PULSE AND A.C. IMPEDANCE STUDIES OF THE ELECTROCHEMICAL SYSTEMS OF TITANIUM IN LiCl-KCl EUTECTIC MELT AT 743 K.
D.M. Ferry, G.S. Picard and B.L. Trémillion
Laboratoire d’Electrochimie Analytique et Appliquée
associé au C.N.R.S. (U.A. 216)
E.N.S.C.P., 11 rue P. et M. Curie
75231 Paris Cedex 05 - France

ABSTRACT
The electrochemical systems of titanium in LiCl-KCl eutectic melt have been investigated by means of pulse techniques and A.C. impedance measurements. Ti$_3^+/Ti$(IV) electrochemical system appears reversible while Ti$_3^+/Ti^{2+}$ is quasi-reversible and metallic titanium deposition from Ti$^{2+}$ is irreversible. Kinetic constants related to these redox systems have been determined as also the thickness of the diffusion layer, the double layer capacitance and the electrolyte resistance.

1. INTRODUCTION

The electrodeposition of metallic titanium from titanium (IV) chloride in molten chlorides melt aroused a lot of investigations since the early fifties. Nevertheless the important discrepancies between the various results available in literature led us to perform a systematic study of the thermodynamic stability of titanium chlorides and oxides in a particular bath, the molten eutectic LiCl-KCl at 743 K.

First, we determined the standard potentials of the three different redox systems of titanium [Ti(0)/Ti(II), Ti(II)/Ti(III) and Ti(III)/Ti(IV)] and the solubility products of all the titanium oxides (1). Secondly, because of the lack of information on the kinetic parameters of the electrochemical systems of titanium, we have undertaken their determination by using pulse and A.C. impedance techniques. This is the subject of this paper.

2. TECHNICAL

2.1. Preparation of melt and apparatus.

The eutectic melt (45 wt % LiCl - 55 wt % KCl) was contained in a pyrex crucible placed inside a pyrex reactor. This mixture was fused under vacuum as described earlier (2), and then maintained at the working temperature (743 K) under an inert atmosphere of dry argon. Heating was achieved by means of a Renat furnace connected to a temperature-controlled device Microcor Chaumon-Arnoux.

2.2. Products and electrodes.

Lithium and potassium chlorides (minimum purity 99%) were supplied by Merck. Solid titanium(III) chloride (purity ≥ 98%), from Alpha Ventron, was kept in a dry glove-box until its use. TiCl$_3$ was added into the melt by means of a "powder burette" (3).
The working and counter electrodes were tungsten wires (surface area \( S = 0.24 \text{ cm}^2 \)) and the reference electrode was the silver-silver chloride (0.75 mol.kg\(^{-1}\)) reference previously described (3). Metallic wires were supplied by Johnson-Matthey (W purity : 99.98 % ; Ag : 15 ppm of impurities). Silver chloride was a Merck product (99 %). Potentials are referred in this paper to the chlorine (1 atm)-chloride electrode whose potential is + 1.023 V versus our reference electrode.

2.3. Pulse techniques.

Chronoamperograms and chronopotentiograms have been recorded by using a PAR Model 176 potentiostat-galvanostat connected, via an interface Model 273, to an Apple Ile microcomputer. Experimental data have been stored onto 5"1/4 flexible disks and then plotted with a 7470 A Hewlett-Packard plotter.

2.4. A.C. Impedance measurements.

Experiments were performed with a Z Computer system Tacussel coupled to a Hewlett-Packard 9826 microcomputer. Measurements have been carried out using a 15 mV amplitude sine wave signal and a frequency range from 100 kHz to 50 mHz. The usual operating precautions (Faraday cage surrounding the electrochemical cell, connecting screened wires,...) were taken. Interpretation of experimental data was realized by comparing them with computerized curves according to a mechanism model. An HP 9000 Series 300 microcomputer and a 7470 A HP plotter was used for that purpose.

3. RESULTS AND DISCUSSION

3.1. Chronoamperometric studies of the oxidation and reduction of titanium(II) solutions.

From \( E = -2.5 \text{ V} \) to \( E = 0 \text{ V} \), it was experimentally observed that chronoamperograms exhibit a current constant value, due to thermal convection, for each potential when times are greater than 10 s. These steady state potential-dependent current values were used for obtaining the i-E curves represented in figure 1a.

We can notice on figure 2a that the diffusion limiting current of the oxidation wave is practically equal to the one of the first reduction wave and to the half of the second reduction wave. Besides, a logarithmic analysis of the i-E oxidation curve (figure 1b) indicates a bilogarithmic behavior when potential is lower than the half-wave potential (current densities less than 13 mA. cm\(^{-2}\)) corresponding to a reversible charge transfer involving one electron suggesting the formation of soluble Ti\(^{4+}\) ions. For potentials greater than the half-wave potential, we observe a deviation from the bilogarithmic behavior which can be explained by considering the solubility of gaseous TiCl\(_4\). By such an analysis, we can verify that the number \( n \) of exchanged electrons is close to the unity (\( n = 1.2 \pm 0.1 \)). From these results, we can deduce that the first step of the Ti\(^{3+}\) ion reduction leads to titanium(II), followed by the reduction of Ti(II) into metallic titanium.

By plotting the variation of the current versus the reciprocal value of the square root of time at a potential corresponding to the diffusion limiting current of the i-E oxidation curve (point P on figure 1a), we demonstrate that experimental data obey
Cottrell's law (figure 1c). The straight line obtained has a slope of 45 ± 6 mA.cm\(^{-2}\).s\(^{-1/2}\) from which the diffusion coefficient \(D\) of Ti\(^{3+}\) ion has been calculated by using for the number of exchanged electrons the value \(n = 1\) determined above. We found \(D = (1.9 \pm 0.5) \times 10^{-5}\) cm\(^2\) s\(^{-1}\). By using (i) this value of \(D\), (ii) the one of the thickness \(\delta\) of the diffusion layer deduced from the limiting current density, and (iii) those of the standard potentials of the electrochemical systems Ti\(^{3+}/Ti^{2+}\) and Ti\(^{2+}/Ti(0)\) [previously determined potentiometrically (1,5,6)], it was possible to obtain a simulated curve (solid line on figure 1a) which fits well the experimental points, thus verifying the consistency of the proposed electrochemical reactions. From this analysis, we have obtained the values of the intrinsic rate constants \(k_0\) and of the transfer coefficients \(\alpha\) of these two redox systems (Table 1). Ti\(^{3+}/Ti^{2+}\) can be considered as quasi-reversible whereas titanium deposition appears irreversible.

3.2. Chronopotentiometric analysis of the titanium electrochemical systems.

\(Ti^{3+}/Ti(IV)\) electrochemical system.

Figure 2a gives typical chronopotentiograms obtained at a tungsten electrode for imposed anodic current density values ranging from 29 to 42 mA.cm\(^{-2}\). We observe waves whose quarter wave potentials \(E_{t/4}\) are very close to the value of the Ti\(^{3+}/Ti(IV)\) standard potential (itself equal to the half wave potential \(E_{1/2}\) of the oxidation curve of figure 1a). For times higher than the transition times \(\tau\), potentials reach values relative to the oxidation of chloride ions into chlorine. Analysis of the variation of the transition time as a function of imposed current density values \(j_0\) (figure 2b) confirms that the electrochemical reaction is diffusion-controlled (Sand's law). From the slope of the straight line obtained by plotting \(j_0\) versus \(\tau^{-1/2}\), we obtained for the diffusion coefficient \(D\) of Ti\(^{3+}\) the value \(D = (1.0 \pm 0.1) \times 10^{-5}\) cm\(^2\) s\(^{-1}\) which is slightly lower than the value determined by chronoamperometry.

Current reversal chronopotentiometry has given the following additional information. By reversing the current at various times of electrolysis (and for several current values) as shown in figure 2c, we have been able to demonstrate that titanium(IV) is produced as a soluble species. In fact, the ratio of \(\tau_{red}\) (transition time corresponding to the reduction of part of the species formed during electrolysis of duration \(t_{ox}\)) to \(t_{ox}\) is close to 1/3 whatever the imposed current values (figure 2d).

\(Ti^{3+}\) reduction.

Concerning the reduction of Ti\(^{3+}\), chronopotentiometric transients show that this reduction effectively occurs in two successive steps (figure 3a). By measuring the corresponding transition times \(\tau_1\) and \(\tau_2\), we observe that \(\tau_2\) is about eight times higher than \(\tau_1\). This result is in good agreement with an exchange of one electron for the first reduction step, and of two electrons for the second one (7a).

By using current reversal techniques (figure 3b), we can prove the formation of...
soluble titanium(II) species during the first electrochemical reaction followed by the electrodeposition of metallic titanium. In fact, the ratio of the reoxidation transition time $t_{ox}$ to the global reduction electrolysis time $t_{red}$ takes the value of 1/3 for potentials ranging from -1.95 to -2.15 V, and takes the value 0.6 for potentials lower than -2.3 V. A value close to 0.6, and not unity which is generally observed for a one step electrochemical deposition, is obtained because of the intermediate step leading to Ti$^{2+}$ ions.

3.3. A.C. Impedance measurements.

The analysis of the i-E reduction curves performed above allowed us to determine the kinetic characteristics of the electrochemical reactions of the Ti$^{3+}$ reduction. Concerning the Ti$^{3+}$/Ti(IV) redox system, which appears reversible from i-E oxidation curve, we had to use another technique for obtaining the corresponding value of the intrinsic rate constant and that of the transfer coefficient. Because of the large frequency range which can be explored, A.C. impedance measurements had proved to be the best method for that study.

Experimental data resulting from measurements performed at a potential equal to -0.50 V are reported in the complex plane (Nyquist plot) in figure 4a and as a function of frequency (Bode plots) in figures 4b and 4c. These spectra clearly show one capacitive loop at high frequencies (from 100 to 5 kHz) and a Warburg behavior for frequencies ranging from 5 kHz to about 0.1 Hz (the phase angle tends towards -45°). Below this last frequency value, as indicated by the Bode phase plot (figure 4c), we can observe a decrease in the phase angle due to the thermal convection leading to a finite thickness diffusion layer $\delta$ (already determined).

Relying on the results obtained by pulse techniques, impedance spectra have been computerized by using a simple model involving two mass transfer steps (Ti$^{3+}$ and produced Ti(IV) diffusions) and one electron charge transfer step. Simulated curves are represented as solid lines in figures 4. The good fit obtained corresponds to the kinetic parameter values given in Table 1, to a double layer capacitance $C_d$ of $(125 \pm 40) \times 10^{-6}$ F.cm$^{-2}$ and to an electrolyte resistance $R_e$ of $(0.08 \pm 0.01)$ $\Omega$ (for a working electrode surface area equal to 1 cm$^2$).

4. CONCLUSION.

By using both pulse and A.C. impedance techniques, it was possible to accurately determine the kinetic parameters characterizing the mass and the charge transfers occurring, in the electrochemical oxidation and reduction reactions of Ti$^{3+}$ ions.

Dahl et al. had estimated the diffusion coefficient of Ti$^{2+}$ ion at 723 K from their study on electrodeposition of titanium from TiCl$_4$ solutions (8). They considered that this diffusion coefficient is in the range of $(1-3) \times 10^{-5}$ cm$^2$.s$^{-1}$. By comparing with our work we can assert that the diffusion coefficients of Ti$^{3+}$ and Ti$^{2+}$ are close to each other. Moreover, we have been able to put a figure to the effect of thermal convection by determining the resulting thickness $\delta$ of the diffusion layer. The value obtained is in good agreement with that which can be estimated by using the relation $\delta = \sqrt{2D_t}$ (7b) knowing...
the value of the diffusion coefficient of Ti$^{3+}$ and that of the duration $t$ for which steady-state diffusion conditions due to thermal convection are reached. In fact from the corresponding value of $t$ (~10 s) deduced from the chronoamperometric measurements, we find $\delta = 0.017 \pm 0.005$ cm.

Concerning the intrinsic rate constants $k_0$ of the electrochemical systems of titanium, only the one related to the Ti$^{2+}$/Ti(0) redox system is available in the literature. Haarberg et al. (9) considered that the electrodeposition of titanium from Ti$^{2+}$ is irreversible, as we have demonstrated in this work. The value of $k_0$ which can be calculated from their work (1.5 $10^{-6} \text{cm}^{-1}$) is very close to ours.

The results described in this paper complete those of our previous work concerning the thermodynamic properties of titanium and its compounds with iron and oxygen (1,4).

ACKNOWLEDGEMENTS.

We wish to thank the C.N.R.S. for its financial support (A.T.P. N° 70.0002).

REFERENCES.

(1) D.M. Ferry, G.S. Picard and B.L. Trémillon, Trans. Inst. Min. Met., Sect. C, (1987), in press.
(2) G. Picard, F. Séon and B. Trémillon, J. Electrochem. Soc., 129 (1982) 1450.
(3) F. Séon, G. Picard and B. Trémillon, Electrochim. Acta, 28 (1983) 209.
(4) D. Ferry, E. Noyon and G. Picard, J. Less Common Metals, 97 (1984) 331.
(5) D.M. Ferry, G.S. Picard and B.L. Trémillon, Communication presented at the EUCHEM Conference on Molten Salts (1986) Geiranger, Norway.
(6) D.M. Ferry, G.S. Picard and B.L. Trémillon, 170th Meeting of the Electrochemical Society, Extended Abstracts, Vol 86-2, p 988, San Diego, California, USA (1986).
(7) A.J. Bard and L.R. Faulkner in "Electrochemical Methods. Fundamentals and Applications". John Willey and Sons Editors, New-York, 1980. a) p 268, b) p129.
(8) G. Dahl, A. Hjelset, W.R. Rolland, Å. Sterten, J. Thonstad and R. Tunold, 34th meeting of the International Society of Electrochemistry; Extended Abstracts; (1983) p. 1131; held in Erlangen (Germany), Sept. 18-23, 1983.
(9) G.M. Haarberg, W.K. Rolland, Å. Sterten, J. Thonstad and S. Øye, Communication presented at the EUCHEM Conference on Molten Salts (1986) Geiranger, Norway.
Figure 1: a) i-E curves in the steady-state conditions due to thermal convection (concentration of $Tl^{3+} = 0.11$ mol.kg$^{-1}$).
b) Bilogarithmic analysis of the oxidation wave.
c) Verification of Cottrell's law at a potential corresponding to the diffusion limiting current (point P in figure 1a).
Figure 2: a) Typical chronopotentiograms for the oxidation of Ti$^{3+}$ ions (concentration of these ions: $8 \times 10^{-2}$ mol.kg$^{-1}$). Current densities: $j = 29$, $33$ and $42$ mA.cm$^{-2}$. b) Verification of Sand's law. c) Chronopotentiograms with current reversal, $j = 62$ mA.cm$^{-2}$. d) Ratio of $\tau_{\text{red}}$ (transition time corresponding to the reduction of the species formed during electrolysis of duration $t_{\text{oX}}$) to $t_{\text{oX}}$ for various current densities.
Figure 3: a) Typical chronopotentiogram for the reduction of $\text{Ti}^{3+}$ into $\text{Ti}^{2+}$ and metallic titanium (concentration of $\text{Ti}^{3+}$: $7.5 \times 10^{-2}$ mol.kg$^{-1}$).

b) Chronopotentiograms with current reversal at potentials corresponding to the first reduction step (formation of $\text{Ti}^{2+}$ ions) and to the second reduction step (leading to the electrodeposition of metallic titanium).

c) Variation of the ratio $\tau_{\text{ox}}/\tau_{\text{red}}$ versus reversal potential.
Figure 4: Nyquist (a) and Bode (b-c) diagrams of the oxidation of Ti$^{3+}$ (imposed potential: -0.5 V) and corresponding simulated curves.
| Electrochemical system | $E^*$ (V) | $k_o$ | $\alpha$  |
|------------------------|---------|------|---------|
| Ti$^{3+}$/Ti(IV)       | -0.44 ± 0.02 | 0.2 ± 0.1 | 0.70 ± 0.05 (ox) |
| Ti$^{2+}$/Ti$^{3+}$    | -1.94 ± 0.01 | (2 ± 1)$10^{-3}$ | 0.50 ± 0.05 |
| Ti(0)/Ti$^{2+}$       | -2.05 ± 0.01 | (3 ± 1)$10^{-6}$ | 0.60 ± 0.05 (red) |

Table 1: Kinetic characteristics of the different redox systems of titanium in LiCl-KCl eutectic melt at 743 K.