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Study on Electrodeposition of Ce(III) at a Tungsten Electrode in a LiCl-KCl Molten Salt Solution

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The electrodeposition of cerium ions at a tungsten electrode in the LiCl-KCl eutectic salt solution was elucidated by linear sweep voltammetry and digital simulation technique. To interpret the electrodeposition process of metal ions, in this work, a program to be able to simulation and curve fittings was developed. Characteristic parameters such as the formal potential ($E^{o'}$), standard rate constant (k^o) and transfer coefficient (α) for the electrodeposition of cerium ions, Ce(III) + $3e^- \rightarrow$ Ce, were extracted by the simultaneous nonlinear regression analysis of multiple linear sweep voltammograms taken in various scan rates. The formal potential, the transfer coefficient and the standard rate constant for the Ce(III)/Ce(0) system proved to be -2.03 V vs. Ag/Ag^+, 0.58~0.63 and 7.5~8.4×10^{-3} cm/s, respectively. It is thought that the methodology introduced in this work can be efficiently applied to analysis of the electrodeposition reactions of the lanthanide and actinide species,

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Keywords: Electrodeposition**,** LiCl-KCl, Molten Salt, Formal Potential, Standard Rate Constant

1. INTRODUCTION

The electrochemical separation in a molten chloride solution, pyrochemical reprocessing technique, is one of the most viable methods for recycling of nuclear fuels and radioactive waste reduction[1-4]. Spent fuels with a huge amount of uranium are converted to metal ingots with transuranic elements (TRUs) and fission products (FPs) as well as uranium metals[5]. In the electrorefining process which is the most important step of the pyrochemical reprocessing, lanthanides (Ln) and actinides (An) elements in the metal ingots are dissolved into molten salt solutions under anodic conditions and then actinides elements are recovered through cathodic deposition at solid cathodes (e.g., graphite)[5]. It is noteworthy that it is hardly to separate pure plutonium in the electrorefining process because the deposition potential of TRUs are very similar to one another. As a result, the pyrochemical reprocessing offers much higher proliferation resistance in comparison with conventional aqueous processes[6,7]. In fact, the actinides deposits can be used as a nuclear fuel of sodium-cooled fast reactors (SFR). To make a high-quality SFR fuel, it is very needed to protect the deposition of Ln elements[8,9]. For this reason, it is prerequisite condition to get exact understanding on the electrochemical properties of lanthanides elements. To date, most of studies have focused on the thermodynamic properties on the electrochemical reaction of Ln elements[10-12]. Recently, we reported the kinetic data such as the standard rate constant (k^o) and the transfer coefficient (α) for both Sm(III)/Sm(II) and Eu(III)/Eu(II) redox couples through non-linear regression analysis of several CV curves by using the DIGISIM software[5,13]. However, the software cannot be applied to electrode reactions such as electrodeposition where one of redox couples exists in the form of solid deposits. So far, to our knowledge, simulation program to interpret electrodeposition process has not been reported. In this work, we present the simulation and curve fitting program for the analysis of the electrode reactions of Ln(III)/Ln(0) or An(III)/An(0) redox couples. To confirm the efficacy of the program, the electrodeposition of cerium (Ce) ions which is one of abundant lanthanides elements in spent fuels was examined by linear sweep voltammetry (LSV) and analyzed by the program[1,3].

2. EXPERIMENTAL SECTION

The high-temperature electrochemical system used for electrodepositing cerium (Ce) ions in the LiCl-KCl eutectic molten salt was described in the previous work[13]. The LiCl-KCl molten-salt solution with 0.10 M Ce(III) was made in a quartz tube using anhydrous LiCl (assay = 99.9%), KCl (assay = 99.9%) and $CeCl_3$ (assay = 99.99%), which were purchased from Aldrich-APL LLC. Electrochemical measurements was performed with a conventional three-electrode system at 773±2 K. The working temperature was monitored by a thermocouple inserted into the quartz cell. A tungsten (W) wire with 1 mm diameter and a glassy carbon rod with 3 mm diameter served as the working and counter electrode, respectively. The practical surface area of the working electrode was measured from the immersion depth of the electrode. A silver-silver chloride (Ag/Ag^+) electrode systems described elsewhere was used as the reference electrode[14]. All potentials were recorded versus the reference electrode.

To elucidate the characteristic parameters ($E^{o'}$, k^o, α) for the electrode reaction of the Ce(III)/Ce(0) redox couple, linear sweep voltammetry (LSV) was carried out at various scan rates in the potential range of -1.40 to -2.15 V with VMP3 potentiostat (BioLogic Science Instruments). Simultaneous nonlinear regression analysis for LSV curves obtained at various scan rates was carried out with homemade software which is newly developed on the basis of the Crank-Nicholson method[15]. The scan rate for the linear sweep voltammetry was chosen between 50 and 1000 mV/s. The *iR* drop compensation was performed for the LSV curves to get accurate potential information. The diffusion coefficient of Ce(III) used in the simultaneous curve fitting of LSV curves was measured by chronoamperometry in which the potential was stepped from -1.40 to -2.15 V in the LiCl-KCl eutectic salt with 0.10 M Ce(III). Pure faradaic chronoamperometric and linear sweep voltammetric response for the electrodeposition of cerium ions were obtained by removing charging currents arising from electrical double layer. The charging current was measured in the LiCl-KCl eutectic solution without Ce(III) ions under same conditions.

3. RESULTS AND DISCUSSION

In case of linear diffusion, the chronoamperometric current is described by the Cottrell equation. Linear diffusion happens at a planar electrode, while nonlinear diffusion occurs at disk or rod-type electrodes[16]. But, diffusion phenomena at disk or rod-type electrodes can be assumed to be linear diffusion in the short time region[16]. For this reason, the chronoamperometric response taken within 1.0 sec was used for the regression analysis on the basis of the Cottrell equation[16]. Fig. 1 shows the curve fitting result for the chronoamperometric response of the electrodeposition of cerium ions in the LiCl-KCl eutectic salt. Most of experimental data were excellently adjusted to the regression curve ($R^2 > 0.999$). Diffusion coefficient of cerium ions proved to be 1.71×10^{-5} cm^2/s, which is a little higher value compared to that (1.56×10^{-5} cm^2/s) reported by Castrillejo et al.[2].

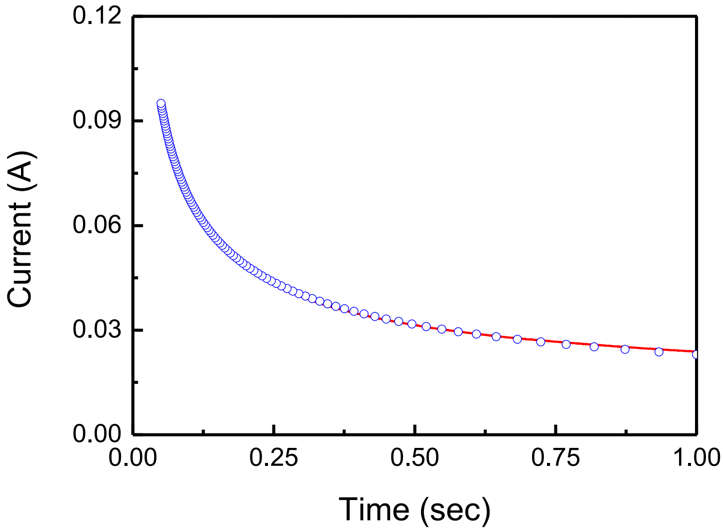

Figure 1. Chronoamperometric current (−) for the electrodeposition of cerium ions to cerium metal at a tungsten electrode in the LiCl-KCl eutectic salt and the corresponding nonlinear regression curve (○).

Digital simulation program coded on the basis of the Butler-Volmer kinetic model, the Fick's diffusion equations and the fast implicit finite difference (FIFD) algorithm was used for the curve fitting of LSV curves [9,17]. For highly accurate nonlinear regression analysis, proper initial values of fitted parameters such as formal potential ($E^{0'}$), standard rate constant (k^o) and transfer coefficient (α) are essential. Before nonlinear regression analysis, the experimental LSV curve taken at scan rate of

500 mV/s was compared with theoretical LSV curves for the electrode reaction of cerium ions, Ce(III) + 3e$^-$ → Ce.

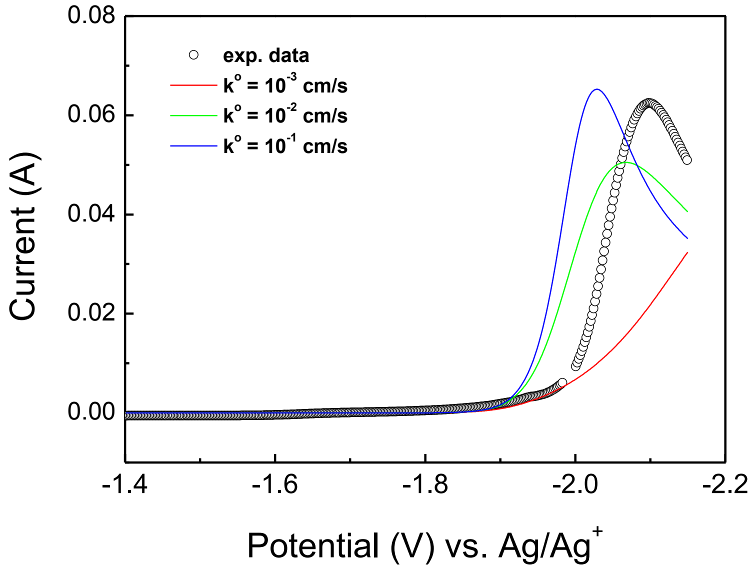

Figure 2. Linear sweep voltammogram (○) for the electrodeposition of cerium ions at a scan rate of 0.5 V/s and the theoretical curves (–) simulated under the following conditions: $E^{0'} = -2.00$; $\alpha = 0.3$; $k^o = 0.1$ to 1.0×10^{-3} cm/s; $D = 1.71\times10^{-5}$ cm^2/s; T = 773 K, scan rate = 0.5 V/s.

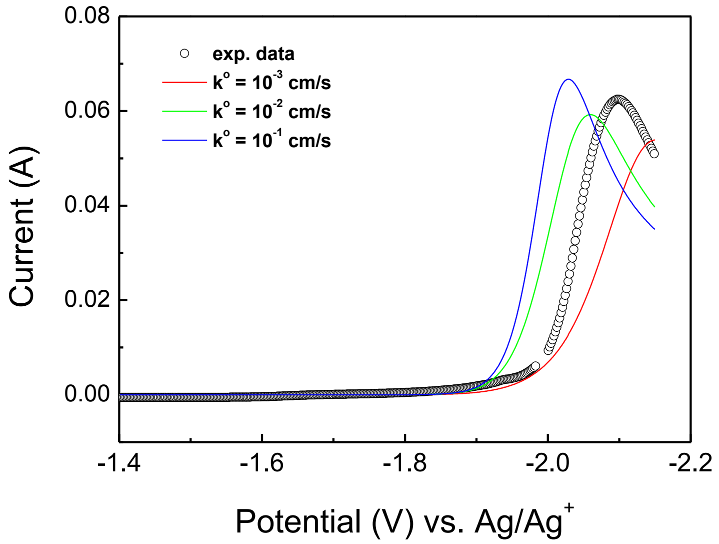

Figure 3. Linear sweep voltammogram (○) for the electrodeposition of cerium ions at a scan rate of 0.5 V/s and the theoretical curves (–) simulated under the following conditions: $E^{0'} = -2.00$; $\alpha = 0.5$; $k^o = 0.1$ to 1.0×10^{-3} cm/s; $D = 1.71\times10^{-5}$ cm^2/s; T = 773 K, scan rate = 0.5 V/s.

Fig. 2 shows the comparison of experimental LSV curves with the theoretical curves simulated at various k^o values (1.0×10^{-3} to 0.1 cm/s) with the fixed α value of 0.30. At α value of 0.30, the theoretical LSV curves were greatly different from the experimental data regardless of k^o value. On the other hand, it was found at the α value of 0.50 that the theoretical LSV curve was similar to the experimental data when k^o value were 1.0×10^{-2} (Fig. 3). In addition, it was observed at α value of 0.70 that the LSV curves simulated at the k^o value of 1.0×10^{-3} closely approached the experimental data (Fig. 4).

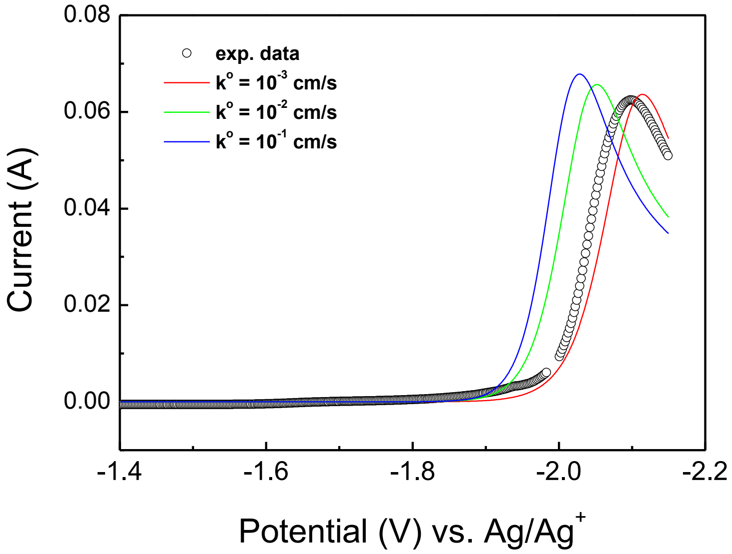

Figure 4. Linear sweep voltammogram (○) for the electrodeposition of cerium ions at a scan rate of 0.5 V/s and the theoretical curves (−) simulated under the following conditions: $E^{0'} = -2.00$; $\alpha = 0.7$; $k^o = 0.1$ to 1.0×10^{-3} cm/s; $D = 1.71\times10^{-5}$ cm^2/s; T = 773 K, scan rate = 0.5 V/s.

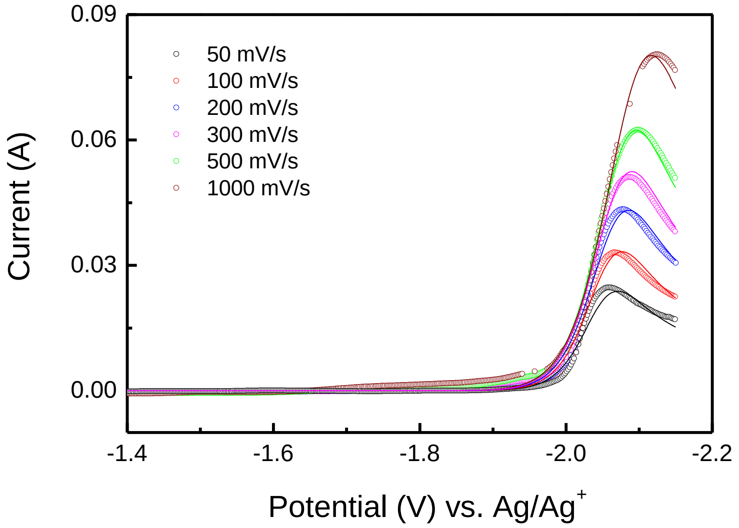

Figure 5. Results (−) of the simultaneous nonlinear regression analysis for the multiple LSV curves (○) taken at the various scan rates of 50, 100, 200, 300, 500 and 1000 mV/s. Initial values of fitted parameters: $E^{0'} = -2.00$; $\alpha = 0.7$; $k^o = 1\times10^{-3}$ cm/s.

According to the expectation, the following three initial value sets for fitted parameters were chosen for nonlinear regression analysis: $E^{o'}$ = –2.00 V, k^o = 1.0×10^{-2} cm/s, α = 0.50; $E^{o'}$ = –2.00 V, k^o = 1.0×10^{-2} and 1.0×10^{-3} cm/s, α = 0.70.

Fig. 5 shows one example of simultaneous curve fitting results for the experimental LSV curves taken at different scan rates. It is clearly seen that most of LSV data (open circle) are excellently fitted to the theoretical curves, indicating the efficacy of the newly developed simulation program and the accuracy of nonlinear regression analysis. Table 1 summarizes the results of curve fittings for the LSV curves, which were performed under the three initial conditions. The values of the fitted parameters were similar to one another regardless of the initial value sets. The standard rate constant for the Ce(III)/Ce(0) redox couple was 7.5~8.4×10^{-3} cm/s which is much higher than that (2.0×10^{-4} cm/s) measured by Castrillejo et al. at 723 K[2]. They used the convolutional analysis of voltammetric curves to get information on the kinetics of the Ce(III)/Ce(0) system, which is not a proper methodology for elucidating the kinetic properties of a redox reaction.

Table 1. Curve fitting results of linear sweep voltammetric curves for the electrodeposition of Ce(III) at a tungsten electrode in the LiCl-KCl eutectic salt.

Initial values			Regression analysis results		
$E^{o'}$ (V vs. Ag/Ag$^+$)	α	k^o (cm/s)	$E^{o'}$ (V vs. Ag/Ag$^+$)	α	k^o (cm/s)
-2.00	0.50	1.0×10^{-2}	-2.03	0.58	8.4×10^{-3}
-2.00	0.70	1.0×10^{-2}	-2.03	0.63	7.8×10^{-3}
-2.00	0.70	1.0×10^{-3}	-2.03	0.61	7.5×10^{-3}

It is well known that thermodynamic ($E^{o'}$) and kinetic (k^o, α) properties can be extracted from the simultaneous nonlinear regression analysis of multiple voltammetric curves based on digital simulation [17]. This approach has been widely applied to measure the thermodynamic and kinetic properties for various electrochemical reactions[5,18,19]. The value of the transfer coefficient (α) for the Ce(III)/Ce(0) redox couple was 0.58~0.63 which was quite different from that (0.4±0.04) reported by Castrillejo et al. at 723 K[2], indicating that the energy barrier for activation was asymmetric and the structure of activated complex was more similar to cerium ions than cerium metals[16].

4. CONCLUSION

In this work, for the first time, the thermodynamic and kinetic properties for the electrodeposition of cerium ions in the LiCl-KCl eutectic salt were measures from the simultaneous nonlinear regression analysis of multiple LSV curves taken at various scan rates. Curve fittings were performed by using the homemade digital simulation program. For effective nonlinear regression analysis, appropriate initial value sets for the characteristic parameters were chosen through the comparison of the experimental LSV curves with the theoretical curves. The formal potential, the transfer coefficient and the standard rate constant for the Ce(III)/Ce(0) redox couple, extracted from the LSV curves fittings, were -2.03 V vs. Ag/Ag^+, 0.58~0.63 and $7.5 \sim 8.4 \times 10^{-3}$ cm/s, respectively. We think that the digital simulation program and the methodology introduced in this work can be usefully applied to elucidate the electrodeposition reactions of the actinide and other lanthanide species, and furthermore the kinetic and thermodynamic information on the electrodeposition of metal ions may be beneficial to the process development and optimization of the pyrochemical reprocessing technique.

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