Elucidation of Electrode Reaction of EuCl₃ in LiCl-KCl Eutectic Melts through CV Curve Analysis

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The electrode reaction of Eu^{3+} in a LiCl-KCl eutectic melt has been re-examined using cyclic voltammetry (CV). In this work, for the first time, the kinetic details of a Eu^{3+}/Eu^{2+} redox system have been completely elucidated, along with the thermodynamic property, through a curve fitting applied to experimental CV data, which were obtained in a wide scan rate range of 0.5 to 10 V/s. The simulated results showed an excellent fit to all experimental CV data simultaneously, even though the curve fittings were performed within a large dynamic range of initial transfer coefficient values, formal potentials, and standard rate constants. As a result, a proper formal potential, transfer coefficient, and standard rate constant for the Eu^{3+}/Eu^{2+} redox system were successfully extracted using the CV curve fitting.

Key Words : Europium chloride, LiCl-KCl, Electrode reaction, CV curve analysis

Introduction

A pyrochemical process based on electrodeposition in molten salts has received great attention as a promising separation and transmutation route of minor actinide (MA) elements for the reuse of nuclear energy in the near future.[1,2] In addition, it has been widely accepted that the process has a proliferation resistance to nuclear materials compared with aqueous processes.

Korea Atomic Energy Research Institute (KAERI) began the development of pyroprocessing in the mid-1990s.[3,4] The pyroprocessing developed at KAERI has aimed to reduce the volume of spent fuel accumulated in domestic nuclear power plant facilities and to recycle recovered actinides in sodium-cooled fast reactors (SFR). Pyroprocessing consists of three distinct steps. First, uranium oxide is electrochemically reduced at the cathode to create a metal ingot containing uranium, and oxygen gas is generated at the anode during the electrolytic reduction process.[3] Next, the metal ingot is transferred to an electrochemical cell of LiCl-KCl molten salt at 773 K for the electrorefining process,[5] where pure uranium metal is recovered through an electrochemical reduction route. Finally, the uranium and transuranium (TRU) nuclides remaining after the electrorefining process are completely recovered during an electrowinning process,[6] where uranium and TRU are co-deposited at a liquid cadmium electrode to create a cadmium-based alloy for nuclear non-proliferation purposes.

To practically use the recovered actinides as a SFR fuel,[7] it is necessary to protect the co-deposition of lanthanide elements. For lanthanide-contaminated fuel, the neutron flux of the transmutation of the actinides is significantly decreased due to certain lanthanide elements with large neutron capture cross sections.[8] Therefore, it is necessary to understand the electrochemical behavior of lanthanides in molten salt in order to efficiently avoid the co-deposition of lanthanide elements and to further improve the efficiency of the electrowinning process.

Some lanthanides properties such as the standard potential, diffusion coefficient, and activity coefficient have been investigated by many researchers.[9-11] Among many lanthanide species, study on europium species in a molten salt has attracted much attention recently due to its peculiar characteristics.[12,18,19] Lanthanide oxides show very poor solubility in a molten salt media.[18] On the other hand, europium oxide (Eu_2O_3) easily dissolves to form Eu(II) ions even though most of lanthanide ions exist as trivalent states in molten salts.[18] So far, few studies on the kinetic properties of europium species have been reported. Recently, Bermejo *et al.*[12] reported the determination of a standard rate constant (k^o), transfer coefficient (α), and half-wave potential ($E_{1/2}$) for a redox reaction of Eu^{3+}/Eu^{2+} through a curve fitting of a single cyclic voltammogram using a simulation computer program (M271 COOL kinetic analysis software). In general, however, the characteristic parameters such as the formal potential, standard rate constant, and transfer coefficient for a given electrode reaction cannot be extracted from a single CV curve because there can be multiple interpretations of a CV curve. Rudolph *et al.* reported a methodology to characterize CV data, which includes non-linear curve fittings of multiple CV curves obtained at many different scan rates over a wide range of timescales.[13] Based on Rudolph's fast implicit finite difference (FIFD) algorithm, an effective computational tool called DigiSim was developed by Bioanalytical Systems, Inc., and the software has been widely used to estimate the thermodynamic and kinetic properties for various electrochemical systems.[14-17]

In this study, the standard rate constant (k^o), transfer

coefficient (α), and formal potential ($E^{0'}$) for the electrode reaction of Eu^{3+}/Eu^{2+} in LiCl-KCl eutectic melts at 773 K were simultaneously determined using nonlinear curve fittings applied to six CV curves taken at a scan rate of 0.5-10 V/s.

Experimental

All experiments were carried out in an Ar-filled glove box, where the concentration of water and oxygen was maintained at less than 3 ppm. Anhydrous LiCl (assay = 99.9%), KCl (assay = 99.9%), and $EuCl_3$ (assay = 99.99%) were purchased from Aldrich-APL LLC and used without further purification. The concentration of Eu in the LiCl-KCl eutectic melts was 0.01 M. A conventional three-electrode cell with a one-compartment quartz cell was used for all measurements, as shown in Figure 1. The temperature of the cell after placed in a furnace was maintained at 773±2 K. Glassy carbon rods (3 mm in diameter, Alfa Aesar Co.) were used as the working and counter electrodes. The electrode area exposed to LiCl-KCl eutectic melts was 1.30 cm^2. An Ag/Ag^+ reference electrode was constructed using a Pyrex glass tube with one end closed. Details of the Ag/Ag^+ electrode are described elsewhere.[19]

To determine the characteristic parameters ($E^{0'}$, k^o, α) for the Eu^{3+}/Eu^{2+} redox reaction, cyclic voltammograms were taken within a potential range of 0.8 to 0.0 V *vs.* Ag/Ag^+ at various scan rates and curve fittings for the CV data were performed using DigiSim software (ver. 3.03, Bioanalytical Systems, Inc.). The scan rate for the cyclic voltammetry was chosen to be between 0.5 V/s and 10 V/s. To obtain a pure faradaic response, ohmic drop (iR_{sol}) compensation was applied to all measurements using the value of solution resistance determined by the electrochemical impedance technique.

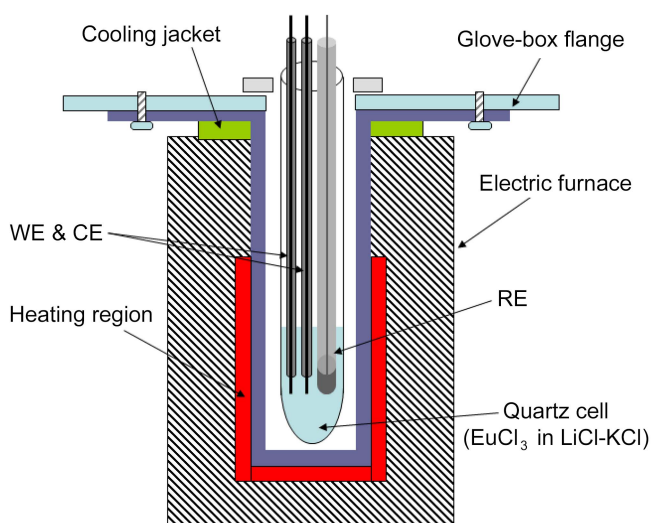To avoid divergence during fitting, the diffusion coefficient was dropped from the fitted parameters. The diffusion

coefficient of Eu^{3+} was determined from the chronamperometric response at the glassy carbon (GC) electrode prior to the CV curve fittings. For the chronoamperometry, an initial potential of 0.8 V was applied to the working electrode for 30 sec, and the potential was then stepped to 0.0 V and kept for 10 sec. The non-faradaic chronoamperometric response due to the electrical double-layer capacitor was measured in the LiCl-KCl eutectic melts without Eu ions. An Autolab PGSTAT302 potentiostat (Eco-Chimie) with specific GPES electrochemical software (version 4.9) was used for the chronoamperometry and cyclic voltammetry.

Results and Discussion

A chronoamperometric faradaic current was obtained from the total current subtracted by the non-faradaic current, which was measured in the same molten salt without Eu ions. The timescale of the analysis was determined by considering the instrumental errors and convection of the electrochemical systems. Instrumental errors originated from potentiostatic limitation within brief times of less than 20 msec. The convection phenomena due to a thermal gradient in an electrochemical cell can disrupt the diffusion layer near the working electrode over longer periods of time. In a number of trials, it was found that the appropriate time region for the linear regression analysis was 0.02-5 sec.

Figure 2 shows the results of linear regression analysis for the chronoamperometric response of the reduction of Eu^{3+} to Eu^{2+}. It can be clearly seen that all the experimental data are well adjusted to the theoretical line known as the Cottrell equation:

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

where *n*, *F*, *A*, *D*, *C*, and *t* are the number of electrons involved in a given electrode reaction, Faraday constant, electrode area, diffusion coefficient, concentration, and time, respectively. The diffusion coefficient of the Eu^{3+} ions determined from the linear regression analysis was 9.21×10^{-6}

Figure 1. Schematic view of the experimental setup for high-temperature electrochemistry in a molten salt system with $EuCl_3$.
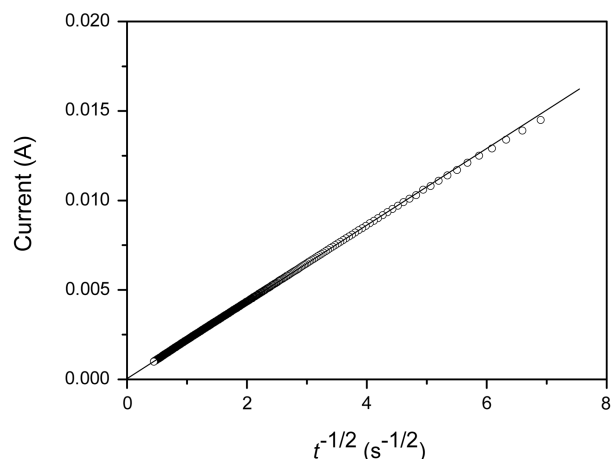

Figure 2. Chronoamperometric response of $EuCl_3$ and a linear regression analysis using the Cottrell equation: experimental data (○); regression line (−).
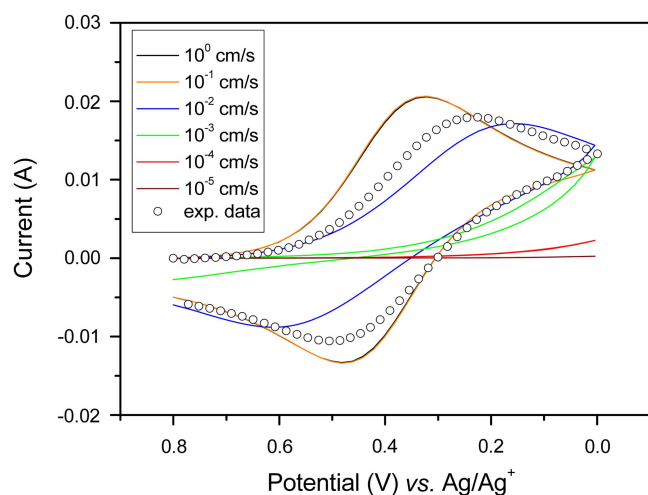
Figure 3. Comparison of experimental CV data (○) and theoretical curves (−) simulated under the following conditions: $E^{0'} = 0.4$; $\alpha = 0.5$; $k^o = 1$ to 10^{-5} cm/s; $D = 9.21 \times 10^{-6}$ cm²/s; T = 773 K, scan rate = 10 V/s.

cm²/s. This value is very similar to the value (9.32×10^{-6} cm²/s) measured using the CV technique.[12]

Figure 3 shows a comparison of experimental data and simulated curves that were obtained at various k^o values (1 to 10^{-5} cm/s), based on the following one-electron transfer reaction:

$$Eu^{3+} + e^- \rightarrow Eu^{2+} \qquad (E^{0'}, \alpha, k^o)$$
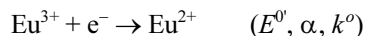
The CV curves simulated at a scan rate of 10 V/s showed quite different characteristics depending on the standard rate constants. One general feature was that well-defined peaks (reversible curves) were observed in k^o values of more than 10^{-1} cm/s, whereas redox peaks disappeared in k^o values of less than 10^{-3} cm/s, indicating that the reaction is irreversible. At k^o values of 10^{-2} cm/s, the cathodic peak potential was shifted in a more negative direction, and the anodic peak potential was shifted in a more positive direction, when compared with the corresponding peaks observed in k^o values greater than 10^{-1} cm/s. This means that a reaction with the k^o values of 10^{-2} cm/s is quasi-reversible. As a result, it can be concluded from the preliminary simulation results that the standard rate constant of a Eu^{3+}/Eu^{2+} redox reaction has a value between 10^{-1} to 10^{-2} cm/s.

In general, the initial values of the main parameters, such as the formal potential, standard rate constant, and transfer coefficient, are very important in CV curve fitting. Thus, curve fittings using DigiSim software were performed under a wide range of initial values: 0.2 to 0.6 V for the formal potential ($E^{0'}$), 0.3 to 0.7 for the transfer coefficient (α), and 10^{-5} to 10^4 cm/s for the standard rate constant (k^o).

Figure 4 shows some examples of the simulated curves (line) adjusted to the experimental CV curves (open circle) taken at six different scan rates (0.5, 1.0, 2.0, 3.0, 5.0, 10 V/s) using a glassy carbon electrode. The simulated curves showed an excellent fit to all the experimental CV data simultaneously at the six scan rates, regardless of the initial
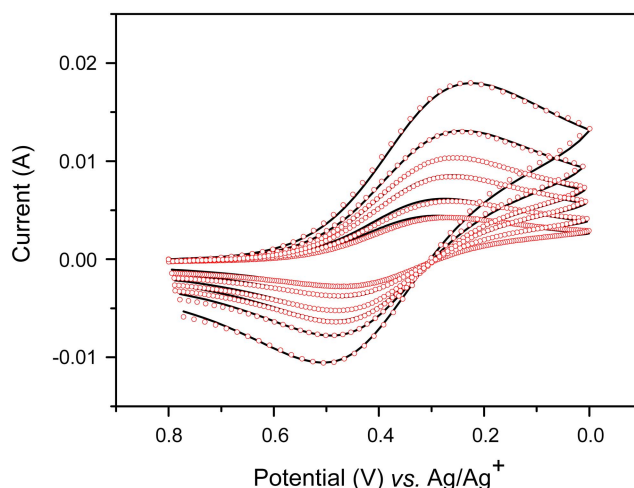

Figure 4. Results (−) of curve fittings to the experimental CV data (○) obtained at the various scan rates of 0.5, 1, 2, 3, 5, and 10 V/s.

Table 1. Fitted parameters for an electrode reaction of Eu^{3+} in a LiCl-KCl eutectic melt at GC

Electrode	$10^6 \times D$ (cm²/s)	$Eu^{3+} + e^- \rightarrow Eu^{2+}$		
		$E^{0'}$ (V)	α	$10^2 \times k^o$
GC	9.2	0.37	0.48	2.2

values of the transfer coefficient, formal potential, and standard rate constant. These excellent fitting results strongly support the accuracy of the present simulation technique. Note that the diffusion coefficients of Eu^{3+} and Eu^{2+} were assumed to be identical in order to avoid divergent behavior during the fitting process. The characteristic parameters ($E^{0'}$, k^o, α) for the electrode reaction were successfully extracted from the curve fitting. The fitted parameters are listed in Table 1. The value of the standard rate constant (2.2×10^{-2} cm/s) was 4.5 times larger than the value (4.9×10^{-3} cm/s) reported by Bermejo *et al.*.[12] When considering the simulated curves shown in Figure 3, it is thought that the k^o value of 2.2×10^{-2} cm/s is more reasonable. In case that the redox couples with the same structural properties are dissolved species, the transfer coefficient (a) value is between 0.4 and 0.6. From the point of view, it seems that the a value of 0.48 obtained in the curve fitting is also acceptable.

Conclusion

To characterize the electrode reaction of Eu^{3+} in a LiCl-KCl eutectic melt, a curve fitting applied to experimental CV data obtained within a wide scan rate range of 0.5 to 10 V/s was performed for a wide range of initial values: 0.2 to 0.6 V for the formal potential ($E^{0'}$), 0.3 to 0.7 for the transfer coefficient (α), and 10^{-5} to 10^4 cm/s for the standard rate constant (k^o). One notable feature in the fitting results is that the simulated results show an excellent fit to all the experimental CV data simultaneously, regardless of the initial values of the transfer coefficient, formal potential and

standard rate constant. The formal potential, the transfer coefficient, and standard rate constant for a Eu^{3+}/Eu^{2+} redox system, which were extracted from the CV curve fitting, were 0.37 V *vs*. Ag/Ag$^+$, 0.48, and 2.2×10^{-2} cm/s, respectively. It is thought that a k^o value of 2.2×10^{-2} cm/s is very reasonable when considering the simulation results at 10 V/s.

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