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*Short Communication*

# Electrochemical Reaction of Yb(III)/Yb(II) at Tungsten Electrodes in LiCl-KCl Eutectic Melts

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The electrode reaction of the Yb(III)/Yb(II) redox couple at W electrodes in the LiCl-KCl eutectic solutions has been studied using linear sweep voltammetry (LSV) and digital simulation method. In this work, the formal potential ($E^{o'}$), standard rate constant ($k^{o}$) and transfer coefficient ($\alpha$) of the Yb(III)/Yb(II) redox system have been determined by a simultaneous curve fitting analysis for a series of LSV curves which were recorded in various scan rates. The regression analysis results showed that the electrode reaction ($Yb^{3+} + e^{-} \rightarrow Yb^{2+}$) is quasi-reversible process. The formal potential, transfer coefficient and standard rate constant for the Yb(III)/Yb(II) redox reaction at W electrodes were –0.49 V vs. $Ag/Ag^{+}$, 0.61, $2.7\times10^{-2}$ cm/s, respectively.

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**Keywords:** Yb(III)/Yb(II)**,** LiCl-KCl Eutectic Melts, W Electrode, Formal Potential, Transfer Coefficient, Standard Rate Constant

## 1. INTRODUCTION

The pyrochemical reprocessing technique has been considered as one of promising routes for the proliferation resistance and the long-term radioactive waste reduction[1,2]. In the electrowinning process, the rare earth element fission products (REEs) are co-deposited with the uranium and transuranium elements at a liquid cadmium cathode. To minimize the deposition of REEs is the key issue of the separation technique because the REEs have neutronic poison effect. It is not easy to effectively separate actinides from REEs since actinides have very similar electrochemical properties to those of REEs. For the optimization of the separation process, it is very important to collect basic information on the electrochemical characteristics of REEs.

Recently, many studies on the thermodynamic properties such as the standard potential of the electrode reactions of REEs have been reported[1,3-5]. So far, however, there is too little information on the kinetic properties of REEs in molten chlorides. Bermejo at al. reported the kinetic and thermodynamic data of the Eu(III)/Eu(II) redox couple from a single CV curve[6]. For a specific CV curve, in general, there could be multiple answers to exactly describe the CV curve. So, it is not a good approach to make a determination of the kinetic and thermodynamic parameters from a single CV curve. Recently, we have reported that the standard rate constant, standard potential and transfer coefficient for the $Sm^{3+}/Sm^{2+}$ can be simultaneously determined by using six CV curves[7].

In this study, we have applied the new approach to elucidate the electrode reaction of Yb which is one of abundant REE fission products. Here, a newly developed homemade program is used to improve accuracy of nonlinear curve fitting. In addition, linear sweep voltammetry (LVS) curves are used instead of CV curves to reduce the complicacy of nonlinear regression analysis.

## 2. EXPERIMENTAL SECTION

The electrochemical experiments were performed at the high-temperature electrochemical cell installed under an Ar-filled glove box. A quartz cell with three electrodes was used to get LSV curves. The concentration of the water and oxygen was controlled below 5 ppm during electrochemical experiments. Anhydrous LiCl (assay = 99.9%), KCl(assay = 99.9%), $YbCl_3$ (assay = 99.99%) were obtained from Aldrich and dehydrated inside a glove box. The final concentration of Yb(III) in LiCl-KCl media was 0.080 M. W rods (1 mm in diameter, Alfa Aesar Co.) were used as the inert working electrodes, and glassy carbon rods (3 mm in diameter, Alfa Aesar Co.) used as the counter electrode. They were immersed into the molten salt solution. The practical surface area of the working electrodes was estimated from the immersion depth of the electrode after each experiment. $Ag/Ag^+$ electrode systems served as a reference electrode, the detail of which was described elsewhere[5]. The temperature of a molten salt solution was maintained at 773±2 K.

To determine the characteristic parameters ($E^{o'}$, $k^o$, $\alpha$) for the Yb(III)/Yb(II) redox couple, linear sweep voltammetry (LVS) curves were taken at various scan rates in the potential range of 0.0 to -1.0 V vs. $Ag/Ag^+$. Simultaneous curve fittings for six LSV curves were carried out with homemade software which was newly developed on the basis of the Crank-Nicholson method[8]. The scan rate for the linear sweep voltammetry was chosen between 0.5 V/s and 10 V/s. To get a pure faradaic response, the ohmic drop compensation was applied.

To avoid divergence in regression analysis, the diffusion coefficient of Yb(III) was determined from the chronoamperometric method. To get the chronoamperometric current (total current) at the LiCl-KCl eutectic melt with $Yb^{3+}$, the step potential of 0.0 to −1.0 V was applied to the W working electrode. Non-faradaic chronoamperometric response (charging current) was measured in the blank solution without $Yb^{3+}$ under the same condition. Pure faradaic currents were obtained by subtracting the charging current from the total current. Chronoamperometric data at a short time region less than 20 msec were not used for the determination of diffusion coefficient ($D$) because of the potentiostatic limitations. All electrochemical measurements were carried out with VMP3 potentiostat (BioLogic Science Instruments).

## 3. RESULTS AND DISCUSSION

The chronoamperometric response for a faradaic reaction is described by the Cottrell equation where current is proportional to $D^{1/2}$ and $t^{-1/2}$. For the linear regression analysis, the chronoamperometric current was plotted versus $t^{-1/2}$.

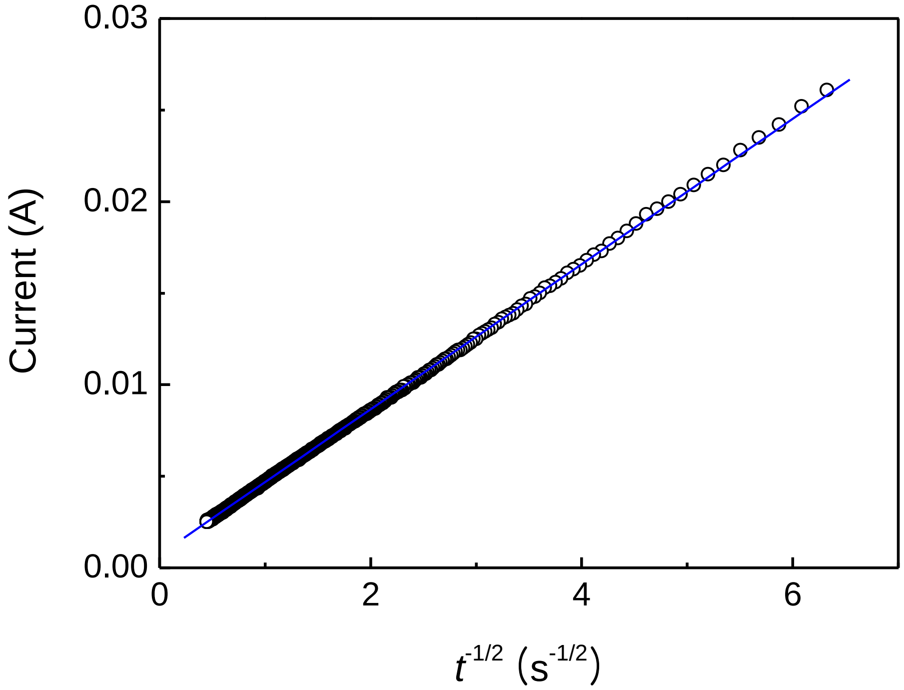

**Figure 1.** Chronoamperometric response (○) for the electrode reaction of Yb(III) to Yb(II) and the corresponding linear regression line (−).

Fig. 1 shows the result of the linear regression analysis of the reduction of Yb(III) to Yb(II). All the experimental data were well fitted to the linear regression line ($R^2 > 0.999$). The diffusion coefficient of Yb calculated from the slope of the regression line was $1.68\times10^{-5}$ $cm^2/s$.

Homemade digital simulation program, which was coded on the basis of the Butler-Volmer kinetic model and the Fick's first and second equations, was used for the regression analysis of LSV curves[9]. In general, the initial values of characteristic parameters such as formal potential, standard rate constant and transfer coefficient are very important in the nonlinear regression analysis. To get appropriate initial value sets for the characteristic parameters, many theoretical LSV curves were simulated at various conditions with the homemade program. One general feature was that the calculated LSV curves were shown to be a reversible system regardless of α value when the standard rate constant is higher than 1.0 cm/s.

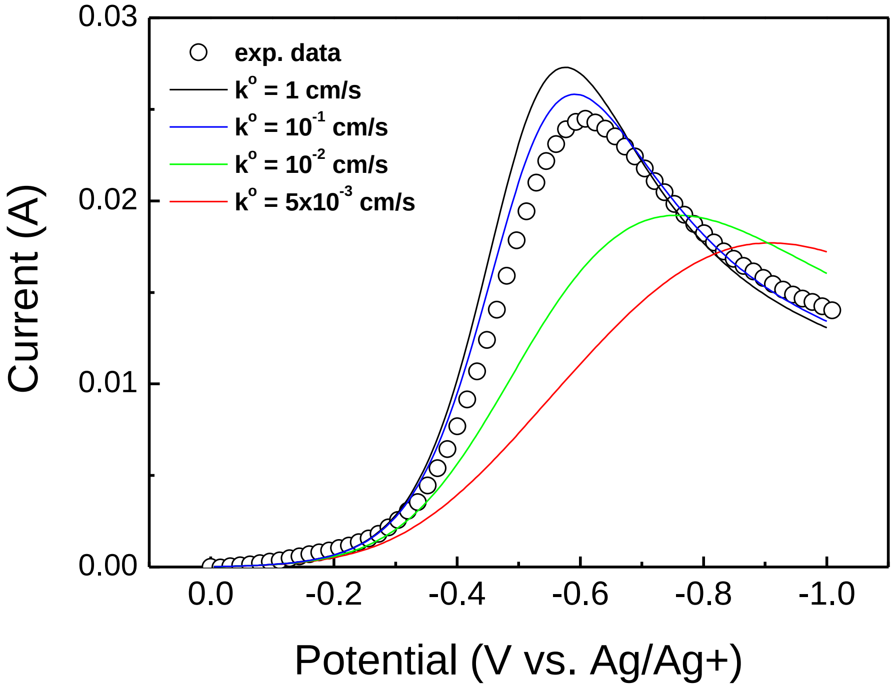

**Figure 2.** Experimental LSV data (○) obtained at a scan rate of 3 V/s and theoretical curves (−) calculated under the following conditions: $E^{0'} = -0.5$; $\alpha = 0.3$; $k^o = 1$ to $5\times10^{-3}$ cm/s; $D = 1.68\times10^{-5}$ cm$^2$/s; T = 773 K, scan rate = 3 V/s.

Fig. 2 shows the comparison of experimental data (scan rate = 3 V/s) with the simulated LSV curves which were obtained at the fixed α value of 0.3 for various $k^o$ values (1.0 to $5\times10^{-3}$ cm/s) for the following electrode reaction of Yb(III) to Yb(II):

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

where $E^{0'}$, $k^o$ and α value are the formal potential, the standard rate constant and the transfer coefficient for the Yb(III)/Yb(II) redox couple, respectively. At α value = 0.3, the theoretical LSV curve was similar to experimental data when the $k^o$ value was $1.0\times10^{-1}$ cm/s. Fig. 3 shows the comparison of experimental data (scan rate = 3 V/s) with the LSV curves simulated at the fixed α value of 0.5. It was found at α value = 0.5 that the LSV curves approximately approached the experimental data when the $k^o$ values were $1.0\times10^{-1}$ and $1.0\times10^{-2}$. In addition, it was observed at α value = 0.7 that the LSV curves simulated with the $k^o$ values of $1.0\times10^{-1}$ and $1.0\times10^{-2}$ closely approximated the experimental data (Fig. 4). In result, the following five initial value sets of main parameters were chosen for effective nonlinear regression analysis: $E^{o'} = -0.5$ V, $k^o = 1.0\times10^{-1}$ cm/s at $\alpha = 0.3$; $E^{o'} = -0.5$ V, $k^o = 1.0\times10^{-1}$, $1.0\times10^{-2}$ cm/s at $\alpha = 0.5$; $E^{o'} = -0.5$ V, $k^o = 1.0\times10^{-1}$, $1.0\times10^{-2}$

cm/s at α = 0.7. The diffusion coefficients of Yb(III) and Yb(II) ions were assumed to be identical to avoid divergence during the nonlinear regression analysis of LSV curves.

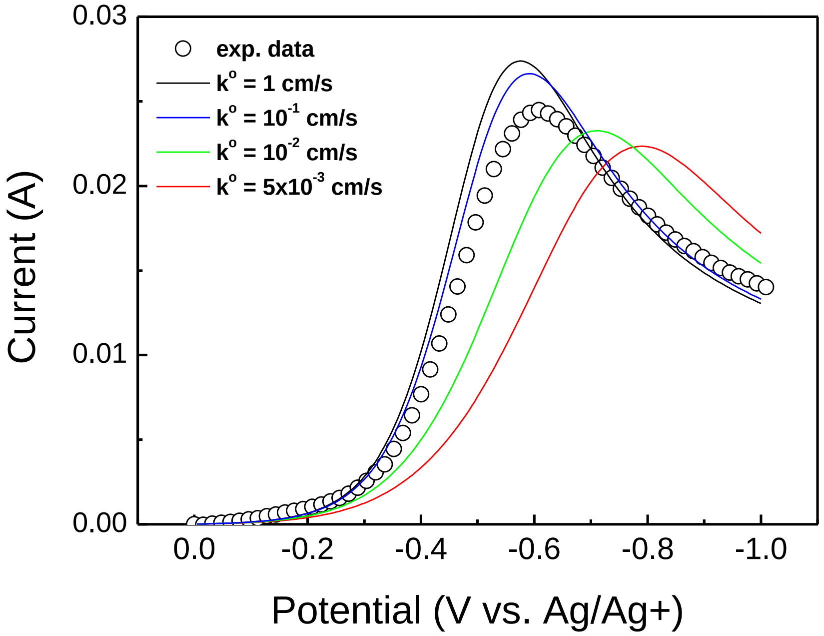

**Figure 3.** Experimental LSV data (○) obtained at a scan rate of 3 V/s and theoretical curves (−) calculated under the following conditions: $E^{0'}$ = –0.5; $\alpha$ = 0.5; $k^o$ = 1 to $5\times10^{-3}$ cm/s; $D$ = $1.68\times10^{-5}$ cm$^2$/s; T = 773 K, scan rate = 3 V/s.

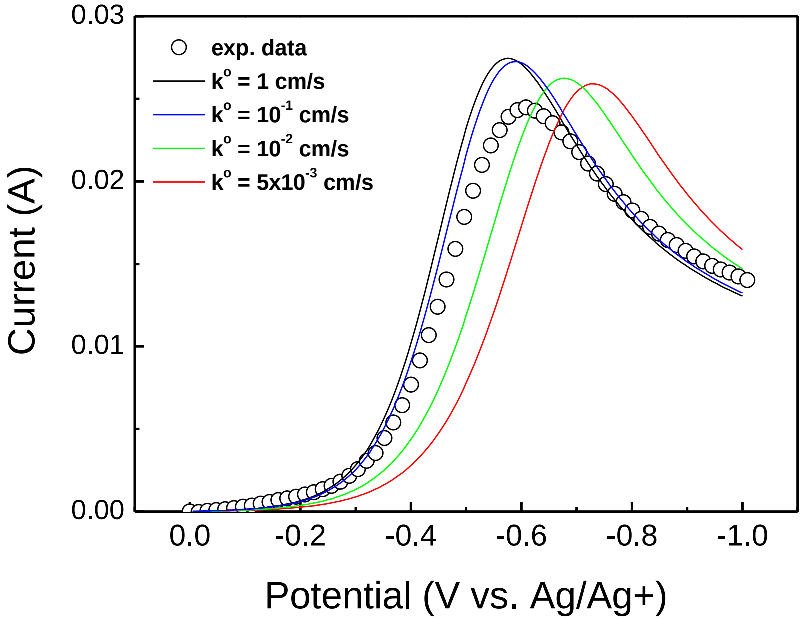

**Figure 4.** Experimental LSV data (○) obtained at a scan rate of 3 V/s and theoretical curves (−) calculated under the following conditions: $E^{0'}$ = –0.5; $\alpha$ = 0.7; $k^o$ = 1 to $5\times10^{-3}$ cm/s; $D$ = $1.68\times10^{-5}$ cm$^2$/s; T = 773 K, scan rate = 3 V/s.

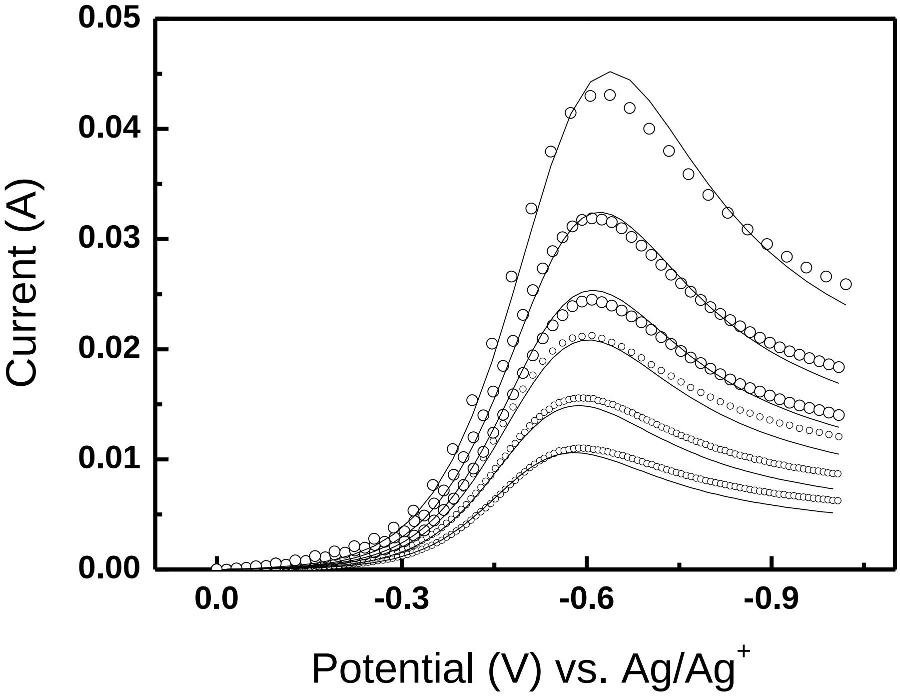

**Figure 5.** Results (−) of simultaneous curve fittings to the experimental LSV data (○) taken at the various scan rates of 0.5, 1, 2, 3, 5 and 10 V/s under the following initial condition: $E^{0'} = -0.5$; $\alpha = 0.5$; $k^o = 1\times10^{-2}$ cm/s.

Fig. 5 shows one example of the simulated curves adjusted to the experimental LSV data (open circle) obtained at different scan rates (0.5, 1, 2, 3, 5, 10 V/s). It is clearly seen that most of experimental data are well fitted to the simulated curves at the six scan rates. The excellent curve fitting results indicate the accuracy of the newly developed simulation technique. Table 1 presents the results of nonlinear regression analysis for the LSV curves, which were carried out at the five initial conditions.

**Table 1**. Fitted parameters for the electrochemical reduction of Yb(III) to Yb(II) in a LiCl-KCl eutectic melt at a W rod electrode.

| Initial values | | Regression analysis results | | |
|---|---|---|---|---|
| α | k$^o$ (cm/s) | E$^{o'}$ (V vs. Ag/Ag$^+$) | α | k$^o$ (cm/s) |
| 0.3 | $1.0\times10^{-1}$ | -0.47 | 0.58 | $2.8\times10^{-2}$ |
| 0.5 | $1.0\times10^{-1}$ | -0.50 | 0.61 | $2.7\times10^{-2}$ |
| 0.5 | $1.0\times10^{-2}$ | -0.49 | 0.61 | $2.9\times10^{-2}$ |
| 0.7 | $1.0\times10^{-1}$ | -0.48 | 0.62 | $2.5\times10^{-2}$ |
| 0.7 | $1.0\times10^{-2}$ | -0.50 | 0.63 | $2.6\times10^{-2}$ |

It was found that the values of the fitted parameters were very similar to one another regardless of the initial values which were predetermined by trial and error. For the first time, to our knowledge, the standard rate constant for the redox reaction of REE was measured from multiple LSV curves. The standard rate constant of the Yb(III)/Yb(II) redox couple was $2.7\times10^{-2}$ cm/s which is slightly higher than that ($1.7\times10^{-2}$ cm/s) of Sm(III)/Sm(II) redox system[7]. The value of the transfer coefficient ($\alpha$) of the Yb(III)/Yb(II) couple was 0.61 which is very similar to that (0.60) of Sm(III)/Sm(II) couple, indicating that the energy barrier for activation is asymmetric[9].

## 4. CONCLUSION

The thermodynamic and kinetic parameters for the Yb(III)/Yb(II) redox couple in LiCl-KCl eutectic melts were simultaneously determined from the LSV curve fittings by the homemade digital simulation program. Nonlinear regression analysis was carried out for the LSV curves obtained at different scan rates of 0.5 to 10 V/s. Various initial value sets of the characteristic parameters such formal potential ($E^{o'}$), transfer coefficient ($\alpha$) and standard rate constant ($k^o$), which were predetermined by trial and error, were applied to the nonlinear regression analysis. It was found that the values of the fitted parameters were very similar to one another regardless of the initial conditions. The formal potential, the transfer coefficient and the standard rate constant for the Yb(III)/Yb(II) redox system, which were extracted from the LSV curve fittings, were -0.49 V vs. $Ag/Ag^+$, 0.61 and $2.7\times10^{-2}$ cm/s, respectively. We think that the basic information on the electrochemical properties of the Yb(III)/Yb(II) redox couple would be usefully used in the development of the pyrochemical separation techniques.

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