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Determination of Electrochemical Parameters for Electrode Reaction of La(III)/La(0) Redox Couple in a High-Temperature Molten Salt Solution

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The electrochemical parameters on the electrodeposition of lanthanum ions in the LiCl-KCl eutectic salts were determined by linear sweep voltammetry and curve fitting program. Thermodynamic and kinetic data for the electrodeposition of lanthanum ions were successfully extracted by the simultaneous nonlinear regression analysis of several linear sweep voltammograms. The formal potential, the transfer coefficient and the standard rate constant for the La(III)/La(0) redox system were estimated to be -2.13 V vs. Ag/Ag^+, 0.61~0.65 and 0.15~0.25 cm/s, respectively.

Keywords: Electrodeposition**,** Molten salts, La(III), Kinetic parameter, Standard rate constant

1. INTRODUCTION

Various pyrochemical reprocessing techniques based on electrochemical methods have been developed[1]. The goal of developing pyrochemical techniques is to recover uranium elements in spent fuels and to reduce radioactive waste[2-7]. They consist of several sequential steps, such as voloxidation, electrolytic reduction, electrorefining, electrowinning and salt purification[3,4]. Metal ingots containing uranium, transuranic elements (TRUs) and fission products were prepared from spent fuels through electrolytic reduction. Most of actinides are recovered in the form of mixtures in the electrorefining process, resulting in a strong proliferation resistance[9,10]. The actinide mixtures have been considered as one of attractive candidates for use in sodium-cooled fast reactors (SFR). Several factors such as purity and composition need to be taken into consideration in order to successfully apply them to a SFR fuel. Efficacy of the nuclear fuels is crucially dependent upon the level of lanthanide contamination[4,11-12]. To achieve a high-quality SFR fuel, precise understanding on the electrochemical behavior of lanthanide elements is required. So far, most of researchers have paid attention to elucidating thermodynamic properties on the electrochemical reaction of lanthanides [13-16]. Actually, study on kinetic properties has been overlooked for reasons of complexity in data interpretation. Recently, we developed analysis program to be able to extract the kinetic data such as the standard rate constant (k^o) and the transfer coefficient (α) for electrodeposition of lanthanide and actinide elements[17]. For the first time, the methodology was applied to determination of kinetic parameters for the electrodeposition of Ce(III) ions. In this work, the electrodeposition of La(III) ions was studied and relevant electrochemical parameters were calculated from the interpretation of linear sweep voltammetric curves.

2. EXPERIMENTAL SECTION

The high-temperature electrochemical cell containing the LiCl-KCl eutectic salt was well described elsewhere[4]. To make the eutectic salt in a quartz cell, anhydrous LiCl (purity = 99.9%, Aldrich) and KCl (purity = 99.9%, Aldrich) were used. A 0.1 M La(III) solution was prepared by adding solid $LaCl_3$ (purity = 99.99%, Aldrich) to the molten salt. Electrochemical experiments were performed with a conventional three-electrode system at 733±2 K. An inert tungsten (W) and a glassy carbon rod were used as the working and counter electrode, respectively. A silver-silver chloride (Ag/Ag^+) redox couple in Pyrex tube was used as the reference electrode[16].

To determine the characteristic parameters ($E^{o'}$, k^o, α) for the electrodeposition of the La(III), linear sweep voltammetry (LSV) was carried out at various scan rates between 50 and 500 mV/s in the potential range of -1.50 to -2.20 V with VMP3 potentiostat (BioLogic Science Instruments). For getting reproducible data, surface of the working electrode was cleaned by electrochemically dissolving La deposits after each experiment. For this, reverse LSV to -1.5 V was performed. To avoid multiple answers which commonly occur in a single LSV curve fitting, simultaneous nonlinear regression analysis for several LSV curves was carried out by using homemade fitting program developed on the basis of the Butler-Volmer kinetic model and the Crank-Nicholson method[18-20]. To simplify the curve fitting of LSV curves, the diffusion coefficient of La(III) was determined from chronoamperometric data measured in the same LiCl-KCl eutectic solution with 0.10 M La(III). Pure faradaic chronoamperometric response for the determination of diffusion coefficient was obtained by subtracting the charging currents due to the electrical double layer on the surface of working electrode. The chronoamperometric current data taken less than 2.0 sec was used to ensure linear diffusion at the rod-type working electrode. For the determination of diffusion coefficient of La(III), linear regression analysis for the chronoamperometric response was performed.

3. RESULTS AND DISCUSSION

It is assumed that diffusion phenomena at a tungsten rod electrode can be considered as linear diffusion in the short time and the chronoamperometric current is described by 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, respectively[19]. Diffusion coefficient of La(III) was calculated from the plots of faradaic current vs. $t^{-1/2}$.

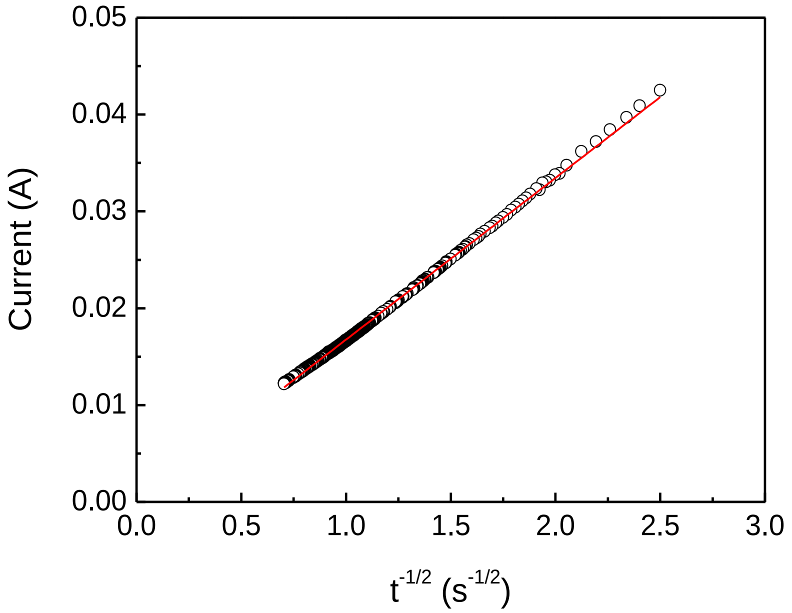

Figure 1. Chronoamperometric current (○) for the electrodeposition of La(III) in the LiCl-KCl eutectic salt at 723 K and the corresponding linear regression line (−).

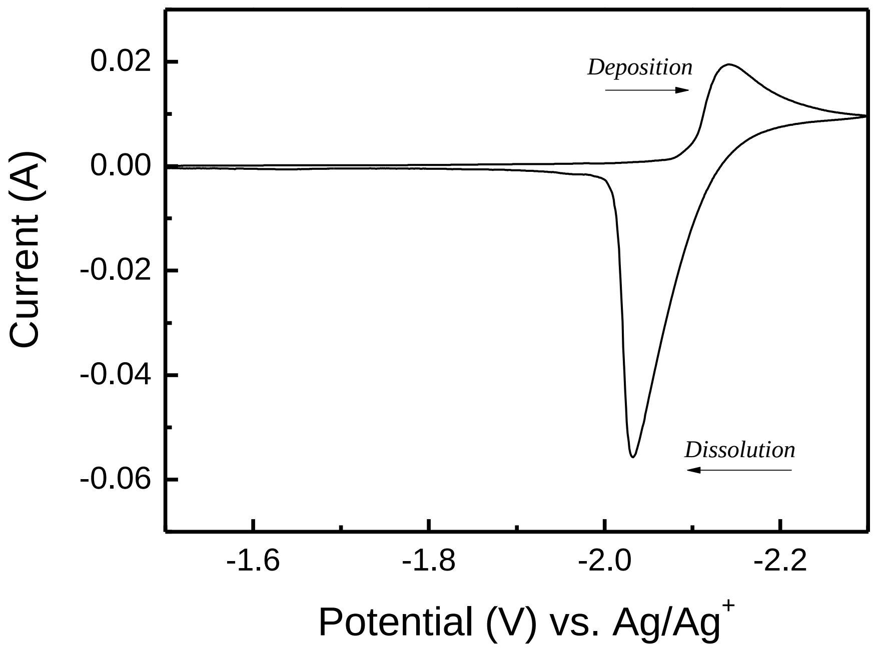

Figure 2. Cyclic voltammogram for La(III)/La(0) redox couple at a scan rate of 0.05 V/s.

Fig. 1 shows the regression analysis result for the chronoamperometric response of La(III) in the LiCl-KCl eutectic salt. Most of experimental data were excellently fitted to the regression line ($R^2 > 0.999$). Diffusion coefficient of La(III) ions was 1.32×10^{-5} cm^2/s, which was very similar to that (1.26×10^{-5} cm^2/s) reported by Yamana group[21].

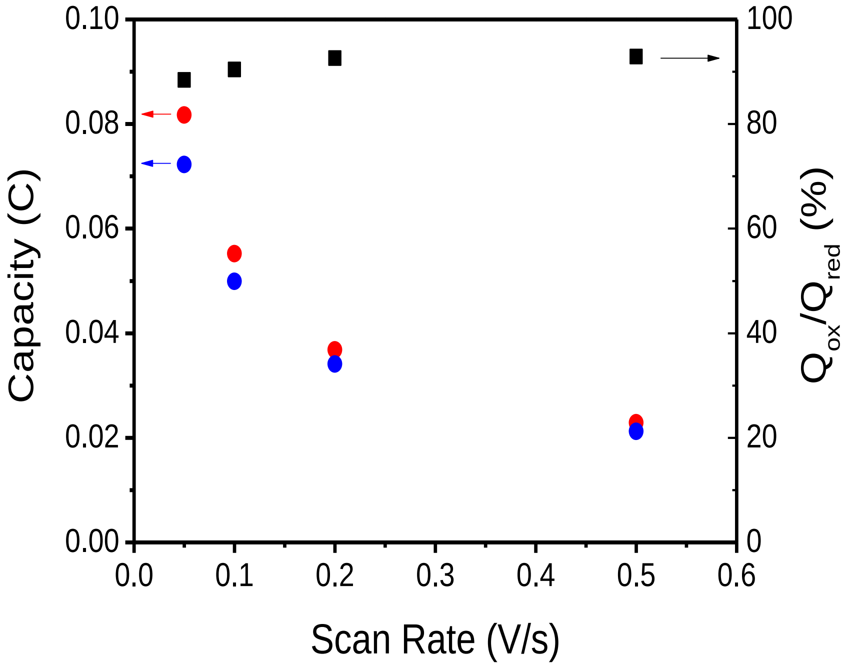

Figure 3. Plots of both deposition capacity (Q_{red}) and dissolution capacity (Q_{ox}) vs. scan rate. Plot of Q_{red}/Q_{ox} vs. scan rate

Fig. 2 shows the typical CV curve of La(III)/La redox couple. Both deposition capacity (Q_{red}) and dissolution capacity (Q_{ox}) were measured from the CV curves taken at various scan rates. Reduction curves are similar to those of general electrode reactions ($O + e^- \rightarrow R$), where both O and R exist in a solution, but oxidation curves are quite different. Dissolution process of La deposits to La(III) occurs in relatively narrow potential range, resulting in sharp anodic peak current.

Fig. 3 shows the plots of both deposition capacity (Q_{red}) and dissolution capacity (Q_{ox}) vs. scan rate. Both Q_{red} and Q_{ox} decreased as scan rate increased, while Q_{red}/Q_{ox} slightly increased with scan rate. At even higher scan rate of 0.5 V/s, a certain amount of La deposits remained on the working electrode at the end of CV experiment. To remove remaining La deposits, initial potential (-1.5 V) was applied to the working electrode for 1 min before next LSV experiment.

Initial values of fitted parameters, such as formal potential ($E^{0'}$), standard rate constant (k^o) and transfer coefficient (α), should be appropriately chosen to do precise regression analysis. For this reason, a number of simulation results were compared with the experimental data. Fig. 4 shows one example of comparison of experimental data with the curves simulated at various k^o values (1.0×10^{-3} to 0.1 cm/s) with the fixed α value of 0.50. It was found that the theoretical LSV curve at the k^o value of 0.1 cm/s closely approached the experimental data, while the theoretical LSV curve at the k^o value of

1.0×10^{-3}cm/s is far from the experimental data. This indicate that kinetics of La(III)/La(0) redox couple should be so rapid[19]. Through a number of trial and error, three initial value sets were chosen for nonlinear regression analysis (Table 1).

Table 1. Summary of nonlinear regression analysis for LSV curves of the electrodeposition of La(III) in the LiCl-KCl eutectic salt.

Initial values			Curve fitting results		
$E^{o'}$ (V vs. Ag/Ag$^+$)	α	k^o (cm/s)	$E^{o'}$ (V vs. Ag/Ag$^+$)	α	k^o (cm/s)
-2.10	0.60	0.1	-2.13	0.63	0.23
-2.15	0.55	0.1	-2.13	0.65	0.25
-2.15	0.60	0.1	-2.13	0.61	0.15

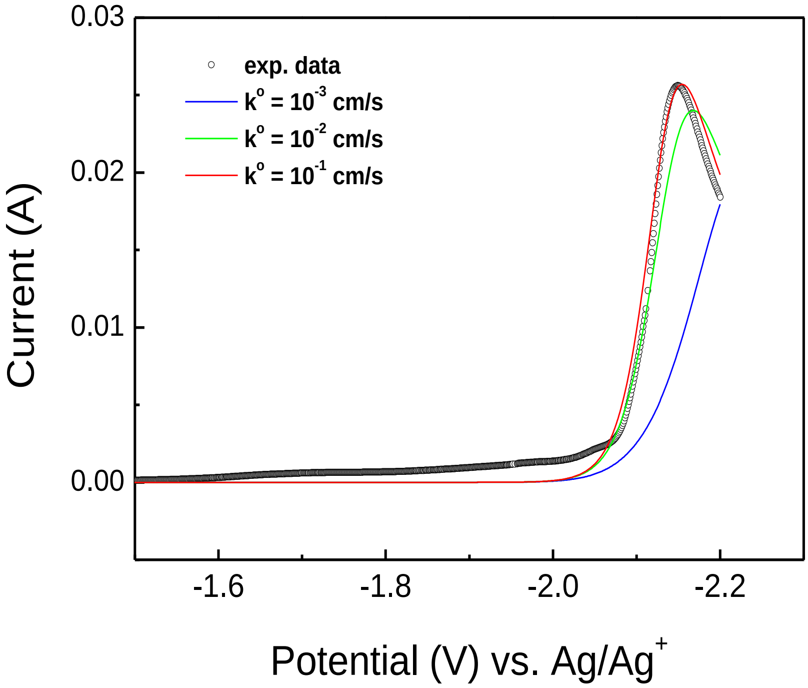

Figure 4. Linear sweep voltammogram (○) for the electrodeposition of lanthanum ions at a scan rate of 0.5 V/s and the theoretical curves (–) simulated under the following conditions: $E^{0'} = -2.15$; $\alpha = 0.5$; $k^o = 0.1$ to 1.0×10^{-3} cm/s; $D = 1.32\times10^{-5}$ cm^2/s; T = 723 K, scan rate = 0.1 V/s.

Fig. 5 shows the simultaneous fitting results for the experimental LSV curves taken at various scan rates. It is clearly seen that the theoretical curves are well adjusted to LSV data (open circle) at four scan rates. Table 1 lists the characteristic parameters determined from the curve fittings. It was found that the values of the fitted parameters were not greatly dependent on the initial value sets. Very interestingly, the standard rate constant for the La(III)/La(0) redox couple was estimated to be 0.15~0.25 cm/s which is so much faster than that (~8.0×10^{-3} cm/s) of Ce(III)/Ce(0). Thus, it is expected in La(III)/La(0) electrochemical system that the mass transfer by diffusion mode rather than the charge transfer step controls the process. The value of the transfer coefficient (α) for the La(III)/La(0) redox couple was 0.61~0.65, implying that the energy barrier for activation was asymmetric and the chemical nature or shape of activated complex resembles that of La(III) ions rather than La elements[19].

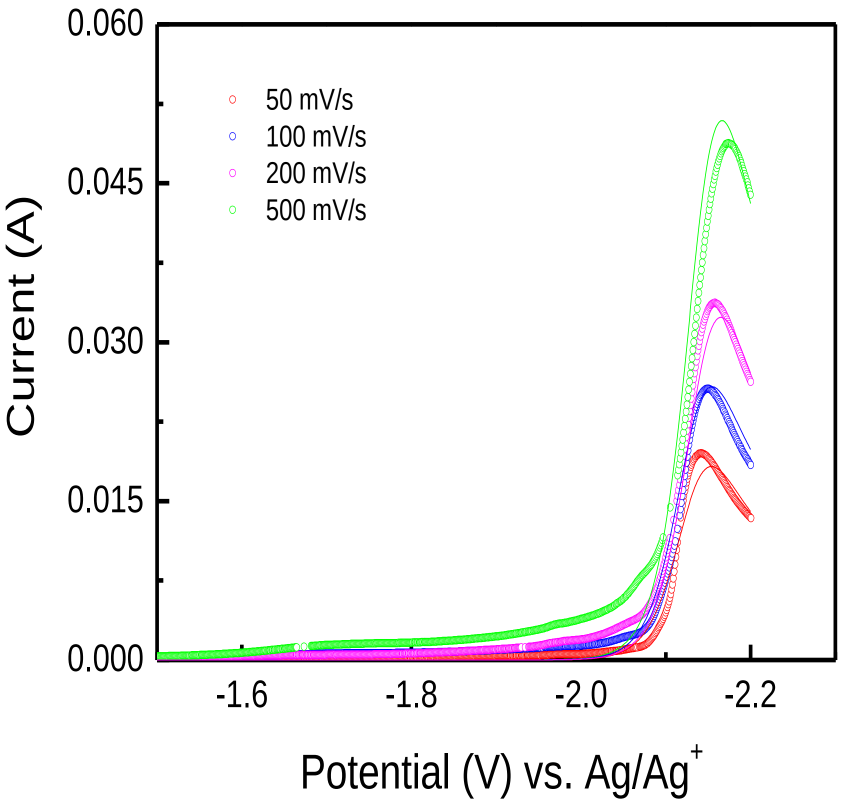

Figure 5. Comparison of nonlinear regression results (−) with experimental LSV curves (○) taken at the various scan rates of 50, 100, 200, 300 and 500 mV/s. Initial values of fitted parameters: $E^{0'}$ = –2.15; α = 0.5; k^o = 0.1 cm/s.

4. CONCLUSION

In this work, the thermodynamic and kinetic properties for the electrodeposition of lanthanum ions in the LiCl-KCl eutectic salts were determined through the simultaneous curve fitting of multiple LSV curves. For effective nonlinear regression analysis, proper initial values for the characteristic parameters were selected through the comparison of experimental LSV curves with simulated curves. The formal potential, the transfer coefficient and the standard rate constant for the La(III)/La(0) redox couple were estimated to be -2.13 V vs. Ag/Ag^+, 0.61~0.65 and 0.15~0.25 cm/s, respectively. We think that the digital simulation program and the methodology can be usefully applied to collecting the kinetic and thermodynamic information on electrodeposition reactions of the actinide and other lanthanide species.

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