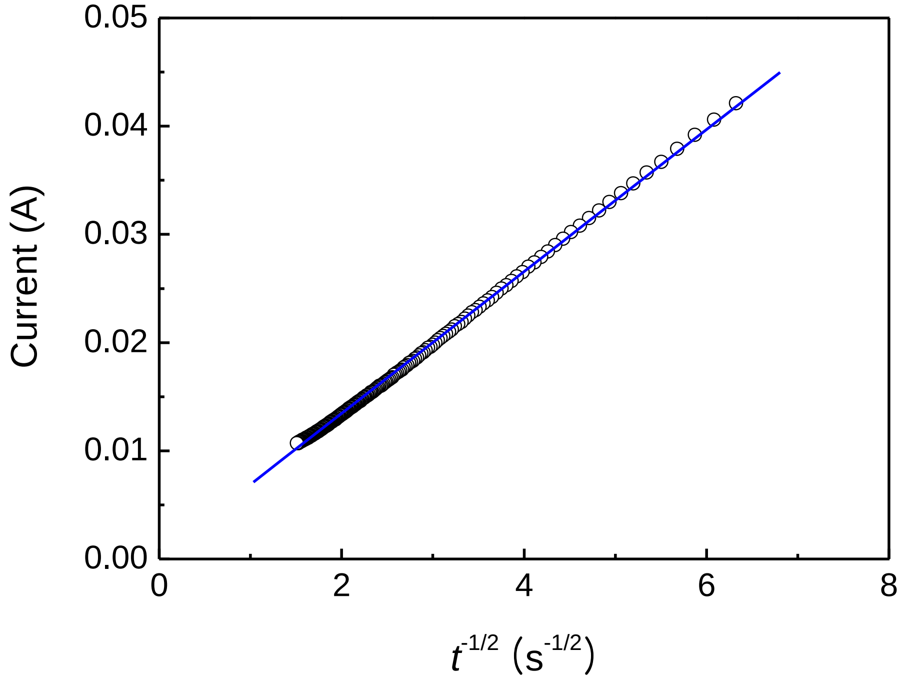

Figure 2. Chronoamperometric current (○) for the reduction of Sm^{3+} to Sm^{2+} and the corresponding linear regression line (−).

Fig. 2 shows the result of linear regression analysis for the chronoamperometric current of the reduction of Sm^{3+} to Sm^{2+}. It is clearly seen that all the experimental data are well fitted to the theoretical line known as the Cottrell equation:

$$i(t) = nFAD^{1/2}C\pi^{-1/2}t^{-1/2}$$

where F, A, D and C are the Faraday constant, the electrode area, the diffusion coefficient and concentration of Sm^{3+}, respectively. Diffusion coefficient of Sm^{3+} ion estimated from the slope of linear regression line (i vs. $t^{-1/2}$) was 1.18×10^{-5} cm^2/s. This value is very similar to the value (1.30×10^{-5} cm^2/s) reported by Cordoba and Carabaca[6].

Fig. 3 shows the comparison of experimental data with calculated curves which were obtained at various k^o values (1 to 10^{-3} cm/s) for the following electrochemical reaction of Sm^{3+}:

$$Sm^{3+} + e^- \rightarrow Sm^{2+} \qquad (E^{0'}, k^o, \alpha)$$

where $E^{0'}$, k^o and α value are the formal potential, the standard rate constant and the transfer coefficient for Sm^{3+}/Sm^{2+} redox reaction, respectively. The theoretical CV curves are obtained under the following assumption: α value = 0.5 and $E^{0'}$ = -0.8 V vs. Ag/Ag^+, which were values estimated on the basis of the curve shape and the peak potentials of preliminary CV data.

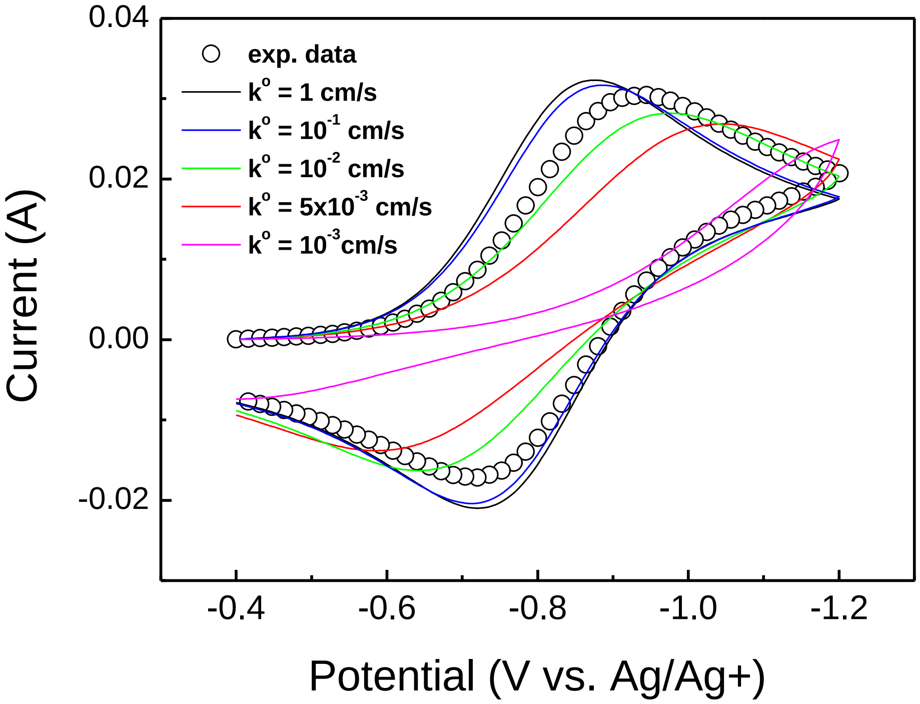

Figure 3. Experimental CV data (○) and theoretical curves (−) calculated under the following conditions: $E^{0'}$ = -0.8; α = 0.5; k^o = 1 to 10^{-3} cm/s; D = 1.18×10^{-5} cm^2/s; T = 773 K, scan rate = 2 V/s.

When the standard rate constant is higher than 10^{-1} cm/s, the calculated CV curves are shown to be a reversible system. On the other hand, the irreversible behavior was observed at the values of standard rate constant less than 5×10^{-3} cm/s. It was estimated from the preliminary CV curve simulation that the standard rate constant of the Sm^{3+}/Sm^{2+} redox reaction may have a value between 10^{-1} and 10^{-2} cm/s.

In general, initial values of main parameters such as the formal potential, the standard rate constant and the transfer coefficient are very important in CV curve fittings. For effective nonlinear regression analysis, however, actual curve fittings using DigiSim software were performed at an appropriate range of initial values: -0.6 to -1.0 V for the formal potential ($E^{o'}$), 0.3 to 0.7 for the transfer coefficient (α), and 10^{-3} to 1 cm/s for the standard rate constant (k^o).

Fig. 4 shows some examples of the simulated curves (line) adjusted to the experimental CV data (open circle) obtained at different scan rates (500, 1000, 2000, 3000, 5000, 10000 mV/s) using a Mo rod as a working electrode. Surprisingly, the simulated curves showed excellent fits to all the experimental CV data simultaneously at the six scan rates, regardless of the initial values of the formal potential, the standard rate constant and the transfer coefficient.

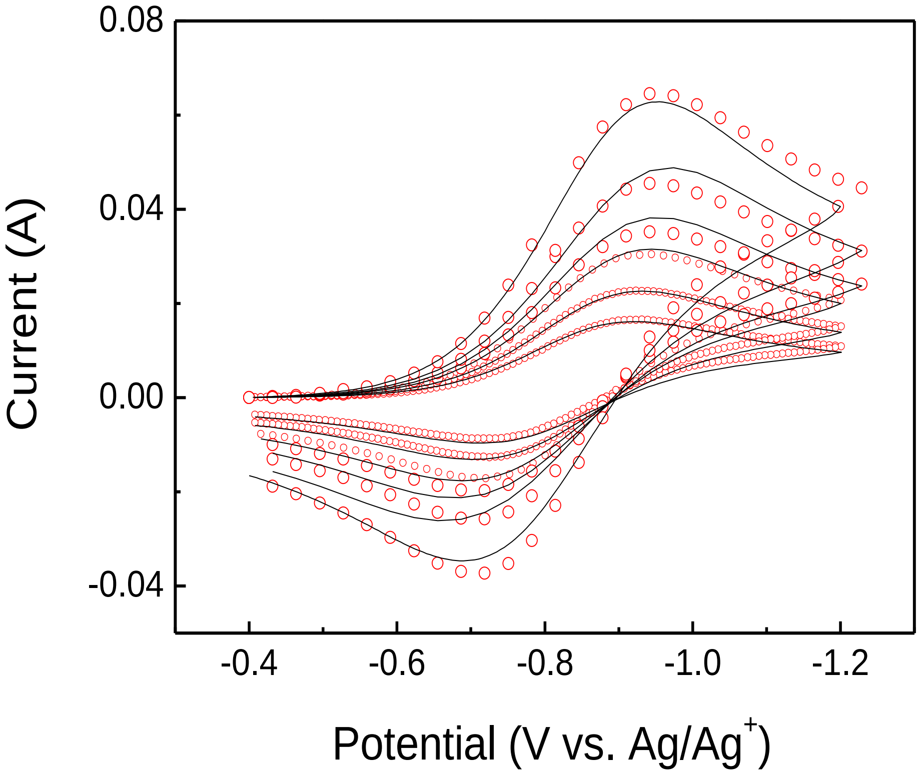

Figure 4. Results (−) of simultaneous curve fittings to the experimental CV data (○) taken at the various scan rates of 0.5, 1, 2, 3, 5 and 10 V/s.

The excellent fitting results strongly support the accuracy of the present simulation technique. Note that the diffusion coefficients of Sm^{3+} and Sm^{2+} ions are assumed to be identical to avoid divergent behavior during CV curve fittings. The characteristic parameters ($E^{o'}$, k^{o}, α) for the Sm^{3+}/Sm^{2+} redox reaction was simultaneously estimated from curve fitting. The fitted parameters are listed in Table 1.

Table 1. Fitted parameters for a reduction of Sm^{3+} to Sm^{2+} in a LiCl-KCl molten salt solution at a Mo rod electrode.

Electrode	$10^6 \times D$ (cm^2/s)	$Sm^{3+} + e^- \rightarrow Sm^{2+}$		
		$E^{o'}$ (V vs. Ag/Ag+)	α	$10^2 \times k^{o}$ (cm/s)
Mo	1.18±0.05	-0.82±0.05	0.60±0.03	1.7±0.2

For the first time to our knowledge, the standard rate constant for the Sm^{3+}/Sm^{2+} redox couple measured was 1.7×10^{-2} cm/s which is slightly smaller than that (2.2×10^{-2} cm/s of Eu^{3+}/Eu^{2+} redox system[10]. The value of the transfer coefficient (α) for the Sm^{3+}/Sm^{2+} redox couple was 0.6 which is higher than that (0.48) of Eu^{3+}/Eu^{2+} redox system, indicating that the energy barrier for activation is asymmetric[10].

4. CONCLUSION

To characterize the electrochemical reduction of Sm^{3+} to Sm^{2+} in a LiCl-KCl molten salt solution, a curve fitting analysis for experimental CV data obtained at different scan rates of 0.5 to 10 V/s was performed for a wide range of initial values: -0.6 to -1.0 V for the formal potential ($E^{o'}$), 0.3 to 0.7 for the transfer coefficient (α), and 10^{-3} to 1 cm/s for the standard rate constant (k^o). It was notable that the curve fitting results showed excellent fits to all the experimental CV data simultaneously. The formal potential, the transfer coefficient and the standard rate constant for a Sm^{3+}/Sm^{2+} redox system, which were extracted from the CV curve fitting, were -0.82 V vs. Ag/Ag^+, 0.60 and 1.7×10^{-2} cm/s, respectively. We think that such data for the Sm^{3+}/Sm^{2+} redox couple would be usefully used in development of on-line monitoring technique for in-situ determination of concentration of Sm species in a molten salt.

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References

1. H. P. Nawada, K. Fukuda, *J. Phys. Chem. Solids* 66 (2005) 647.
2. K. Uozumi, M. Iizuka, T. Kato, T. Inoue, O. Shirai, T. Iwai, Y. Arai, *J. Nucl. Mater*. 325 (2004) 34.
3. L. Cassayre, C. Caravaca, R. Jardin, R. Malmbeck, P. Masset, E. Mendes, J. Serp, P. Soucek, J. P. Glatz, *J. Nucl. Mater*. 378 (2008) 79.
4. J. N. Mathur, M. S. Murali, K. L. Nash, *Ion Exch. Solvent Extr*. 19 (2001) 357.
5. V. Smolenski, A. Novoselova, A. Osipenko, C. Caravaca, G. Cordoba, *Elctrochim. Acta* 54 (2008) 3 82.
6. G. Cordoba, C. Caravaca, *J. Electroanal. Chem*. 572 (2004) 145.
7. H. Yamana, B. G. Park, O. Shirai, T. Fujii, A. Uehara, H. Moriyama, *J. Alloy Comp*. 408 (2006) 66.
8. T. J. Kim, Y. K. Jeong, J. G. Kang, Y. Jung, D. H. Ahn, H. S. Lee, *J. Radioanal. Chem*. 286 (2010) 283.
9. M. R. Bermejo, F. Rosa, E. Barrado, Y. Castrillejo, *J. Electroanal. Chem*. 603 (2007) 81.
10. T. J. Kim, Y. Jung, S. H. Kim, S. W. Paek, D. H. Ahn, *Bull. Korean Chem. Soc*. 32 (2011) 863.
11. E. Levillain, F. Gaillard, P. Leghie, A. Demortier, J. P. Lelieur, *J. Electroanal. Chem*. 420 (1997) 16 7.
12. Y. Jung, S. Kim, B. S. Kim, D. H. Han, S. M. Park, J. Kwak, *Int. J. Electrochem. Sci*. 3 (2008) 566.