

# Electrochemical behaviour of titanium(II) and titanium(III) compounds in molten lithium chloride/potassium chloride eutectic melts

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The nature of the open circuit potentials of Ti and TiC electrodes in titanium(II) and titanium(III) chloride solutions, the apparent valency of the titanium ions in the melt immediately after the anodic dissolution of TiC and Ti, as well as the anodic dissolution of Ti, have been investigated in order to explain the oxidation-reduction process of titanium in lithium chloride-potassium chloride eutectic melts. It is shown that the standard electrode potential for TiC/Ti(III) exceeds that for the oxidation of Ti(II) to Ti(III). The anodic dissolution of TiC anodes give stable Ti(III) species at the standard electrode potentials the contrary to the behaviour of Ti metal anodes where the stable species are Ti(II) ions. Titanium electrodes in TiCl<sub>3</sub> solutions of molten lithium chloride-potassium chloride melts behave according to the Ti(III)/Ti(II) redox electrode potential of the reaction:  $\text{Ti} + \text{TiCl}_3 \rightleftharpoons 3\text{TiCl}_2$ . An anodic dissolution mechanism compatible with all the experimental facts is proposed.

## 1. Introduction

The electrochemistry of titanium subchlorides in molten salts and the deposition of metallic titanium from titanium chlorides have been the subject of many investigations [1-10]. Despite the extensive investigations, as well as the advantages in economics and product quality, the electrolysis of titanium from chloride melts has not found commercial application, mainly because titanium is present in the electrolyte in different valencies which may favour reoxidation and disproportionation reactions, resulting in a very low current density [11]. There is also considerable disagreement in the literature, even in the measured standard potential values of the three different titanium redox systems, Ti(II)/Ti(0), Ti(II)/Ti(III), and Ti(III)/Ti(IV), in molten LiCl-KCl eutectic melts as well as their kinetic characteristics [12-13].

The cheapest way to obtain metal from its oxide is to reduce the oxide with carbon. Unfortunately, the reduction of titanium oxide with carbon does not yield pure titanium metal, but does yield TiC. Fortunately, however, TiC can be refined electrolytically by using the TiC as an anode to yield pure titanium metal. Thus, determining the nature of the open circuit potentials of Ti and TiC electrodes in titanium(II) and titanium(III) chloride solutions, the apparent valency of the titanium ions in the melt immediately after the anodic dissolution of the TiC and Ti, as well as the mechanism of the anodic dissolution of Ti in molten salts, is of importance for understanding the

oxidation-reduction process of titanium in lithium chloride-potassium chloride eutectic melts.

## 2. Experimental details

The eutectic mixture of 41 mol % (m/o) potassium chloride and (59 m/o) lithium chloride at 723 K was used as the solvent system. The solvent was purified by a method described elsewhere [14-15].

The cell used in this experiment has been previously described [16]. Within this cell and under an atmosphere of dry, oxygen-free argon, the solvent was allowed to collect into the fritted compartments which were used as experimental cells. At the end of the experiment the volume of each compartment was determined by titrating its chloride content and using the known density of the melt at 723 K.

All electrochemical measurements were carried out using a PAR Model 273 potentiostat-galvanostat connected via a model 273 interface, to an IBM computer. Experimental data were stored and plotted using a 7470 Hewlett-Packard plotter.

The reference electrode comprised a platinum foil in contact with a titanium(II) solution. This reference electrode was used instead of a chlorine reference electrode because titanium has more than one stable valency state under the prevailing experimental conditions and chlorine gas can oxidize these titanium valence states from the lower to the higher. The platinum reference electrode has been shown to be reproducible and non-polarizable over a long period

of time [17–20]. The carbon electrode, which served as a counter electrode in all electrochemical investigations in molten salts, was constructed as described by Propp [21]. The titanium indicator electrode was prepared by adding anhydrous titanium chloride (III) to titanium metal forming  $\text{TiCl}_2$ . A pure titanium electrode rod was then immediately immersed into the  $\text{TiCl}_2$  solution at equilibrium. Dilute solutions of titanium chlorides in the LiCl–KCl eutectic melt were prepared by anodic dissolution of scrap metal and TiC. Carbon-bonding in the TiC anode was achieved by forming a mixture of the carbide with pitch, molding to shape, and baking at 1000–1200°C in an inert atmosphere to drive off pitch volatiles. Anodes formed in this way had a good electrical conductivity and their use permitted complete electrolytic extraction of Ti from TiC.

All chemicals used in this study were of reagent grade. Those chemicals containing water of hydration were vacuum dried at 383°C before being added to the melt. A blanket of pure argon gas was kept over the melt at all times to exclude oxygen and water vapor. The argon gas was purified by a method described elsewhere [14, 15].

### 3. Results and discussion

#### 3.1. Open circuit potential measurements

The equilibrium of the Ti/Ti(II) system was studied with the Ti/Ti(II), LiCl–KCl || LiCl–KCl,  $\text{PtCl}_2/\text{Pt}$  cell where the Pt electrode was used for convenience instead of measuring against the chlorine electrode directly. Using the precise data for the potential of the Pt/PtCl<sub>2</sub>(1 M), LiCl–KCl || LiCl–KCl/Cl<sub>2</sub> cell [22]:

$$E_{\text{Pt}/\text{PtCl}_2(1\text{M})/\text{LiCl-KCl}}(\text{V}) = -0.3223 + 0.00034(T - 450) \quad (1)$$

where  $T$  represents the temperature of the cell in K, the titanium electrode potentials measured with respect to the platinum reference electrode were normalized to the chlorine electrode. Thus, the potentials obtained are numerically the same as the potential difference for the Ti/TiCl<sub>2</sub>, LiCl–KCl || LiCl–KCl/Cl<sub>2</sub> cell which corresponds to the formation of titanium(II) chloride in the melt.

Figure 1 plots the titanium electrode potential plotted against the logarithm of the Ti(II) concentration for five temperatures and shows a linear dependence. The slope of these curves, that is, the change in potential with respect to the change in concentration,  $(\partial E/\partial(\log [C_{\text{Ti(II)}}]))_T$ , as measured from Fig. 1 and as calculated from the Nernst equation:

$$E_{\text{Ti}/\text{Ti}^{2+}} = E_{\text{Ti}/\text{Ti}^{2+}}^0 + 2.303 \frac{RT}{nF} \log (C_{\text{Ti}^{2+}}) \quad (2)$$

assuming two electrons are transferred, are in close agreement, indicating that a two electron transfer process is occurring in this system.

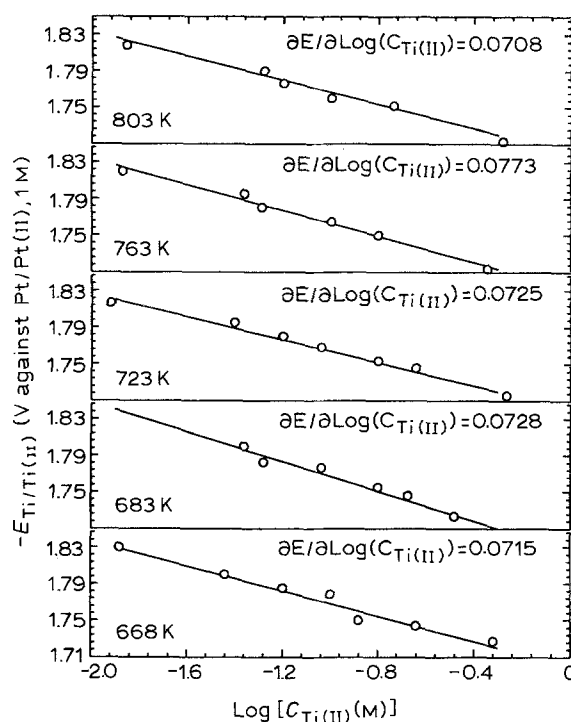


Fig. 1. Titanium electrode potentials as a function of the Ti(II) concentration in the LiCl–KCl melt.

The standard potential of Ti/Ti(II) has been determined to be  $-2.010$  V with respect to a Cl<sub>2</sub> reference electrode and at 723 K, the free energy of formation of titanium(II) chloride in a 1 M solution was calculated to be  $-38.7$  kJ mol<sup>-1</sup>. Figure 2 shows the variation of the Ti/Ti(II) electrode potential with temperature for different TiCl<sub>2</sub> concentrations in the melt. Values for  $(\partial E/\partial T)_P$  obtained from this figure for each concentration were used to calculate the molar entropy which was determined to be  $29$  J mol<sup>-1</sup> K<sup>-1</sup>.

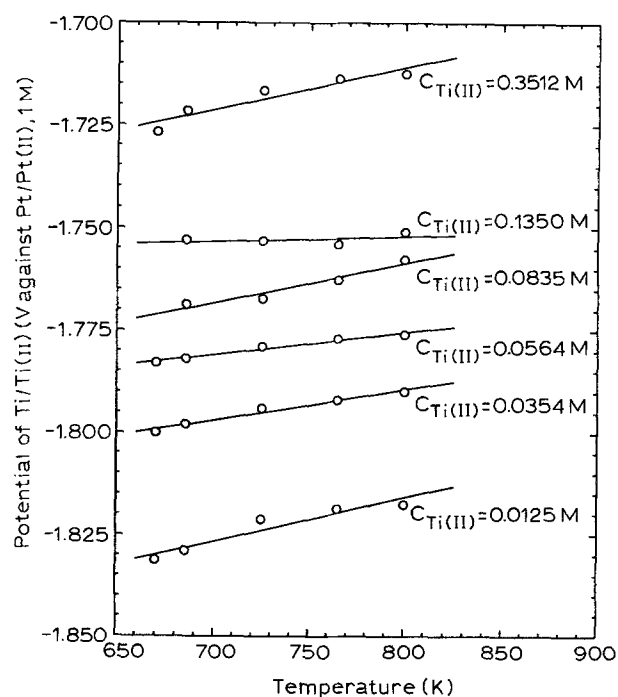


Fig. 2. Temperature dependence of titanium electrode potentials for different Ti(II) concentrations.

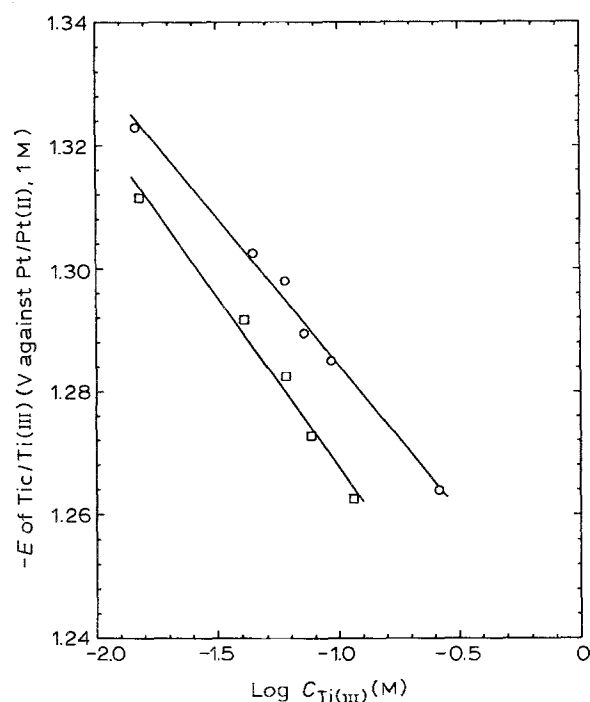


Fig. 3. TiC electrode potentials as a function of the Ti(III) concentration in the melt. (O) 723 K and (□) 873 K.

The apparent valency of the titanium ions in the melt after the anodic dissolution of TiC was examined at various current densities and at various concentrations of the titanium chloride (within  $1.4 \times 10^{-2}$  to 0.623 M). The preparation and composition of the TiC anode is given in the experimental section of this paper. The composition of the titanium chloride in the melt was obtained by measuring the weight decrease of the TiC anode. The apparent valency of the titanium ion in the melt was then determined from the charge passed during the electrolysis and the weight decrease of the TiC anode using Faraday's law.

In Fig. 3, the TiC electrode potentials are plotted against the logarithm of the titanium ion concentration for two temperatures. The change in potential with respect to the change in concentration,  $(\partial E / \partial (\log [C_{Ti^{3+}}]))_T$ , measured for each temperature as well as calculated using the Nernst equation (assuming a three electron process) are shown in Table 1, showing a close agreement in the slopes. Standard potential measurements for the TiC/Ti(III), LiCl-KCl, PtCl<sub>2</sub>/Pt system are given in Table 2. From the results obtained one can conclude that the standard electrode potential for TiC/Ti(III) exceeds that for the oxidation of Ti(II) to Ti(III). Hence, one should expect that a TiC anode

Table 1. Experimental and Nernst behaviour of a TiC electrode in a molten LiCl-KCl melt

Temperature (K)	$\frac{\partial E}{\partial (\log [C_{Ti^{3+}}])_T}$	
	Calculated	Observed
723	0.0477	0.0487
873	0.0576	0.054

Table 2. Standard potential measurements for the TiC/Ti(III) system

$C_{Ti(III)}$ (M)	$\log [C_{Ti(III)}]$	$E$ (V)*	$E$ (V) <sup>†</sup>	$E^0$ (V)
0.0140	-1.853	-1.273	-1.323	-1.235
0.0450	-1.347	-1.254	-1.303	-1.240
0.0575	-1.240	-1.249	-1.299	-1.243
0.0705	-1.152	-1.240	-1.290	-1.246
0.0903	-1.031	-1.236	-1.286	-1.238
0.2630	-0.580	-1.214	-1.264	-1.244

\* Measured

<sup>†</sup> Against a 1 M Pt reference electrode.

will give stable Ti(III) species at these potentials, contrary to the behaviour of Ti metal anodes where the stable species are Ti(II) ions.

The electrode potentials of TiC were also measured at the same temperature range and at, approximately, the same concentration range with the TiC/Ti(III), LiCl-KCl || LiCl-KCl, PtCl<sub>2</sub>/Pt cell. A known amount of reagent grade TiCl<sub>3</sub> was inserted into the melt and the solution was allowed to equilibrate. The TiC electrode potentials were plotted against the logarithmic concentration of Ti(III) species added to the eutectic melt and the slopes measured again indicated that a three electron process was occurring.

Open circuit potentials of the Ti/Ti(III), LiCl-KCl || LiCl-KCl, PtCl<sub>2</sub>/Pt cell were measured using a rotating disc electrode. The titanium electrode potentials were plotted against the logarithmic concentration of Ti(III) ions which showed an almost linear dependence, as shown in Fig. 4. The change in potential with respect to the concentration,  $\partial E / \partial \log (C_{Ti(III)})$  measured from Fig. 4 is 85 mV decade<sup>-1</sup> and as calculated from the Nernst equation (assuming  $n = 3$ ) is 47.8 mV decade<sup>-1</sup>. The discrepancy in these results indicate that the standard titanium potential is not controlled solely by the concentration of Ti(III) in the melt. For the Ti(III)/Ti(IV) cell, one should expect that the equilibrium potentials be more positive than

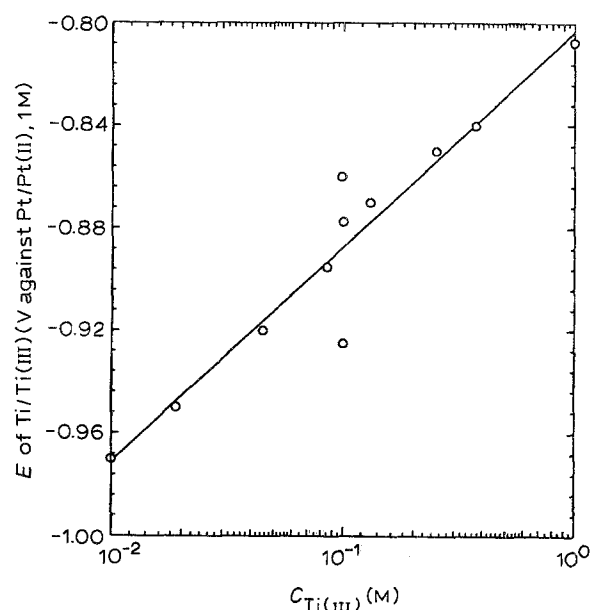


Fig. 4. Titanium electrode potentials as a function of the Ti(III) concentration in the LiCl-KCl melt.

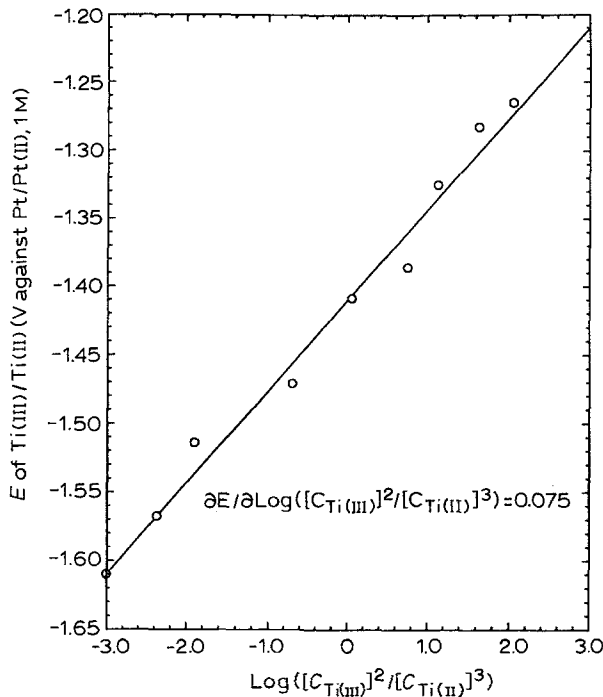
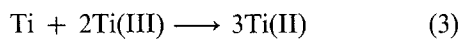


Fig. 5. Titanium electrode potentials as a function of the rate of the Ti(III) concentration to the Ti(II) concentration.

the measured potentials of  $-0.98$  to  $-1.5$  V with respect to Pt reference electrode, thus, precluding the possibility that Ti(III) is oxidized to Ti(IV). The results can only be explained by taking into account that titanium reacts with Ti(II) ions chemically by the chemical redox reaction:



The Ti(III)/Ti(II) redox potential, according to Reaction 3, is given by the Nernst equation:

$$E = E_{\text{Ti(III)/Ti(II)}}^0 + 2.303 \frac{RT}{2F} \log \frac{[\text{Ti(III)}]^2}{[\text{Ti(II)}]^3} \quad (4)$$

which has a slope (at 723 K):

$$\frac{\partial E}{\partial \log \left[ \frac{(C_{\text{Ti}^{3+}})^2}{(C_{\text{Ti}^{2+}})^3} \right]} = 0.072 \text{ V decade}^{-1} \quad (5)$$

This slope compares favourably to our experimental value of  $0.075 \text{ V decade}^{-1}$  as shown in Fig. 5. For a constant Ti(II) concentration, the slope as determined from Equations 4 is:

$$\left[ \frac{\partial E}{\partial \log C_{\text{Ti(III)}}} \right]_{[\text{Ti(II)}]} = 0.144 \text{ V decade}^{-1} \quad (6)$$

Our experimentally obtained slope from Fig. 5 is smaller indicating that the concentration of Ti(II) species should be taken into account according to the Reaction 3.

### 3.2. Cyclic voltammetry of the Ti(III)-LiCl-KCl system

Figure 6 shows a cyclic voltammogram obtained for  $6.3 \times 10^{-2} \text{ M TiCl}_3$  prepared by anodic dissolution of titanium metal in a molten LiCl-KCl eutectic melt at 723 K and at a sweep rate of  $0.05 \text{ V s}^{-1}$ . In a separate experiment, a known amount of reagent grade  $\text{TiCl}_3$  was introduced in the eutectic melt and the solution was allowed to equilibrate. A carbon indicator electrode was used to obtain the cyclic voltammogram as shown in Fig. 6.

Dilute solutions of titanium(III) species were prepared by the anodic dissolution of the metal at high current densities. At low current densities the anode dissolves to yield reduced titanium chlorides at concentrations determined by the equilibrium of Reaction 3. At higher current densities one should expect an increasing amount of Ti(III) to be produced because of anodic polarization.

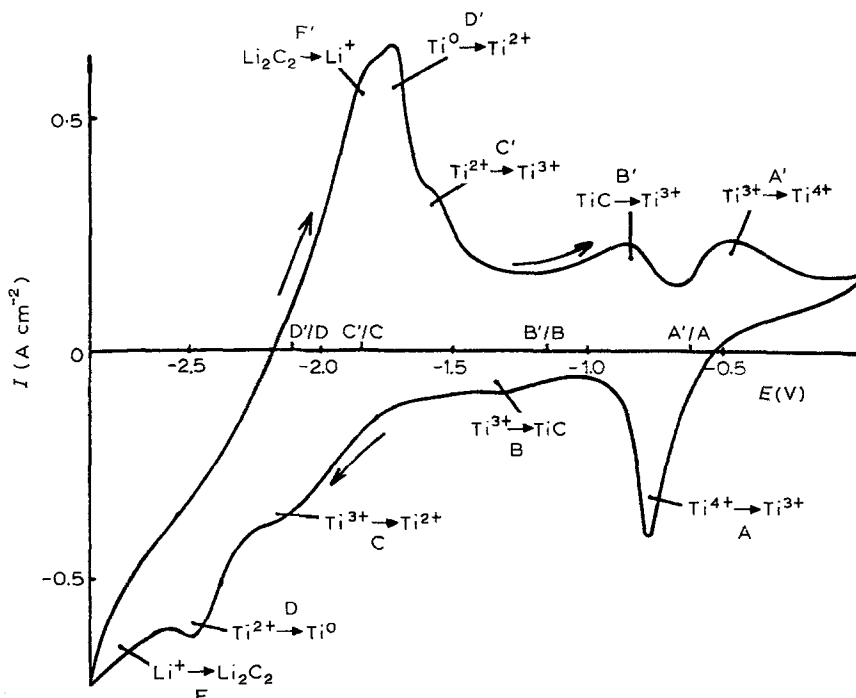
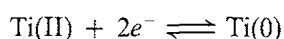
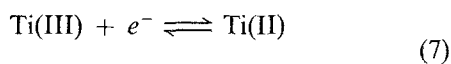
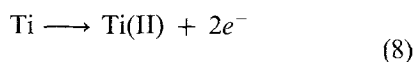


Fig. 6. Cyclic voltammogram for Ti(III) in  $6.3 \times 10^{-2} \text{ M TiCl}_3$  at a scan rate of  $0.05 \text{ V s}^{-1}$ .

It can be seen that during negative going potential scans, two well distinguished peaks appear at  $-2.1$  and at  $-2.4$  V with respect to chlorine reference electrode. Similar results were obtained by Ferry *et al.* [6]. These cathodic peaks are attributed to the reactions:



We limit our attention here to the analysis of the behaviour of Ti during its active dissolution. During positive going potential scans two consecutive anodic peaks appear at  $-1.78$  V and at  $-1.62$  V/Cl<sub>2</sub> and are respectively attributed to the reactions:



The peak at  $-1.78$  V/Cl<sub>2</sub> is a sharp peak and can be attributed to the dissolution reaction of Ti. During successive cycles a small increase in the peak current from 10 to 15 mA was observed. The results can be explained taking into account that a parallel chemical reaction occurs at the anode in which electrochemically formed Ti(III) ions react with metallic titanium to yield reduced titanium chloride at a concentration set by the equilibrium Reaction 3.

For sweep rates higher than  $0.005$  V s<sup>-1</sup> the peak current at  $-1.62$  V/Cl<sub>2</sub> increases, indicating that under such conditions a higher concentration of Ti(II) is formed in the melt at  $-1.72$  V, which is further oxidized at higher potentials ( $-1.62$  V/Cl<sub>2</sub>) to Ti(III).

Calculated standard redox potentials,  $E_0^0$ , and redox potentials,  $E^0$ , taken from the cyclic voltammogram shown in Fig. 6 are shown in Table 3 for the Ti(IV)/Ti(III), Ti(III)/Ti(II), Ti/Ti(II), and Ti/Ti(III) systems indicating that the titanium electroactive species do not have a great tendency to form complexes in the melt.

The interaction of chemical reaction and anodic oxidation of titanium metal is certainly of high importance for the cathodic deposition of titanium metal from molten salts containing Ti(III) species, since the subsequent reduction of  $\text{Ti(III)} + e^- \rightleftharpoons \text{Ti(II)}$  and  $\text{Ti(II)} + 2e^- \rightleftharpoons \text{Ti(0)}$  interferes with the reaction  $2\text{Ti(III)} + \text{Ti} \rightarrow 3\text{Ti(II)}$ . One should expect that the significant velocity of the chemical redox reaction might hinder or slow the electron exchange in the reaction,  $\text{Ti(II)} + 2e^- \rightleftharpoons \text{Ti(0)}$  compared to the faster oxidation-reduction reaction of  $\text{Ti(III)} + 3e^- \rightleftharpoons \text{Ti(0)}$ . Thus, determining the mechanism of the titanium dissolution process in the presence of titanium (III) chloride ions in a LiCl-KCl eutectic melt is of importance for understanding the oxidation-reduction process of titanium in molten salts.

### 3.3. Tafel behaviour

Polarization curves with sufficiently small scan rates can be taken as quasi-stationary state polarization

Table 3. Calculated standard redox potentials,  $E_0^0$ , and redox potentials,  $E^0$ , taken from cyclic voltammetry

Equilibrium	$E_0^0$ (calculated) (V)*	$E^0$ (V)*
A: $\text{Ti(IV)} + e^- \rightleftharpoons \text{Ti(III)}$	-0.923	-0.610
B: $\text{Ti(III)} + \text{C} + 3e^- \rightleftharpoons \text{TiC}$	-1.420	-1.120
C: $\text{Ti(III)} + e^- \rightleftharpoons \text{Ti(II)}$	-1.730	-1.820
D: $\text{Ti(II)} + 2e^- \rightleftharpoons \text{Ti}$	-2.080	-2.140
E: $2\text{Li(I)} + 2\text{C} + 2e^- \rightleftharpoons \text{Li}_2\text{C}_2$	-3.390	-2.500

\* The potentials are given vs a Cl<sub>2</sub>/Cl<sup>-</sup> reference electrode in a molten LiCl-KCl eutectic melt.

curves as presented in Fig. 7 for Ti in a 0.5 M TiCl<sub>3</sub>-LiCl-KCl eutectic solution at a scan rate of  $0.1$  mV s<sup>-1</sup>. The anodic curve has a Tafel like behaviour with a slope of  $90$  mV decade<sup>-1</sup> while the cathodic curve shows a slope of  $100$  mV decade<sup>-1</sup>. In different experiments, the anodic curves, measured for different concentrations of Ti(III), ranged from  $80$  to  $95$  mV decade<sup>-1</sup>. The position of the anodic polarization curve in the diagram changes with the change of Ti(III) concentration. Actually, this change is controlled by the Ti(III) reaction order,  $\omega_{\text{Ti(III)}}$ , for the anodic reaction. The reaction order can be determined from the change of the current with respect to the electrode potential at a constant concentration of the reduced species as a function of the change in Ti(III) ion concentration with respect to the electrode potential:

$$\left[ \frac{\partial \ln i}{\partial E_{\text{eq}}} \right]_{C_{\text{Ti(III)}}} = \omega_{\text{Ti(III)}} \left[ \frac{\partial \ln C_{\text{Ti(III)}}}{\partial E_{\text{eq}}} \right]_{C_{\text{Ti(II)}}} + \frac{\beta F}{RT} \quad (9)$$

where  $\beta$  is the anodic transfer coefficient. By using Fig. 4 and Equation 9, a straight line dependence of

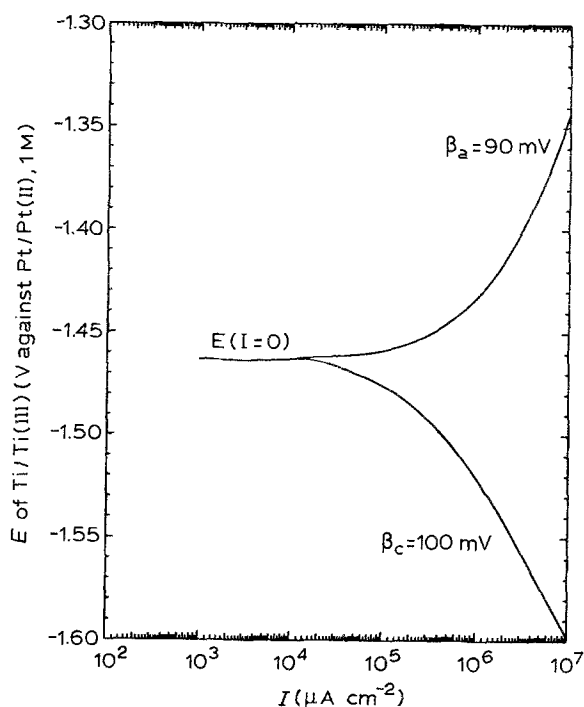


Fig. 7. Potentiodynamic curve obtained for the Ti electrode in a 0.5 M TiCl<sub>3</sub>-LiCl-KCl solution at 723 K, at a scan rate of  $0.1$  mV s<sup>-1</sup>.

85 mV decade<sup>-1</sup> was obtained which corresponds to a reaction order,  $\omega_{\text{Ti(III)}}$ , of one when  $\beta_a$  is 90 mV decade<sup>-1</sup>.

Considering that the multistep electrode process consists of two electron transfer steps, one of which is slow and rate limiting and the other of which is fast, the Butler–Volmer equation has the following form:

$$i = i_0 \left[ \exp\left(\frac{-\alpha F\eta}{RT}\right) - \exp\left(\frac{(1 + \beta)F\eta}{RT}\right) \right] \quad (10)$$

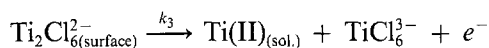
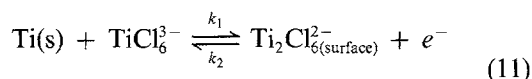
where  $\alpha = \alpha_{\text{app}}$  is the apparent cathodic transfer coefficient and  $1 + \beta = \beta_{\text{app}}$  is the apparent anodic transfer coefficient [27].

For the case of oxidation of a two electron process, where the second step is rate limiting, the apparent cathodic and anodic transfer coefficients are expected to be approximately  $\alpha_{\text{app}} = 0.5$  and  $\beta_{\text{app}} = 1.5$ .

### 3.4. Mechanism of the anodic reaction

Tafel slopes for Ti dissolution in Ti(III) chloride solutions were 90 mV decade<sup>-1</sup> which gives an apparent transfer coefficient,  $\beta_{\text{app}}$ , of 1.55. With the observed reaction order,  $\omega_{\text{Ti(III)}}$ , equal to one, a direct two electron exchange mechanism is not probable [23].

The spectrum of Ti(III) was measured by Gruen and McBeth [24] in the LiCl–KCl eutectic melt at temperatures from 400 to 1000°C. The spectrum underwent large changes when the temperature was changed. These changes were attributed to an equilibrium between tetrachloro and hexachloro titanium(III) ions in which  $\text{TiCl}_6^{3-}$  predominated in LiCl–KCl at 450°C. On the other side, numerous intercalation reactions are known in which one reactant enters the lattice of the other. Such behaviour is conveniently illustrated by the references of two recent studies [25, 26]. Lithium undergoes a low temperature (298 K) topochemical reversible reaction with transition metal compounds (for example,  $\text{TiS}_2$ ,  $\text{NbSe}_3$ ) in which the host lattice structure may be partially retained (for example, in  $\text{Li}_x\text{TiS}_2$ ,  $\text{Li}_3\text{NbSe}_3$ ). The reaction  $\text{Ti} + \text{TiB}_2 \rightleftharpoons 2\text{TiB}$  proceeds by surface migration of titanium [26]. Taking into account the above characteristics of titanium species into the eutectic melt, the results obtained for anodic titanium dissolution are consistent with the following mechanism:



where the second step is rate limiting giving the rate:

$$i = Fk_3C_{\text{Ti}_2\text{Cl}_{6(\text{surface})}^{2-}} \exp\left(\frac{\beta FE}{RT}\right) \quad (12)$$

Hence, the reaction determining the equilibrium potential,  $E_{\text{eq}}$ , is  $\text{Ti} + 2\text{TiCl}_3 \rightleftharpoons 3\text{Ti(II)}$  where  $k_1$  is the rate constant for the first step and  $E = E_{\text{eq}} - E_1^0$ , where  $E_1^0$  corresponds to the potential of the second step of the titanium dissolution reaction.

Theoretically, the cathodic Tafel slope for the

suggested mechanism, assuming a constant bulk concentration of the reducing species, should depend upon the reduction of Ti(III) and Ti(II) species. When polarized cathodically, a pseudo-limiting current occurs which at higher cathodic polarizations, changes the slope to 100 mV decade<sup>-1</sup> representing the  $\text{Ti(III)} \rightarrow \text{Ti(0)}$  reduction with  $\alpha = 0.5$ .

### 4. Conclusions

The reduction of  $\text{TiCl}_3$  in a pure LiCl–KCl eutectic melt proceeds at  $-2.1 \text{ V/Cl}_2$  and at  $-2.4 \text{ V/Cl}_2$  through the reactions:  $\text{Ti(III)} + e^- \rightleftharpoons \text{Ti(II)}$  and  $\text{Ti(II)} + e^- \rightleftharpoons \text{Ti(0)}$ , respectively. Two consecutive anodic peaks appear at  $-1.78 \text{ V/Cl}_2$  and at  $-1.62 \text{ V/Cl}_2$  and are attributed to the reactions:  $\text{Ti} \rightarrow \text{Ti(II)} + 2e^-$  and  $\text{Ti(II)} \rightarrow \text{Ti(III)} + e^-$ . The standard electrode potential for  $\text{TiC/Ti(III)}$  ( $E^0 = -1.51 \text{ V/Cl}_2$ ) exceeds that for the oxidation of  $\text{Ti(II)}$  to  $\text{Ti(III)}$  ( $E^0 = -1.77 \text{ V/Cl}_2$ ).  $\text{TiC}$  anodes give stable  $\text{Ti(III)}$  species at these potentials in contrast with the behaviour of  $\text{Ti}$  metal anodes where the stable species are  $\text{Ti(II)}$  ions. It is shown that the open circuit potential of titanium electrodes in  $\text{TiCl}_3$  solutions of molten lithium chloride–potassium chloride melts behave according to the  $\text{Ti(III)/Ti}$  redox electrode potential of the reaction:  $\text{Ti} + 2\text{TiCl}_3 \rightleftharpoons 3\text{TiCl}_2$ . A parallel chemical reaction occurs at the anode in which electrochemically formed  $\text{Ti(III)}$  ions react with metallic titanium to yield reduced titanium chloride at a concentration set by the equilibrium Reaction 3.

The mechanism for anodic dissolution of  $\text{Ti}$  is proposed, considering two transfer steps, where the second step is rate limiting. The cathodic Tafel slopes for the suggested mechanism, assuming a constant bulk concentration of the reducing species, depend upon the reduction of  $\text{Ti(III)}$  and  $\text{Ti(II)}$  species. When polarized cathodically, a pseudo-limiting current occurs which at higher cathodic polarizations, changes the slope to 100 mV decade<sup>-1</sup> representing the  $\text{Ti(III)} \rightarrow \text{Ti(0)}$  reduction with  $\alpha = 0.5$ .

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