Rotating Disk Electrode Study of a Ti$^{3+}$/Ti Electrode in LiCl–KCl Eutectic and NaCl–MgCl$_2$–KCl Melt†

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The electrochemical behavior of Ti$^{3+}$/Ti electrodes in alkali-chloride melts has been studied using the rotating disk electrode (RDE) technique. The steady state polarization curves and results from the RDE analysis revealed that the cathodic reduction of the Ti$^{3+}$/Ti electrode in LiCl–KCl eutectic consists of a two-step reduction in which the latter step, corresponding to the reduction of Ti$^{2+}$ to Ti, is accompanied by the following inverse-disproportionation reaction,

$$2\text{Ti}^{3+} + \text{Ti} \rightarrow 3\text{Ti}^{2+}.$$  

Comparison of the cathodic behavior of the Ti$^{3+}$/Ti electrode in LiCl–KCl eutectic with that in NaCl–MgCl$_2$–KCl melt indicates that the lower valence Ti$^{2+}$ is stable in the latter melt where high cathodic current results in a smooth deposit. The diffusion coefficients of Ti$^{3+}$ in these melts were found to be $4.6 \times 10^{-10}$ (LiCl–KCl eutectic) and $1.7 \times 10^{-10}$ m$^2$s$^{-1}$ (NaCl–MgCl$_2$–KCl melt), respectively.

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Keywords: rotating disk electrode, LiCl–KCl eutectic, tri-valent titanium ion, titanium electrodeposition

I. Introduction

The electrochemical behavior of Ti ions in molten salts has been studied using electrochemical and chemical methods$^{(11-40)}$. Metal/Metal ion electrodes in LiCl–KCl eutectic melts have been extensively studied using the electrochemical polarization technique, the voltage sweep method and the impedance method. The electrochemical study of Ti ions, with respect to the kinetic parameters, thermodynamic equilibrium constants and morphology of the electrodeposits has attracted a great deal of interest. In the case of Ti ion reduction in LiCl–KCl eutectic, Ti$^{3+}$ ions proceed via a two step reaction. However, there still exists a lack of understanding of the electrochemical behavior of the Ti$^{3+}$/Ti system in molten salts. It is difficult to determine the reaction mechanism only on the basis of steady state polarization data, i.e. an electrochemical technique is instructive in evaluating the contribution of the diffusion process to the cathodic reduction of a metal ion.

On the other hand, LiCl–KCl eutectic is known as a hygroscopic melt, which necessitates careful handling and a dehydration pretreatment$^{(5)}$. Further, a reliable masking of the electrode surface is very important for the determination of current density in molten salt systems.

When a rotating disk electrode (RDE) is successfully prepared with a non-conducting sheath surrounding a disk electrode, the kinetic current is extrapolated from the measured current.

In this study, RDE analysis has been applied to the mechanistic study of the Ti$^{3+}$/Ti system in alkali-chloride melts. Tokumoto et al.$^{(00)}$ reported that metallic Ti was electrochemically deposited in NaCl–MgCl$_2$–KCl melt. However, there have only been a few electrochemical studies on the deposition mechanism. RDE analysis has also been applied to the study of the cathodic behavior of Ti$^{3+}$/Ti electrodes in NaCl–MgCl$_2$–KCl melt.

II. Experimental

1. Electrolyte An eutectic mixture (LiCl–KCl=41:59 mol%) was used as a base electrolyte. After melting the mixture under vacuum, the melt was dehydrated using dry HCl and then dry Ar was passed through the melt for 10 ks. MgCl$_2$-BaCl$_2$-CaCl$_2$-KCl-NaCl (22.73:20.45:13.64:4.55:38.63 mol%) was also used as an electrolyte. Crystal water within the reagents was removed by heating under dry Ar and maintained in an oven. This dehydrated mixture was treated in the same manner as above. The procedure for adding TiCl$_3$ and Ti powder to the melt is described as follows; the reagent was transferred from its bottle to the capsule under a flow of dry Ar. The carefully weighed TiCl$_3$ was introduced to the melt through an addition tube. The addition of alkali chloride was performed in the same manner as above$^{(2)}$.

Chemical analysis of the Ti ions$^{(00)}$ was made by sampling the quenched melts. The samples were dissolved in a dilute acidic solution where Ti$^{3+}$ is oxidized to Ti$^{4+}$ qualitatively according to the reaction,


\[
\text{TiCl}_3 + \text{HCl} \rightarrow \text{TiCl}_4 + \frac{1}{2}\text{H}_2. \tag{1}
\]

The amount of \(\text{Ti}^{2+}\) was determined by measuring the amount of \(\text{H}_2\) evolved into a gas burette\(^{(10)}\). The total amount of Ti ion was determined by an oxidation-reduction titration method\(^{(1)}\). The concentration of \(\text{Ti}^{2+}\) was calculated by subtracting the amount of \(\text{Ti}^{2+}\) from the total amount of Ti ions.

2. Electrode A rotating disk electrode (RDE) was prepared from a rod (\(\phi 3 \text{ mm}, 0.5 \text{ m in length}\) of Ti and austenitic stainless steel (SUS304). The rods were degreased and inserted into an alumina tube (outer diameter \(8 \text{ mm}\)). The gap between the rod and the tube was filled with a powder of Pyrex glass. These rods were heated to melt down the glass powder for 7.2 ks at \(1523 \text{ to } 1573 \text{ K}\). The RDE was prepared by cutting one end of the rod and polishing the cross-sectional area with \#1500 grid emery paper. The RDE was washed with acetone before the experiments. The other end of the Ti rod was wound and welded with Ni wire (\(\phi 0.5 \text{ mm}\)) to create an electrical lead. The reference electrode consisted of a Ag/Ag\(^+\) (0.1 m.f.\;) electrode with a millilitre membrane. Electrode potentials were referred to the Ag/Ag\(^+\) (0.1 m.f.\;) electrode. The counter electrode was a spiral of Pt or Ti wire (\(\phi 1.0 \text{ mm}\) \(4 \times 10^{-4} \text{ m}^2\) in surface area.

3. Apparatus An electrolytic cell was made from an alumina crucible which was placed at the center of an Infra-red Gold Furnace (Shinku Riko Co. Ltd.). The temperature of the melt was kept constant at \(773 \text{ K}\) for the LiCl–KCl eut. and at \(993 \pm 1 \text{ K}\) for NaCl–MgCl\(_2\)–KCl melt. Ar was dried through silica gel, CaCl\(_2\) and P\(_2\)O\(_5\) columns. The experimental apparatus is shown in Fig. 1. It consists of a motor drive machine (Nikko Keisoku RRDE-1, SC-3), a three electrode type electrochemical cell and a transmission for providing rotation force. Thus, a shaft of the RDE is linked to a motor drive indirectly by a V-belt. An electrical contact between the RDE and potentiostat was made using an Ag brush surrounding the shaft. All the equipment, RDE devices, furnace, etc. were installed in a glove box under a flow of nitrogen gas. The electrical noise and mechanical vibration related to the RDE device was greatly reduced by repeated technical trials.

III. Results and Discussion

1. Cathodic polarization curves of the \(\text{Ti}^{2+}/\text{Ti}\) electrode in LiCl–KCl eut.

The cathodic polarization curves for the \(\text{Ti}^{2+}\) on the Pt electrode reveal three reduction peaks at \(-0.7 \text{ to } -0.8, -1.2 \text{ and } -1.5 \text{ V} \) (cf., Fig. 2). Since the appearance of the current peaks at \(-0.7 \text{ to } -0.8 \text{ and } -1.2 \text{ V}\) has not yet been elucidated, the cathodic currents corresponding to two peaks and a plateau are referred to the onset potentials of these current waves (nobler ones than those of the current peaks), those of which are \(-0.6, -0.8 \text{ and } -1.2 \text{ V}\). The nobler reduction wave at \(-0.6 \text{ V}\) was shown to be attributable to the catalytic reduction of \(\text{Ti}^{4+}\) to \(\text{Ti}^{3+}\) \((2)\).

At \(-0.8 \text{ V}\), the reduction wave corresponds to the discharge reaction of \(\text{Ti}^{3+}\) to \(\text{Ti}^{2+}\) (eq. (2)). At potentials of less than \(-1.2 \text{ V}\), the second step appeared as a limiting current and was due to the consecutive reduction of \(\text{Ti}^{2+}\) to Ti where the reduction is controlled by the diffusion of \(\text{Ti}^{2+}\) (eq. (4))\(^{(10)}\). The reduction of \(\text{Ti}^{3+}\) occurred in a two step mechanism, depending on the potential. The data obtained are consistent with those published by Ferry et al.\(^{(10)}\). It was noted that the increase in \(\text{Ti}^{3+}\) concentration in the melt results in the precipitation of TiCl\(_3\) due to its extremely low solubility\(^{(10)}\). Matsumoto et al.\(^{(10)}\) reported that a cyclic voltammogram for a \(\text{Ti}^{3+}/\text{Ti}^{2+}\) redox electrode showed a rather complicated behavior in relation to the disproportionation reaction eq. (3),
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Fig. 2. Cathodic polarization curves for the Ti$^{3+}$/Ti electrode on Pt in LiCl-KCl eut. containing TiCl$_3$ and Ti at 773 K. Sweep rate: $1 \times 10^{-3}$ V s$^{-1}$.

\[
\begin{align*}
\text{Ti}^{3+} + e^- & \rightarrow \text{Ti}^{2+} \quad (2) \\
2\text{Ti}^{2+} + \text{Ti} & \rightarrow 3\text{Ti}^{2+} \quad (3) \\
\text{Ti}^{2+} + 2e^- & \rightarrow \text{Ti}. \quad (4)
\end{align*}
\]

These results suggest that the first reduction step of Ti$^{2+}$ to Ti$^{3+}$ stimulates to a lesser extent the formation of Ti$^{2+}$ at the electrode surface due to the low solubility and the influence of the chemical reaction eq. (3). Then, as the above reactions proceeded, the equilibrium concentration of Ti$^{3+}$ and Ti was established. Consequently, only a black powder of TiCl$_3$ was deposited in the melt during the reduction at $-1.2$ V. At $-1.3$ V, dendritic Ti was deposited on the Pt substrate. The dendritic deposit was identified as Ti metal using XRD$^{(2)}$. It is inferred that during the discharge at $-1.3$ V the cathodic reduction of Ti$^{2+}$ occurs in a manner controlled by a diffusion process accompanied by the preceding reaction eq. (3)$^{(0,2)}$.

2. RDE voltammograms for Ti$^{3+}$/Ti on SUS304 electrode in LiCl-KCl eut.

As discussed above, the cathodic reduction of Ti$^{3+}$ is affected by the preceding chemical reaction of eq. (3). Therefore, the RDE analysis is an effective method for understanding the reduction mechanism of Ti$^{3+}$. The RDE analysis has been applied to the electrode processes and has proved to be useful in the study of a chemical reaction coupled with an electron transfer reaction.

If the preceding reaction is represented by eq. (5), and the forward and backward rates are high, then the electron transfer step, eq. (6), involves an electroactive species, O, generated by a preceding chemical reaction,

\[
\begin{align*}
k_f \\
Y & \rightleftharpoons O \quad (5) \\
k_b \\
O + ne^- & \rightleftharpoons R \quad (6)
\end{align*}
\]

where eqs. (5) and (6) correspond to eqs. (3) and (4) respectively. In this case, a species Y and species O (eq. (5)) correspond to Ti$^{3+}$+Ti and Ti$^{2+}$ (eq. (3)), respectively. For the reaction of Ti$^{3+}$+Ti (eq. (3)) we obtain the forward reaction rate as a function of the concentration of Ti$^{3+}$ and the total surface area of Ti powder supposing that both the reactions proceed in the vicinity of Ti surfaces under an equilibrium state. Similaryl for the reaction of Ti$^{2+}$ we obtain the backward reaction rate as a function of Ti$^{3+}$. Since it is inconvenient to calculate the real surface area of the finely dispersed Ti powders, we can simplify the preceding reaction kinetics by writing both the rates as the first order reactions with Ti$^{3+}$ and Ti$^{2+}$, irrespective of the Ti surface area. Hence, the kinetic equation for the forward reaction is found to be pseudo first reaction order, because the addition of excess Ti powder gives regular Ti suspended solution (similar to solid metal fog), which behaves like a reactant saturated solution. Whenever, the existence of sponge Ti keeps a large amount of Ti surface area, the rate of the forward reaction would not be affected explicitly by the amount of Ti powder added.

The disk current density, $i$, under such conditions was derived by Levich et al.$^{(10)}$ in terms of a rotating rate $\omega = 2\pi f$ as,

\[
i = \frac{nFDC^*}{1.61D^{1/3}\omega^{-1/2}v^{1/6} + D^{1/2}/Kk^{1/2}} \quad (7)
\]

\[
K = k_f/k_b \quad (8)
\]

\[
k = k_f + k_b \quad (9)
\]

\[
C^* = C_O + C_Y \quad (10)
\]

where $C_O$ and $C_Y$ are the bulk concentrations of the O and Y species, and $k_f$ and $k_b$ are the rate constants of the forward and backward reactions, respectively. $K$ is the equilibrium constant for eq. (5). The first term in the denominator represents the Nernst diffusion layer thickness $\delta$,

\[
\delta = 1.61D^{1/3}\omega^{-1/2}v^{1/6}. \quad (11)
\]

The diffusion limiting current $i_L$ is proportional to the square root of $\omega$, (Levich equation),

\[
i_L = D/\delta = 0.62nFv^{-1/2}C^*\omega^{1/2} \quad (12)
\]

where $v$ is kinematic viscosity defined as $\eta/\rho$. The second term is defined as the reaction layer thickness,

\[
\mu = (D/k)^{1/2}. \quad (13)
\]

As can be seen in eq. (7), the kinetic current ($i_k$) is separated with increasing $\omega (\delta \approx \mu K)$, irrespective of whether $k_f$ is involved in a purely charge transfer or an electron transfer coupled with a chemical reaction. The kinetic current is expressed as,
\[ i_k = nFD^{1/2}C^*Kk^{1/2}. \]  

(14)

At low \( \omega (\delta \gg \mu K) \), the second term in the denominator is negligible, and the current is the diffusion controlled \( i_k \). Alternatively, eq. (7) is also modified in the following\(^{14} \),

\[ \frac{i}{\omega^{1/2}} = \frac{i_k}{\omega^{1/2}} - i \frac{D^{1/6}}{1.61V^{1/6}KK^{1/2}}. \]

(15)

Thus, \( K \) can be obtained from the slope of a straight line of an \( i/\omega^{1/2} \) plot at less noble potentials corresponding to the discharge of \( \text{Ti}^{2+} \). The graph (Fig. 3) shows a straight line from which the value of \( Kk^{1/2} \) was calculated to be 2.48 s\(^{-1/2} \). This is not the case where the \( i/\omega^{1/2} \) plot shows the values independent of \( i \), assuming that the charge transfer reaction is wholly controlled by diffusion as given by eq. (12). In this way, the value of \( K \) is obtained from that of \( k_t \) and \( k_n \), both of which need to be estimated from the experimental data. The rate constant \( k_t \) for the reduction of \( \text{Ti}^{2+} \) to \( \text{Ti}^{2+} \) is expected to be similar to that of \( \text{Ti}^{2+} + \text{Ti}^{2+} \) in LiCl–KCl eut. assuming that the activity of \( \text{Ti}^{2+} \) is unity. Therefore, we can adopt the reported value of \( k_t = 2.9 \times 10^7 \) s\(^{-1} \) in LiCl–KCl eut. as a first approximation\(^{12} \). Taking into account of the activity of the Ti solid as unity in eq. (3), the value of \( k_n \) was calculated to be 6.9 \times 10^7 s\(^{-1} \). The equilibrium constant \( K_s \) calculated from the values of \( k_t \) and \( k_n \), indicates that the equilibrium of the preceding reaction, eq. (3), is shifted to the left side so that the prevailing ion is \( \text{Ti}^{2+} \) even when Ti powder is introduced to increase the \( \text{Ti}^{2+} \) concentration in the LiCl–KCl eut.

It is informative to compare the voltammograms on the Pt with that of the RDE on Ti. Figure 4 shows the voltammograms on the Ti electrode at various rotation rates in the range 100 ~ 800 min\(^{-1} \). The immersion potential of the Ti electrode showed a less noble potential compared with that of the Pt electrode (Fig. 2) even if the experimental conditions were similar. The cathodic current increases when shifting the potential towards the cathodic direction from the equilibrium potential, and reaches a limiting current which increases with an increase of the rotation rate. The \( 1/i - \omega^{-1/2} \) plot, known as a Koutecky-Levich plot, at \( -1.5 \) V shows a straight line which crosses at the origin. For the plots at \( -1.6 \sim -1.9 \) V, the slopes of the straight lines were lower than those at potentials of \( -2.0 \sim -2.3 \) V. Therefore, at a less noble potential than \( -2.0 \) V, the reactant differs from that at nobler potentials, which suggests a co-operative discharge of \( \text{Li}^+ \) with \( \text{Ti}^{2+} \) ions. As is shown in Fig. 2, the cathodic current in the blank melt increases gradually with decreasing the potential below \( -2.0 \) V, where the \( \text{Li}^+ \) deposition contributes the cathodic reduction.

3. RDE voltammograms for \( \text{Ti}^{2+}/\text{Ti} \) on SUS304 in NaCl–MgCl\(_2\)–KCl melt

If the current is controlled by both mass transport and an activation reaction, the measured current is given by\(^{13} \)

\[ \frac{1}{i} = \frac{1}{i_{ac}} + \frac{1}{0.61nFC^*D^{1/3}v^{-1/6}k^{1/2}}. \]

(16)

where \( i_{ac} \) is an activation-controlled current which can be evaluated by extrapolating the \( 1/i - \omega^{-1/2} \) plot to infinite rotation rate.

Figure 5 shows the voltammograms for SUS304 RDE in NaCl–MgCl\(_2\)–KCl melt at various rotation rates in the range 100 ~ 800 min\(^{-1} \). The currents at these rotation rates increased rapidly in the vicinity of the immersion potential. With decreasing potential, the current exhibits a linear relation to the potential indicating no diffusion limiting current. As is shown before, at potentials below \( -1.3 \) V a limiting current is observed in LiCl–KCl eut.
Fig. 5 Cathodic polarization curves for the Ti$^{4+}$/Ti electrode on SUS304 at various rotation rates in NaCl-MgCl$_2$-KCl melt at 993 K. TiCl$_3$: 0.857 mol%.

(c.f., Fig. 2), while the polarization behavior exhibits a steep rise of the cathodic current below $-1.4$ V in this melt. These cathodic reduction behaviors of Ti$^{2+}$ in LiCl–KCl eut. and this melt are related to the difference of Ti$^{2+}$ stability, which indicated that Ti$^{2+}$ in NaCl-MgCl$_2$–KCl melt is much more stable than that in LiCl–KCl eut. according to the results of the chemical analysis (Table 1).

At potentials below $-1.4$ V, the current increased with potential in an exponential manner, which is characterized by the so-called Tafel behavior. The magnitude of these currents is $0.1 \sim 1.0 \times 10^4$ A m$^{-2}$. As is shown in Figs. 6(a) and (b), the plots of $1/i$ vs. $\omega^{-1/2}$ at potentials of $-0.6$ to $-1.3$ V have straight lines whose slopes depend on the potential. The slopes at $-0.6$ and $-0.8$ V are almost 2.5 and 4 times higher than those at $-1.0$ and $-1.3$ V. From eq. (15), the slope of the $1/i$ vs. $\omega^{-1/2}$ plot is represented by $1.61(nFC^*)^{-1}D^{-2/3}v^{1/6}$. This equation involves the unknown values $nC^*$ and $D^{-2/3}\omega^{1/6}$, where the latter term assumes the same value for Ti$^{2+}$ and Ti$^{4+}$ because $D$ and $v$ for Ti$^{2+}$ and Ti$^{4+}$ do not differ greatly. Further, if the reduction of Ti$^{4+}$ proceeds via two-steps, similar to that described for the LiCl–KCl eut., the value of $nC^*$ for the first step at nobler potentials is 3 times higher than that of $nC^*$ for the second step at less noble potentials. Since this is consistent with the experimental results, it is likely that the first reduction of Ti$^{4+}$ occurs predominantly in the potential range $-0.6$ to $-0.8$ V and the consecutive reduction of Ti$^{2+}$ to Ti occurs at potentials of less than $-1.0$ V. Figure 7 shows the plot of the kinetic currents obtained by extrapolating the $1/i$ vs. $\omega^{-1/2}$ graphs, which reveal first and second current waves, both of which seemed to obey the Tafel relation. Assuming $\alpha=0.5$, the number of electrons transferred is calculated to be 1.36 for the first wave and 1.77 for the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Equilibrium concentrations of Ti ions in LiCl–KCl eut. and NaCl-MgCl$_2$–KCl melt with the existence of TiCl$_3$ and excess amount of Ti powder.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A bath LiCl–KCl eut. (mol%)</td>
<td>B bath NaCl-MgCl$_2$–KCl melt (mol%)</td>
</tr>
<tr>
<td>Ti$^{2+}$</td>
<td>0.2</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>1.4</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>$&lt;2.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

--- Less than detectable limitation.
second wave. Thus, the number of electrons transferred is close to unity and two for the first and second wave, respectively. In Fig. 7, the first current wave shows a diffusion-limited current of $1.75 \times 10^2$ A m$^{-2}$. The dotted line represents the extrapolated Tafel line for the reduction of Ti$^{2+}$ to Ti, which is curved towards the potential axis around the equilibrium potential of Ti$^{2+}$/Ti. In the figure, the reversible potentials of the Ti$^{2+}$/Ti$^{3+}$ and the Ti$^{2+}$/Ti$^{3+}$ Ti electrodes were estimated from the data in NaCl–MgCl$_2$–KCl melt$^{[15]}$. At potentials below $-1.0$ V, the cathodic current is attributed to the reaction of eq. (4), because the reduction of Ti$^{2+}$ to Ti occurs predominantly at less noble potentials than those of Ti$^{4+}$/Ti$^{3+}$ and Ti$^{3+}$/Ti$^{2+}$ electrodes thermodynamically.

4. Chemical stability and mass transfer of Ti$^{2+}$ in LiCl–KCl eut. and NaCl–MgCl$_2$–KCl melt

Preliminary experiments were performed to evaluate the chemically stable Ti ions in the chloride melts. The attainment of an equilibrium condition is dependent on time and the particular atmosphere. Therefore, after the addition of TiCl$_3$ and Ti powder into the melt the mixtures were kept under a flow of dry Ar for 12–35 h to complete the reaction. The results of the chemical analysis are shown in Table I, where LiCl–KCl eut. and NaCl–MgCl$_2$–KCl melt are abbreviated as the bath A and the bath B respectively. The amount of Ti$^{4+}$ is found to be negligibly small even in the high temperature bath B. The difference between the two baths is that the bath A holds the less amount of Ti$^{3+}$ introduced, while the Ti$^{2+}$ concentration in the bath B is higher than Ti$^{3+}$, the Ti$^{2+}$ being mostly converted from Ti$^{3+}$ by eq. (3) in the presence of Ti powder.

The diffusion coefficient of Ti$^{2+}$ was determined by analysis of the voltammograms using eq. (15) for the bath A and eq. (16) for the bath B. The value of \( \nu \)

| Table 2 Diffusion coefficient of Ti ions in molten salts. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Electrolyte                    | Temperature (K) | Measurement     | Reaction         | Diffusion coefficient (m$^2$ s$^{-1}$) | Reference |
| LiCl–KCl                       | 773             | Cronoamperometry | Ti$^{2+}$ + 2e$^-$ → Ti | 4.1 × 10$^{-10}$ | (2) This work |
|                                |                 | RDE             |                  | 4.6 × 10$^{-10}$ |                  |
| LiCl–KCl                       | 743             | Cronoamperometry | Ti$^{2+}$ + e$^-$ → Ti$^{3+}$ | 1.9 ± 0.5 × 10$^{-9}$ | (1)          |
|                                |                 | Cronopotentiometry |              | 1.0 ± 0.1 × 10$^{-9}$ |                  |
| LiCl–KCl                       | 729             | Linear sweep    | Ti$^{2+}$ + 2e$^-$ → Ti | 1.1 × 10$^{-9}$ | (16)         |
| NaCl–KCl                       | 1023            | Linear sweep    | Ti$^{4+}$ + e$^-$ → Ti$^{3+}$ | 1.5 ± 0.5 × 10$^{-9}$ | (17)         |
| MgCl$_2$–BaCl$_2$–CaCl$_2$–NaCl–KCl | 893 | RDE             | Ti$^{2+}$ + 2e$^-$ → Ti | 1.7 × 10$^{-10}$ | This work |
| AlCl$_3$–NaCl                  | 458             | Cronoamperometry | Ti$^{2+}$ → Ti$^{3+}$ + e$^-$ | 2.6 × 10$^{-10}$(1) | (20)         |
|                                |                 | Cronopotentiometry |              | 3.3 × 10$^{-10}$(2) |                  |
|                                |                 | Linear sweep    |                  | 2.5 × 10$^{-10}$(1) |                  |
|                                |                 |                  |                  | 3.0 × 10$^{-10}$(2) |                  |
|                                |                 |                  |                  | 3.1 × 10$^{-10}$(1) |                  |
|                                |                 |                  |                  | 3.9 × 10$^{-10}$(2) |                  |
| LiF–NaF–KF                     | 773             | Linear sweep    | Ti$^{4+}$ + e$^-$ → Ti$^{3+}$ | 2.6 ± 0.5 × 10$^{-10}$ | (18)         |
|                                |                 | Cronoamperometry |              | 1.9 ± 0.4 × 10$^{-10}$ |                  |
| LiF–BeF$_2$–ZrF$_4$            | 773             | Linear sweep    | Ti$^{3+}$ → Ti$^{4+}$ + e$^-$ | 1.0 ± 0.1 × 10$^{-10}$ | (18)         |
|                                |                 | Cronopotentiometry |              | 1.9 ± 0.2 × 10$^{-10}$ |                  |
| NaBF$_4$                       | 693             | Linear sweep    | Ti$^{4+}$ + e$^-$ → Ti$^{3+}$ | 2.6 ± 0.5 × 10$^{-10}$ | (19)         |
|                                |                 | Cronopotentiometry |              | 1.3 ± 0.3 × 10$^{-10}$ |                  |

(1) Ti$^{3+}$: 5.91 × 10$^{-2}$ M. (2) Ti$^{2+}$: 3.34 × 10$^{-2}$ M.
\( (=\eta/\rho) \) is calculated from the values of \( \eta \) and \( \rho \). The values of \( \eta \) and \( \rho \) in LiCl–KCl eutectic are calculated to be \( 2.44 \times 10^{-8} \text{Ns m}^{-2} \) \((15)\) and \( 1.684 \text{kg/dm}^3 \) \((15)\) neglecting the temperature dependence of these values. In MgCl\(_2\)-NaCl–KCl melt (50:30:20 mol\%) at 748 K, these values are approximated to be \( 2.1 \times 10^{-3} \text{Ns m}^{-2} \) and \( 2.0 \text{kg/dm}^3 \) \((15)\). Table 2 shows the diffusion coefficient of Ti\(^{2+}\) and Ti\(^{3+}\), together with the conditions of electrolysis. The diffusion coefficient of Ti\(^{2+}\) using the RDE method is consistent with that obtained by chronom-perometry in LiCl–KCl eutectic. However, the diffusion coefficient of Ti\(^{2+}\) in the bath B was lower than expected. This is because the value of kinematic viscosity \( \nu \) in NaCl–KCl–MgCl\(_2\) melt at 748 K was used without any temperature correction. Further, the progress of the reaction shown in eq. (3) causes the conversion of Ti\(^{3+}\) and Ti to Ti\(^{2+}\), and therefore the initial amount of Ti\(^{3+}\) presumably decreases to some extent. These two factors have the opposite effect on eq. (16). Since the temperature correction of \( \nu \) for NaCl–MgCl\(_2\)–KCl melt is small, the diffusion coefficient of Ti\(^{2+}\) would be slightly higher than that obtained using the RDE measurement with making an appropriate correction for Ti\(^{2+}\) concentration.

In electrodeposition, the cathodic reduction of metal ions to adsorbed atoms is the first step, this being followed by nucleation and crystal growth processes. In the discharge of Ti ions, the parameters such as diffusion coefficient and solubility of Ti ions, can take part in mass transport characteristics. Hence, these parameters are inherently responsible in controlling the morphology of deposits. For example, high solubility of metal ions in a bath would be necessary for controlling the morphology because the cathodic current is increased without any limitation from mass transportation. Thus, fine grain deposits are obtainable by applying a high overpotential on an electrode process. The bath B, containing a high concentration of Ti\(^{2+}\) is advantageous for obtaining a smooth deposits, as described in the patent \( 9\). On the other hand, in bath A the cathodic current is associated with two-electron transfer of Ti\(^{3+}\), which is electrochemically produced by the first reduction step of Ti\(^{3+}\). Thus, a high overpotential during the cathodic reduction of Ti\(^{2+}\) can not be expected to be due to a relatively low concentration of Ti\(^{2+}\) in the bath A. Since the diffusion process mainly contributes to the cathodic reduction of Ti\(^{2+}\), the co-operative discharge of Li\(^+\) would deteriorate the electrodeposits.

IV. Conclusion

A steady state polarization study and RDE analysis of a Ti\(^{3+}\)/Ti electrode in LiCl–KCl eutectic showed a two-step reduction in which the latter step was a well defined two-electron transfer reaction accompanied by a chemical reaction at potentials below \(-1.3\) V. The RDE analysis in NaCl–MgCl\(_2\)–KCl melt showed that the discharge of Ti\(^{2+}\) proceeds via a two-step reaction, which exhibits the first and second Tafel lines for the reduction of Ti\(^{3+}\) to Ti\(^{2+}\) and Ti\(^{2+}\) to Ti. The diffusion coefficient of Ti\(^{2+}\) in NaCl–MgCl\(_2\)–KCl melt was several times lower than that in LiCl–KCl eutectic.

REFERENCES