Electrochemical Studies on Lanthanum Ions in Molten LiCl-KCl-eutectic Mixture

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We have investigated the electrochemical behaviour of lanthanum ions in a eutectic molten mixture of LiCl and KCl, using linear sweep voltammetry, as well as semi-integration and semi-differentiation of cyclic voltammograms. It was found that the reduction of La^{3+} is quasi-reversible, and that the obtained diffusion coefficient of La^{3+} is consistent with that estimated from thermodynamic data. The electrochemical reduction, diffusion of La^{3+} in LiCl-KCl, and the structure and stability of the complex ion are discussed.

Key words: Diffusion Coefficient; Electrochemical Behavior; Lanthanum; Molten Salts.

We have investigated the electrochemical behavior of La^{3+}, using cyclic voltammtery, and measured the diffusion coefficient of La^{3+} in LiCl-KCl eutectic.

Experimental

The reagents were LiCl (Wako Chem. Ind. Ltd.: $>$ 99.5%), KCl (Wako Chem. Ind. Ltd.: $>$ 99.5%) and anhydrous LaCl$_3$ (Aldrich, 99.99%). The LiCl-KCl eutectic mixture was introduced into a quartz cell, dehydrated by heating under vacuum at 573 K for 24 hr, and then melted. Anhydrous LaCl$_3$ was used without pretreatment because of its high purity. All measurements were carried out under an atmosphere of carefully purified argon. A schematic view of the experimental apparatus is shown depicted in Figure 1. The temperature was kept within ±1 K by a PID controller.

Tungsten wire of 1 mm diameter was employed as working- and counter electrode. Its surface was polished with No. 2000 enemy paper, washed in diluted nitric acid and in distilled water with an ultrasonic cleaner. A Pt wire of 1 mm diameter was applied as quasi-reference electrode because also at high temperature its potential was sufficiently stable. The electrochemical measurements were made with a potentio/galvanostat (Type 2001, Toho Tech.) with an X-Y recorder (Model F-45D, Riken Denshi Co. Ltd.).

Results and Discussion

The kinetic parameters and the diffusion coefficients were obtained by conventional, semi-integral and semi-differential methods. The derived properties were compared with each other as follows.

(a) Conventional electroanalysis of a series of voltammograms: Cyclic voltammograms with LaCl$_3$ in molten LiCl-KCl mixtures at 773 K are presented in Figure 2. One notices one peak around -1.0 V, which was attributed to the reduction of La^{3+}, estimating from the concentration of LaCl$_3$ and the standard electromotive forces [1]. The shape of the peak suggests the formation of an insoluble compound. The corresponding oxidation peak occurs around -0.6 V. As can be seen in Fig. 3, the peak current is proportional to the square root of the sweep rate of potential, and the peak potential becomes more negative area with increasing sweep rate. In keeping with the theory of linear voltammetry, the analysis of this dependence shows that the reduction of La^{3+} in this melt is an irreversible step under diffusion control. The number of electrons participating for the reduction was calculated from the equation [2].

$$E_\mathrm{p} - E_{\mathrm{p}/2} = 1.857RT/\alpha n_\mathrm{a}F, \tag{1}$$

where E_p and $E_{\mathrm{p}/2}$ are the peak potential and the half peak potential, respectively, α is a transfer coefficient, and F the Faraday constant. The diffusion coefficient of La^{3+} was determined using the following equation for the case of a diffusion-controlled formation of a substance insoluble in the melt:

$$i_\mathrm{p} = 0.6105 \cdot 10^{-3} nFCAD^{1/2}v^{1/2}(nF/RT)^{1/2}, \tag{2}$$

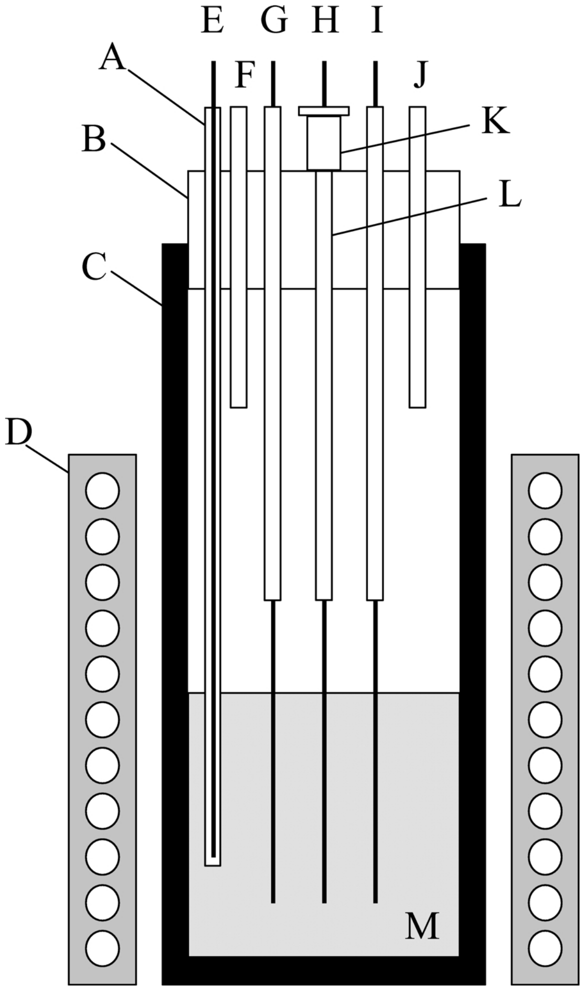

Fig. 1. The schematic view of the apparatus used in the electrochemical measurements A: Quartz tube, B: Silicon stopper, C: Quartz vessel, D: Electric furnace, E: Thermocouple, F: Ar gas inlet, G: Pt quasi-reference electrode, H: Tungsten working electrode W. E., I: Tungsten counter electrode, J: Ar gas outlet, K: Spacer adjusting the surface area of W. E., L: Quartz tube (covering W. E.), M: Molten salts.

where i_p is the peak current, C the bulk concentration, A the surface area, and v the sweep rate. This equation is widely used in electrochemical works cited in reference [3]. The obtained electron transferred and diffusion coefficient are tabulated in Table 1.

(b) Semi-integral and semi-differential electroanalysis of the cathodic voltammogram: The computer treatment of the results allows convolution of the voltammograms. An example of convolution with functions $t^{\pm 1/2}$ (semi-integration and semi-differentiation) of the voltammogram of the process

Table 1. The kinetic parameters and the diffusion coefficient of La^{3+} in molten LiCl-KCl eutectic at 773 K.

$\alpha n_a{}^*$	$k^0 \cdot 10^6$/ $(m \cdot s^{-1})^{**}$	$D \cdot 10^5$/ $(cm^2 \cdot s^{-1})^*$	Method
2.97 ± 0.06	–	2.1 ± 0.5	conventional
2.87 ± 0.12	1.7 ± 0.6	2.9 ± 0.4	semi-integration
2.84 ± 0.08	–	2.4 ± 0.5	semi-differentiation

* The errors of αn_a and D are due to the potential and current in the voltammogram. ** The error of k^0 is due to the least squares method.

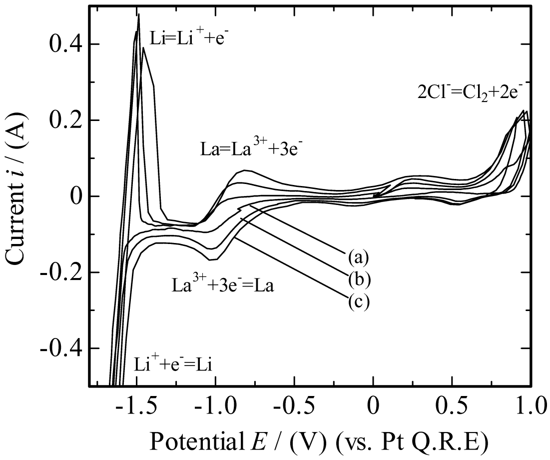

Fig. 2. Cyclic voltammograms of $LaCl_3$ in molten LiCl-KCl with various sweep rates, (a) 0.1 V/s, (b) 0.3 V/s, (c) 0.5 V/s at 773 K.

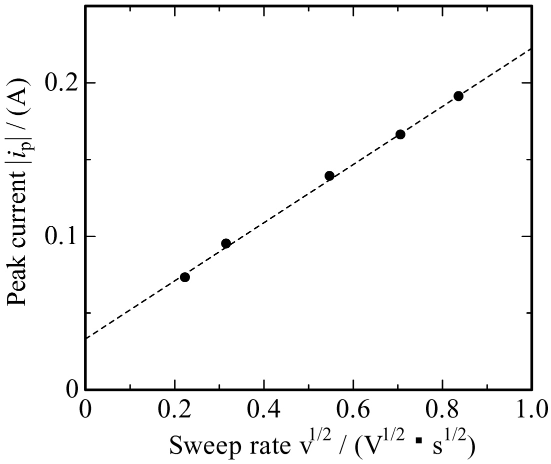

Fig. 3. Relation between the square root of the sweep rate and the peak current for the reduction of La^{3+} at 773 K.

of reduction for La^{3+} is presented in Figure 4. Semi-integration of the cyclic voltammogram results in the production of an S-shaped curve (Fig. 4(b)), where the peaks on the voltammograms are displayed with waves similar to the polarographic ones. In this case,

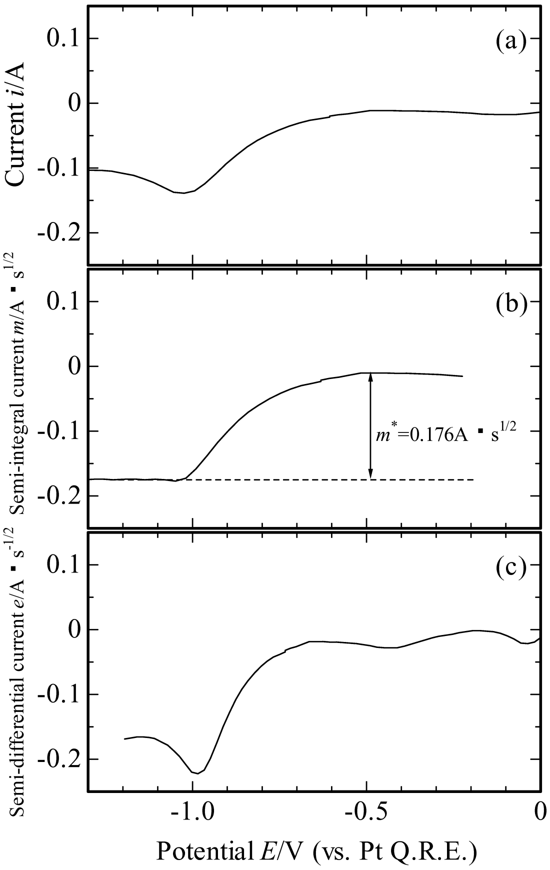

Fig. 4. The reduction peak of La^{3+} by (a) voltammogram with 0.3 V/s, (b) semi-integral analysis curve and (c) semi-differential analysis curve in molten LiCl-KCl eutectic at 773 K.

the height of the wave does not depend on the sweep rate and is not sensitive to the IR drop. For sweep rates between 0.1 and 0.9 V/s, the convolution current had a constant value of $m^* = 0.176\text{A} \cdot \text{s}^{1/2}$. The occurrence of a plateau in the region of the cathodic potential proves that the rate of transfer is limited by diffusion; the height of the plateau is given by [4 – 6]

$$m^* = n_\text{a} FAC\sqrt{D}. \tag{3}$$

Assuming that the number of electrons transferred is 3, this equation enables to calculate the diffusion coefficients listed in Table 1. In addition, the kinetic parameters for the reduction peak of La^{3+} are evaluated as an irreversible or a quasi-reversible system by adopting the equation

$$E = E^0 + \frac{RT}{\alpha n_\text{a} F} \ln \frac{k^0}{D^{1/2}} + \frac{RT}{\alpha n_\text{a} F} \ln \frac{m^*(t)}{i(t)}, \tag{4}$$

where E is the apparent standard potential, E^0 the equilibrium potential, m a semi-integral value calculated from the current as a function of time t, and i the current. According to (4), a plot of E vs. $\ln\{(m^* - m(t))/i(t)\}$ gives a straight line having a slope of $RT/\alpha n_\text{a} F$. The standard rate constants calculated by the semi-integral electroanalysis are summarized in Table 1. This value obeys the Matsuda and Ayabe criterion [7] for a quasi-reversible system

$$2.0 \cdot 10^{-7}(n_\text{a} v)^{1/2} < k^0 < 0.3 \cdot 10^{-2}(n_\text{a} v)^{1/2}$$

which yields in our conditions

$$1.9 \cdot 10^{-7} < k^0 < 2.8 \cdot 10^{-3}.$$

Semi-differentiation of a voltammogram (Fig. 4(c)) makes it possible to determine the number of valence electrons included in the electrode reaction and the diffusion coefficient, using

$$W_\text{p} = 2.94RT/\alpha n_\text{a} F. \tag{5}$$

In the semi-differential electroanalysis, which provides a clearer peak than the conventional cyclic voltammogram, the diffusion coefficient can be calculated from the equation

$$e_\text{p} = \frac{\alpha n_\text{a}^2 F^2 AvCD^{1/2}}{3.367RT} \tag{6}$$

for the peak height e_p [8 – 10].

The obtained kinetic parameters, calculated from above equations, are given in Table 1. The values estimated from a series of conventional and convolutional analysis show good agreement with each other.

(c) Electrochemical behavior of La^{3+} in LiCl-KCl and stability of complex ions: From a series of electrochemical researches, the cathodic electrodeposition of lanthanum metal was three-electrons reaction and was ascertained as a quasi-reversible reaction estimating from the standard rate constant according to the convolutional electroanalysis. The diffusion coefficients obtained from various electroanalyses show good agreement with each other. The propriety for the temperature dependence of the diffusion coefficients was discussed as follows.

There are some data about the activation energies, ΔH, for diffusion of lanthanum, which are calculated from the following equation obtained by Smirnov [11] and Sokolovskii [12].

$$-\frac{\Delta H}{2.3R} = \frac{\partial \log D}{\partial (1/T)}. \tag{7}$$

From these data it is expected that the interdiffusion in the LiCl-KCl eutectic melt depends largely on the characteristics of the diffusing cations, probably the coulombic interaction between the cations and surrounding anions, or the stability of the complex ions. The trivalent lanthanide trivalent ions in LiCl-KCl are expected to exist in the form of octahedral complex ions. It is supposed that, the smaller the center cation, the higher the stability of the complex ion, i. e. the bonding between the center metal cation and chloride ions. This relation between ionic radii of the lanthanide ions and the stability of their complex ions could also be expected from the thermodynamic data. Diffusion data of other lanthanides and computational studies of the structure and transport processes in molten salts would be necessary for a more quantitative analysis.

Conclusion

For a feasible recovery process of lanthanides, electrochemical measurements on diluted $LaCl_3$ were performed in eutectic LiCl-KCl melts. The convolution voltammogram results did show that the reduction process of La^{3+} is quasi-reversible. The diffusion coefficients of La^{3+} agree well with the values determined by electroanalysis and were discussed in connection with the stability of the complexes.

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