

Electrochemistry of Titanium Tetrachloride in 1-Butyl-2,3-dimethyl Imidazolium Tetrafluoroborate

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The electrochemistry of titanium tetrachloride has been examined in trialkyl-substituted imidazolium tetrafluoroborate at 65 °C. Ti(IV) reduction was studied with chronopotentiometry and cyclic voltammetry in melts with different concentrations of TiCl₄. The diffusion coefficient of Ti(IV) ranged between $1.1 \cdot 10^{-7}$ and $7 \cdot 10^{-8}$ cm² s⁻¹. The electroreduction of Ti(IV) was found to proceed via the sequence of one-electron steps, the relative stability of the low valence intermediates being dependent on the concentration of TiCl₄ in the electrolyte. The kinetics of an overlapping disproportionation reaction of Ti(II) was examined and its rate constant at low concentration (0.025 mol/l) of TiCl₄ was found to be $k = 2 \cdot 10^6$ cm³ mol⁻¹ s⁻¹, Ti(0) being the final product of the stepwise reduction process at higher concentrations (0.03–0.14 mol/l).

Key words: Titanium; Electrochemistry; Ionic Liquids; Cyclic Voltammetry; Chronopotentiometry.

1. Introduction

Electrodeposition of titanium has always been attractive to researchers. Therefore the electrochemistry of Ti was widely investigated in high temperature molten chlorides and fluorides by Taranenko et al. [1], Makyta et al. [2] and Shapoval et al. [3].

The deposition of Ti from highly concentrated alkaline solutions, claimed by E. Pokorney in 1930 [4], could not be reproduced. In strongly acidic molten salts at a ambient temperature, Ti(IV) also proved to be impossible to reduce to Ti(0) [5]. Although Al-Ti alloy was deposited from an oversaturated Ti(II) solution in an 1-ethyl-3-methylimidazolium chloride melt by Tsuda et al. [6], as well as from Ti(II) in an AlCl₃:NaCl melt [7].

Lisowska and Bialozor [8] investigated the electroreduction of TiCl₄ in DMSO and reported the mechanism as an irreversible reduction of Ti(IV) to Ti(III) followed by a secondary chemical reaction. The reduction to Ti metal was not achieved.

The electrochemistry of Ti-organometallic complexes has been studied in aromatic solvents by Ab-

bot et al. [9]. The authors received dendritic Ti deposits.

The introduction of low temperature ionic liquids (ILs) as electrolytes opened new possibilities to the electrochemistry of refractory metals. Water-free, low melting and completely ionic media seemed to be perfect candidates for studying the possibility of obtaining new coatings with desirable characteristics.

Mukhopadhyay et al. investigated Ti in disubstituted imidazolium-based ILs and managed to deposit micro-quantities of Ti on highly oriented graphite [10] and gold (111) [11]. In both cases, in situ electrochemical scanning tunnelling microscopy was applied for detecting the deposit.

There is still no clear understanding of the processes and intermediate products of Ti compounds during reduction reactions in imidazolium-based ILs. The 1,2,3-trialkylated imidazolium-based ILs exhibit higher electrochemical stability. Therefore they were chosen for studying the electrochemical reduction behaviour of TiCl₄.

Cyclic voltammetry (CV) and chronopotentiometry (CP) techniques have proven to be useful for determin-

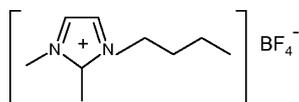


Fig. 1. Structure of BMMIM- BF_4 .

ing the multistep reaction mechanism of Ge(IV) [12], Si(IV) [13], U(IV), Nb(V) and Hf(IV) [14] electroreduction in high temperature molten salts. In the present work, we applied these techniques for studying the Ti(IV) electrochemistry in trialkylated imidazolium-based ILs.

2. Experimental

2.1. Chemicals

1-Butyl-2,3-dimethylimidazolium tetrafluoroborate (BMMIM- BF_4) (Fig. 1) was obtained from H. Schottenberger, University of Innsbruck, Institute of General, Inorganic and Theoretical Chemistry, Austria. The IL was dried under vacuum (0.004 mbar) at 65 °C overnight and kept under argon (99.999% purity) at all times.

Titanium tetrachloride (99.9%), obtained from Aldrich, was used as received.

Handling of the chemicals and cell assembling were performed in a glove-box (MBraun Labstar) filled with argon (99.999% purity). The oxygen and water contents were always less than 5 ppm.

2.2. Electrochemical Studies

Electrochemical studies were performed in a standard three-electrode electrochemical cell, using a Pt-disc (0.031 cm^2) as working electrode, a glassy carbon rod as auxiliary electrode, and an Ag/AgCl reference electrode in BMMIM- BF_4 solution oversaturated with AgCl. The reference electrode compartment was separated from the IL by a highly porous Vicor tip. All the electrochemical measurements have been carried out with a Voltalab PGZ301 system (Radiometer Analytical). The temperature was maintained at 65 °C.

3. Results and Discussion

The purity of the IL is of great importance for getting reproducible results. Prior to the experiments, voltammetry of the BMMIM- BF_4 IL has been performed. After establishing a constant potential of the Pt electrode in the melt, cathodic and anodic curves were recorded consequently. The anodic sweep was started from the equilibrium potential as well.

It was found that the pure IL is electrochemically stable in the range of -1.8 to $+2$ V vs. an Ag/AgCl reference electrode (Fig. 2). The cathodic limit is caused by reduction of the imidazolium-based cation. In the anodic direction, oxidation of the tetrafluoroborate anion, with BF_3 and fluorocarbons formation, limits the electrochemical window [15, 16]. The anodic peak at

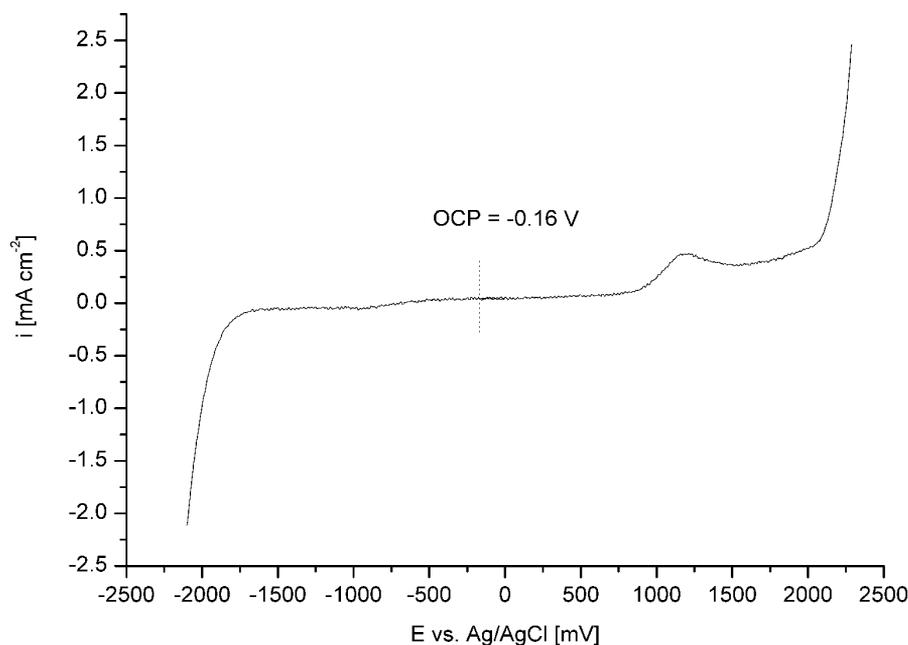


Fig. 2. Cathodic and anodic curves of pure BMMIM- BF_4 IL; sweep rate, 0.1 V/s, temperature, 65 °C.

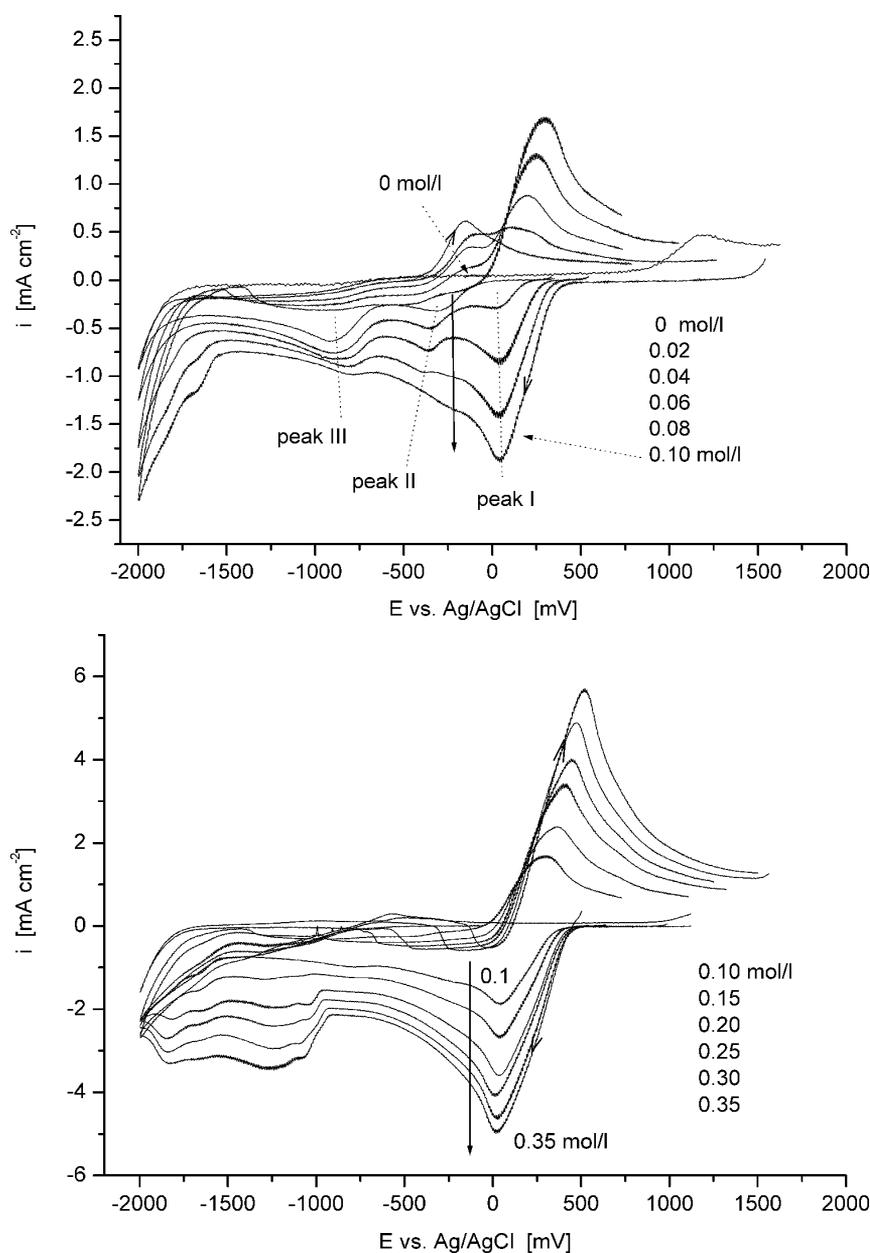


Fig. 3. Cyclic voltammograms of TiCl_4 solutions in BMMIm- BF_4 . Top: 0 to 0.1 mol/l in concentration steps of 0.02 mol/l; bottom: 0.1 to 0.35 mol/l in concentration steps of 0.05 mol/l; scan rate, 0.1 V s^{-1} .

+1.2 V is attributed to the chloride oxidation [15]; the impurity of Cl^- results from the synthesis.

The presence of TiCl_4 in the melt results in cathodic and anodic peaks, increasing with the concentration of TiCl_4 (Fig. 3). The observed pattern differs depending on the concentration. The CV of diluted solutions (Fig. 3, left) shows a first cathodic peak within the range -0.36 to -0.38 V. At higher concentrations from 0.02 mol/l, an additional cathodic peak appears

at $+0.03$ to 0.05 V. These two cathodic peaks gradually merge at increasing concentrations. Up to the concentration 0.1 mol/l, a third cathodic peak is observed at -0.9 V (Fig. 4, circles).

The dependency of the peak current density on the concentration for the first cathodic peak (I) consists of two linear branches (Fig. 4, squares), indicating an influence of the saturation of the IL with TiCl_4 (drops of TiCl_4 were observed at higher concentrations). In addi-

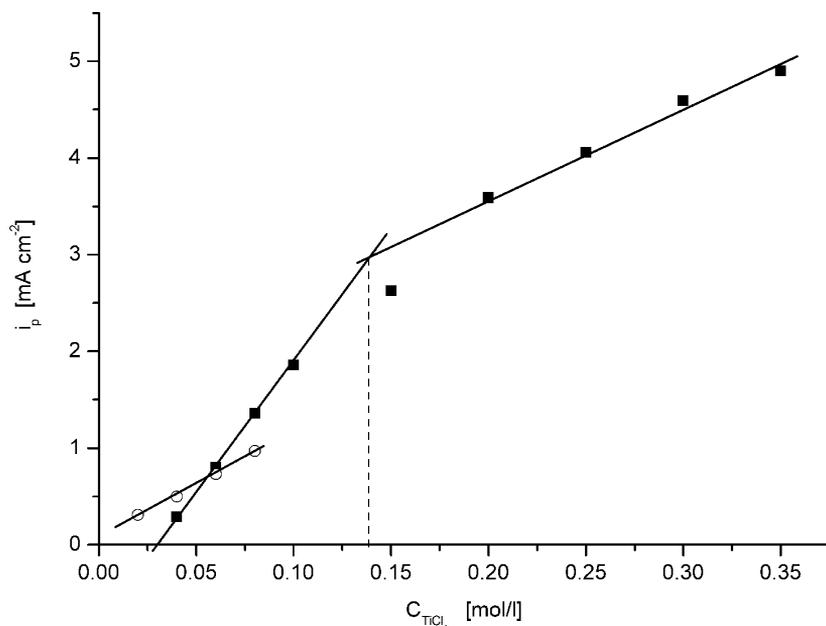


Fig. 4. Current of cathodic peak I (■) and peak III (○) vs. concentration.

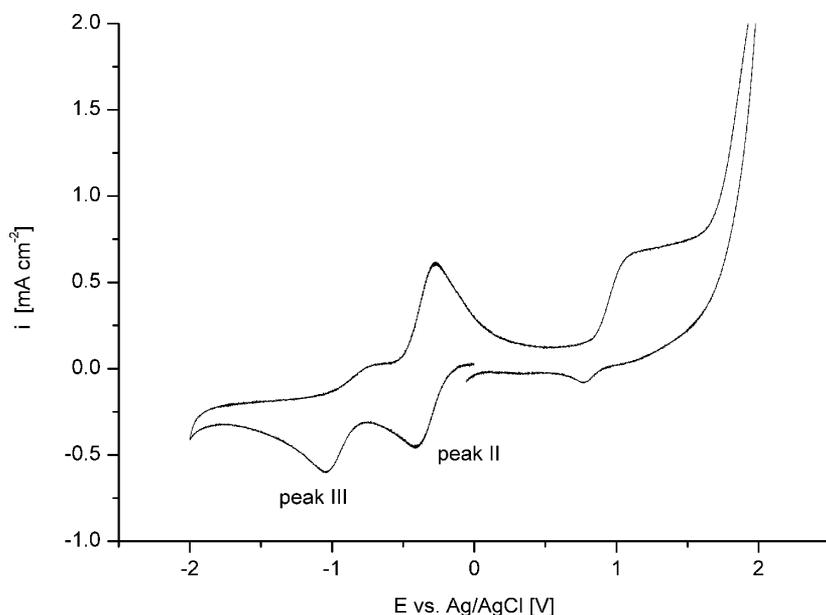


Fig. 5. CV curve of 0.025 mol/l TiCl_4 in BMMIm- BF_4 at 0.1 V/s.

tion, the peak at -0.9 V vanishes and, instead, a broad irregular cathodic wave appears at approx. -1.25 V.

Thus, the preliminary study of system TiCl_4 -BMMIm- BF_4 by cyclic voltammetry revealed at least three concentration regions where the electrochemical behaviour of dissolved TiCl_4 is essentially different: 1.) “diluted solution”, $C < 0.03$ mol/l; 2.) “medium concentration”, $0.03 < C < 0.14$ mol/l; and 3.) “con-

centrated solution”, $C > 0.14$ mol/l. The reduction processes in these three concentration regions were studied by CV and CP.

3.1. Diluted Solution (0.025 mol/l TiCl_4 in BMMIm- BF_4)

Cyclic voltammograms at different sweep rates were recorded, as well as chronopotentiograms for a

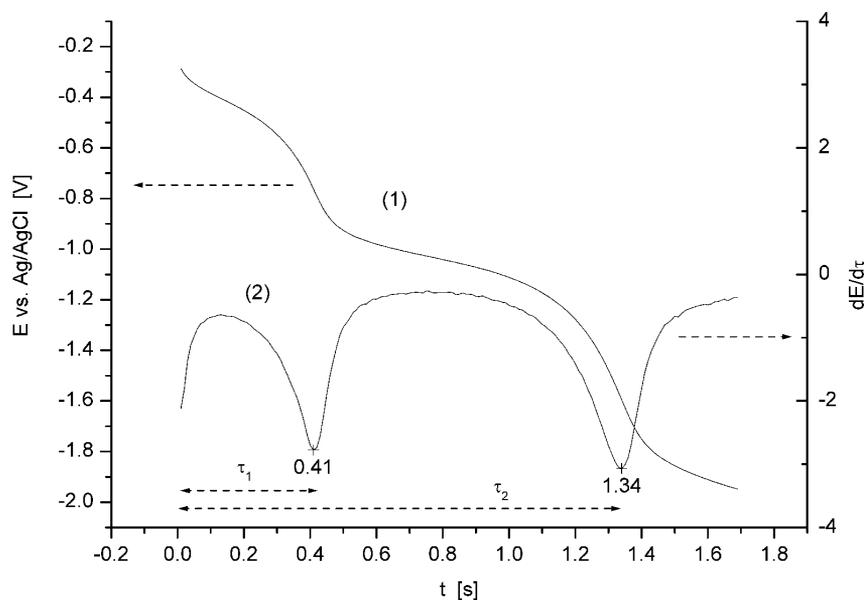


Fig. 6. Potential response to a current step of -1.45 mA cm^{-2} (curve 1) and its 1st derivative (curve 2).

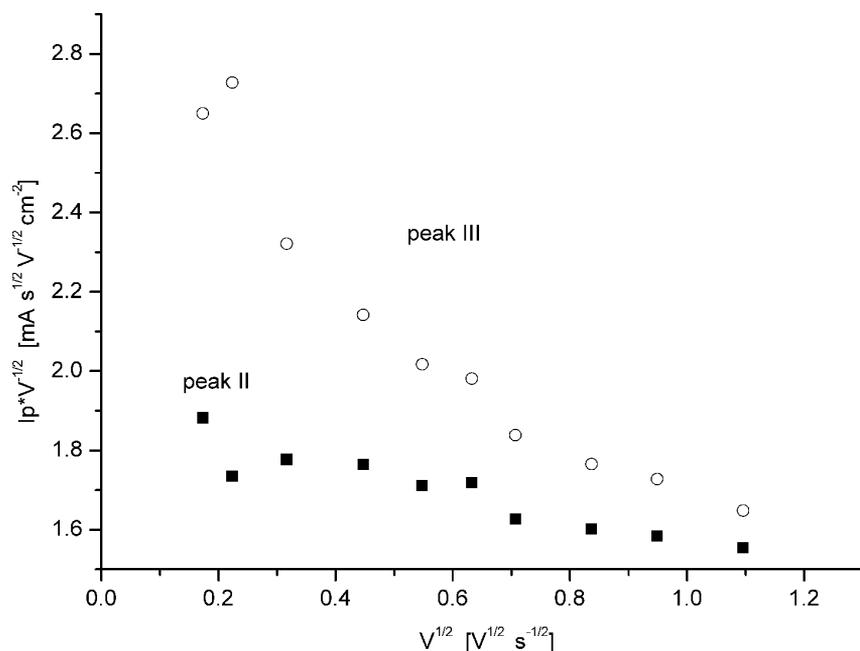


Fig. 7. Voltammetry peak current analysis.

range of transition times starting at 0.3 s up to 14 s. Two cathodic waves were distinctly observed, both in cyclic voltammograms and chronopotentiograms, in this concentration region (Figs. 5, 6).

Voltammetry data was analyzed in terms of the Sevcik-Randles equation [17]

$$\frac{i_p}{v^{1/2}} = 0.4463 \cdot \left(\frac{F^3}{RT}\right)^{1/2} n^{2/3} A D_o^{1/2} C_o^* \quad (1)$$

where i_p is the peak current, v the sweep rate, n the number of electrons involved in the reaction, A the area of the electrode, D_o the diffusion coefficient and C_o^* is the bulk concentration of the depolarizer. Peak currents were determined for the two cathodic peaks and $\frac{i_p}{v^{1/2}}$ was plotted as a function of \sqrt{v} (see Fig. 7). For analysis of CP data, the Sand equation was applied [17]:

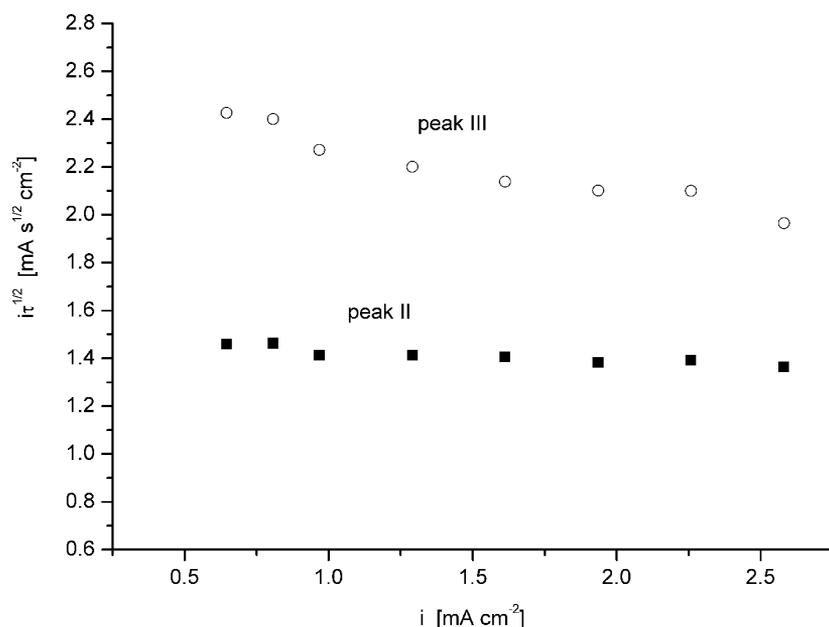


Fig. 8. Transition times analysis.

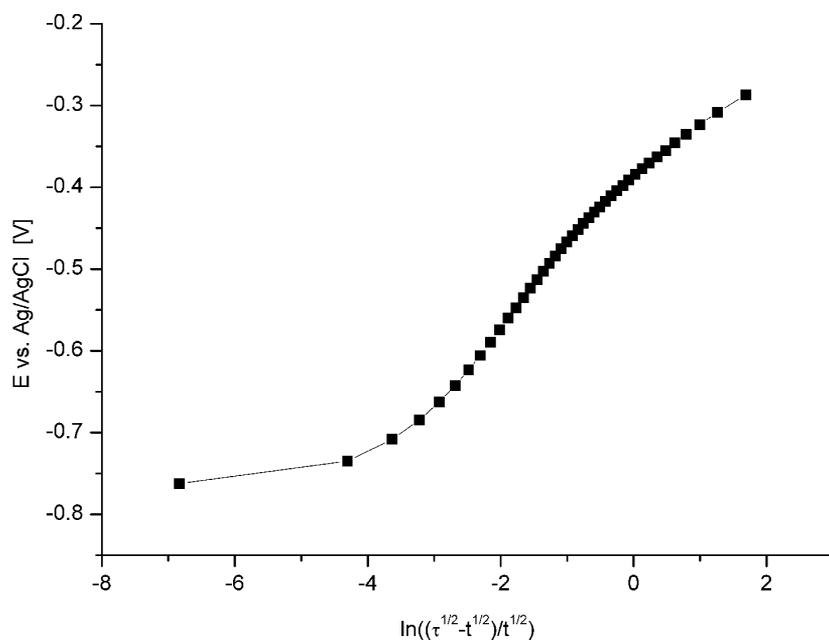


Fig. 9. Karaoglanov plot of the potential-time curve in the potential range of peak II.

$$i \cdot \tau^{1/2} = \frac{1}{2} \pi^{1/2} F n A D_0^{1/2} C_0^* \quad (2)$$

where i is the applied current, τ the transition time, and n the number of electrons involved in the reaction.

Analysis of transition times and peak currents showed that the reduction processes have some ki-

netic complications and are different for the two peaks, where peak II indicates a diffusion-controlled reaction (Figs. 7, 8).

Analysis of the shape of the potential-time curve is given in terms of the Karaoglanov equation

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (3)$$

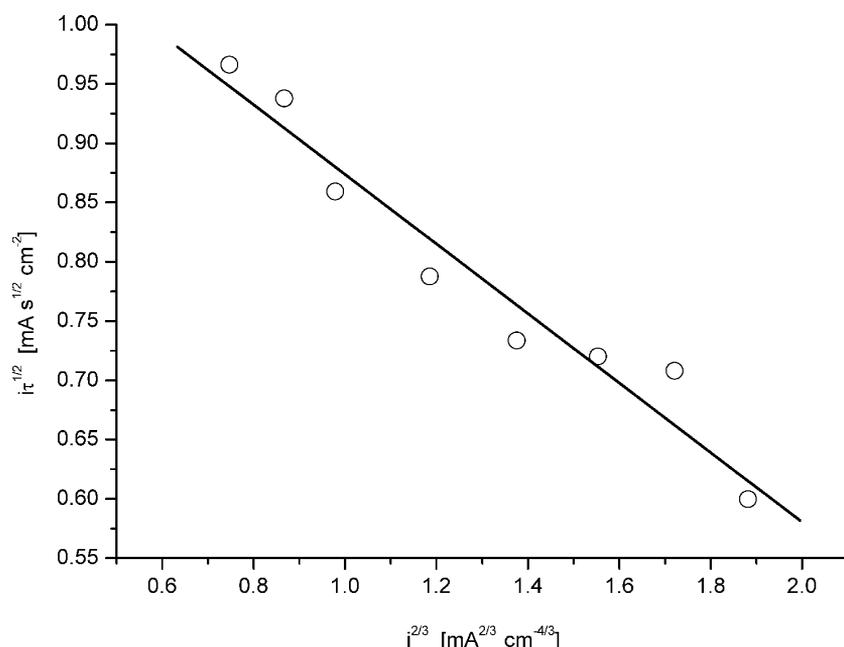
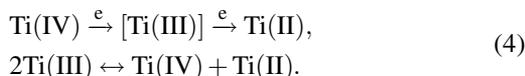


Fig. 10. Transition times analysis in terms of the Fischer-Dračka theory [20].

in Figure 9. This plot is S-shaped, which can be attributed to a 2-electron wave with the formation of a thermodynamically unstable intermediate in the equilibrium with the initial reactant and the product of the first visible peak [18]. A proposed process for peak II is:



Assuming the first wave process (peak II) as (4), the diffusion coefficient of Ti(IV) was calculated from the Sand equation (2), resulting for $n = 2$ in $D_{\text{Ti(IV)}} = (1.09 \pm 0.03) \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This value is in good agreement with studies of titanium(IV) chloride in strong Lewis acidic ILs [5]. In water and DMSO solutions, studies of the Ti(IV)/Ti(III) couple have shown a diffusion coefficient to be an order of magnitude higher ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [19].

The second wave (peak III) corresponds to a process with some kinetic complications. Following general criterions is useful for the determination of the character of kinetic complications [12].

Provided the conditions for semi-infiniteness and linearity of diffusion are obeyed,

- the derivative $\frac{d(i\tau^{1/2})}{di} > 0$, if the conjugated reactions of depolarizer's inactivation (auto-inhibiting) take place or the diffusion process is partially over-

lapped by the discharge process of a surface layer (slow adsorption);

- the derivative $\frac{d(i\tau^{1/2})}{di} < 0$, if the depolarizer is partially replenished by antecedent or subsequent (auto-catalytic) chemical reactions.

The negative slope of the $i\sqrt{\tau}(i)$ plot (Fig. 8) evidences a chemical reaction with partial replenishment of the depolarizer. Since the first reduction step (peak II) is practically pure diffusion-controlled, the chemical reaction cannot be related to a pre-dissociation of some inactive complex of Ti(IV). Most probably, it is a disproportionation of the product according to the following general scheme, which was theoretically considered by Fischer and Dračka [20]:



According to their theory, the chronopotentiometric function $i\sqrt{\tau}$ should depend linearly on $i^{2/3}$ according to the equation

$$\begin{aligned} i\tau^{1/2} &= C_0 F \pi^{1/2} D_A^{1/2} \\ &- \left(\frac{3}{16}\right)^{1/3} \pi^{1/2} D_A^{-1/2} D_B^{2/3} F^{1/3} k^{-1/3} i^{2/3}. \end{aligned} \quad (6)$$

Figure 10 shows the dependency of the function $i\sqrt{\tau} = i\sqrt{\tau_{\text{peak III}}} - i\sqrt{\tau_{\text{peak III}}}$ on $i^{2/3}$. It is linear, which con-

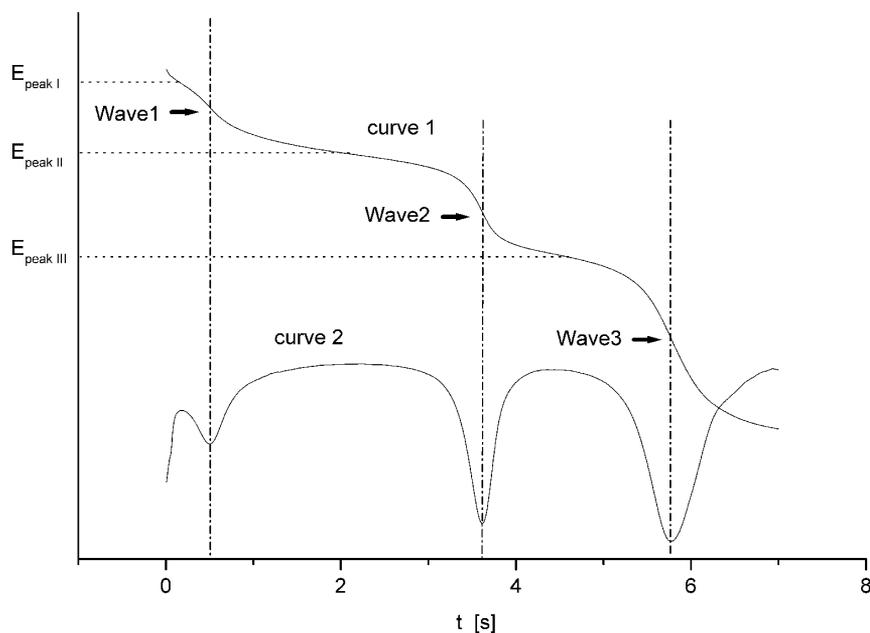
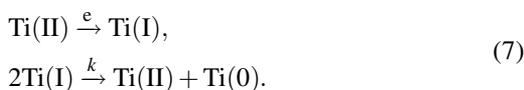


Fig. 11. Potential response to a current step of -0.97 mA cm^{-2} (curve 1) and its 1st derivative (curve 2).

firms the validity of general reaction mechanism (5) for the second reduction wave (peak III). Obviously, in our case A is Ti(II) and B is Ti(I), and the two-step mechanism is



Considering the chemical reactions (7) as totally irreversible, the diffusion coefficient of Ti(II) and the rate constant of (7) were calculated from the fitting of experimental data with equation (6) (Fig. 10): $D_{\text{Ti(II)}} = (7.45 \pm 0.2) \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $k = (1.95 \pm 0.05) \cdot 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

3.2. Medium Concentration (0.05 mol/l TiCl₄ in BMMIm-BF₄)

Three consecutive separated waves were observed in the “medium” concentration range (Fig. 3a). The first wave (peak I) appeared at more positive potentials ($\sim 0 \text{ V}$), corresponding to the formation of the first intermediate, Ti(III), which becomes more stable as the concentration increases (the relative height of the peak was growing). Figure 11 shows the potential response to a current step in the electrolyte with 0.05 mol/l TiCl₄.

The independency of the $i\tau^{1/2}$ on the current density is an evidence of a diffusion-controlled reac-

tion (see Fig. 12). The $i\tau^{1/2}$ ratios are approximately equal to: $i\tau^{1/2}_1 : i\tau^{1/2}_2 : i\tau^{1/2}_3 = 1 : 3 : 4$, which could be attributed to the formation of Ti(III), Ti(I) and Ti(0) reduction products at the end of each reduction step. A similar pattern is observed at the concentration 0.1 mol/l.

Using (2), the diffusion coefficient for Ti(IV) was calculated from the CP data. The value in this intermediate concentration region is somewhat lower: $D_{\text{Ti(IV)}} = (6.9 \pm 0.2) \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.

3.3. Concentrated Solution

Further increase of the concentration resulted in a phase separation in the melt: small drops of undissolved TiCl₄ were clearly visible on the surface and in the bulk of the electrolyte.

Accordingly, the reduction pattern becomes much more complicated at potentials more negative than -1 V . A series of poorly resolved waves appear in the potential region ranging from about -1 to -2 V in the cyclic voltammograms (Fig. 3b) and up to 5 peaks are observed in the derivative curve of the CP data (Fig. 13).

Transition time analysis for these peaks is given in Fig. 14. One can see that these transition times can hardly be interpreted in terms of a simple stepwise reduction mechanism.

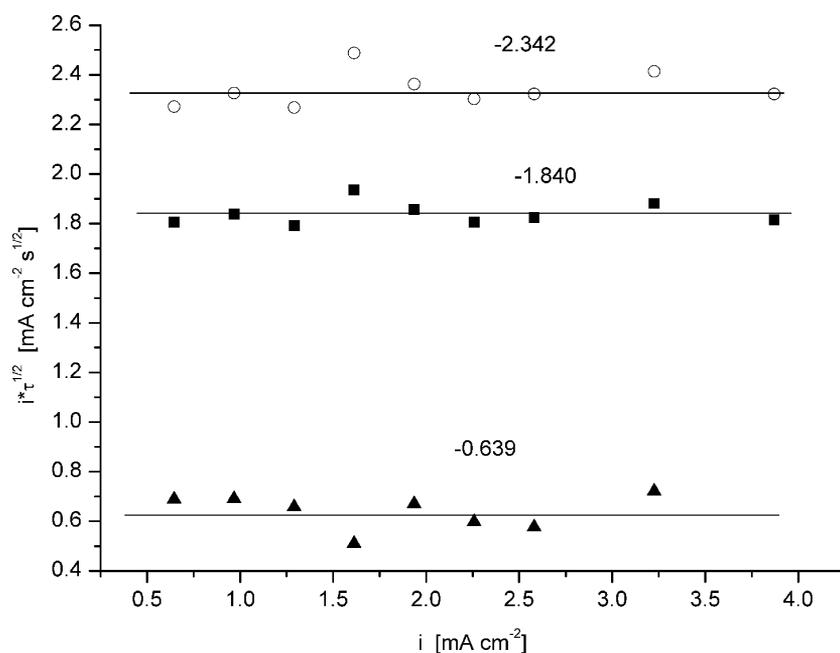


Fig. 12. Transition times analysis in terms of the Sand equation for three consecutive cathodic waves: \blacktriangle – peak I at 0.03 V; \blacksquare – peak II at -0.4 V; \circ – peak III at -0.9 V.

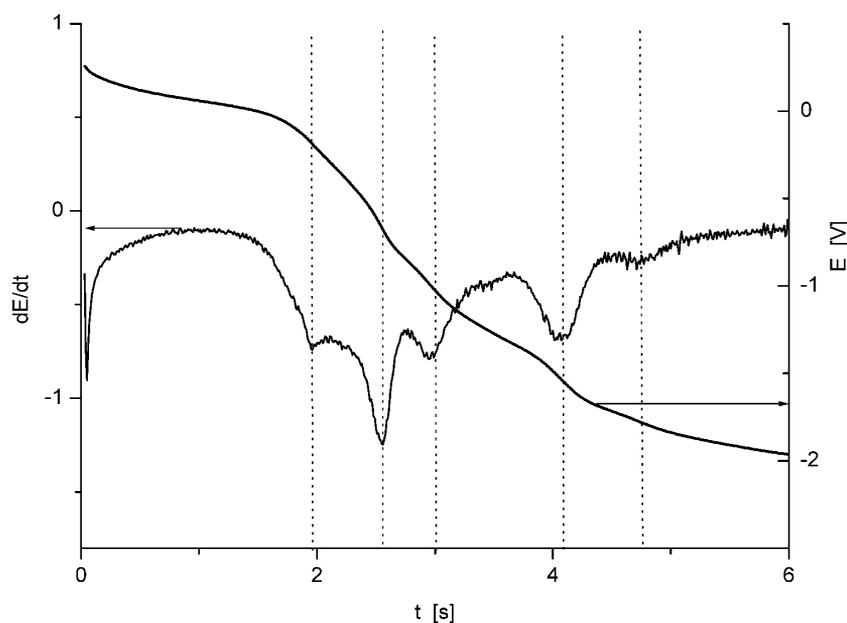


Fig. 13. Potential response to a current step (-3.0 mA cm^{-2}) and its 1st derivative for $C_{\text{TiCl}_4} = 0.2 \text{ mol/l}$.

The reason of such behaviour can be related to the phase separation, which is observed in “concentrated” solutions. In fact, the electrochemical process takes place in the heterogeneous system containing two liquid phases – IL saturated with TiCl_4 and vice versa. There are no theoretical studies of this case in the literature yet.

4. Conclusions

As shown from our results, the overall electrochemical reduction mechanism can be represented in terms of the general scheme, which was first proposed in [12]: sequence of one-electron reduction steps with accompanying disproportionation reactions, $2\text{Ti}(i) \rightleftharpoons$

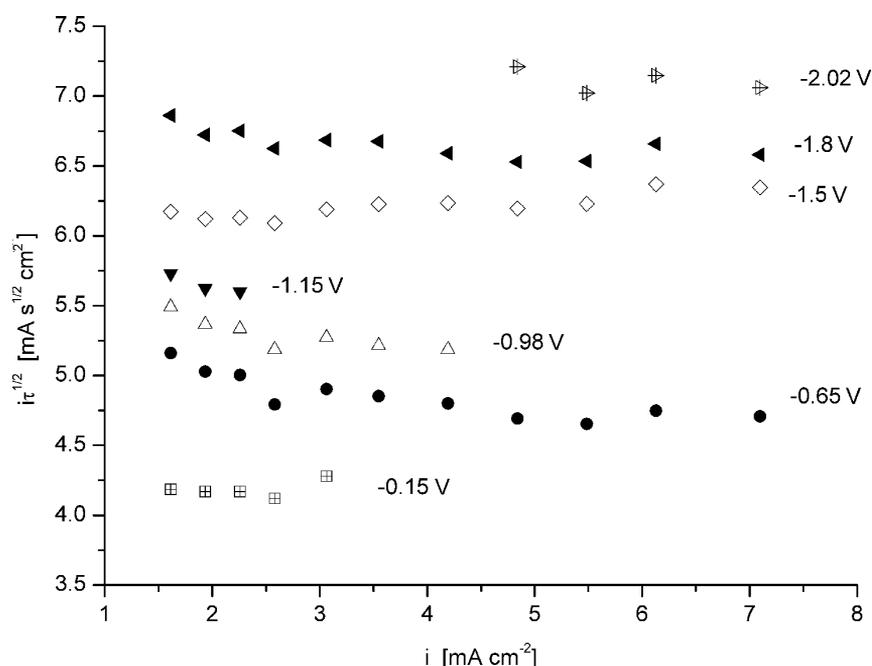


Fig. 14. Transition times analysis in terms of the Sand equation, $C_{\text{TiCl}_4} = 0.2 \text{ mol/l}$. Potentials in the plot correspond to potentials of the process transition times.

$\text{Ti}(i+1) + \text{Ti}(i-1)$, with possible formation of each species in the intermediate oxidation states. In diluted solutions, the $\text{Ti}(\text{II})$ intermediate is more stable, and also the disproportionation kinetics of $\text{Ti}(\text{I})$ can be detected. Total four-electron reduction to $\text{Ti}(\text{0})$ is observed with the formation of $\text{Ti}(\text{III})$ and $\text{Ti}(\text{I})$ as the relatively stable intermediates. At concentrations higher than 0.14 mol/l the limit of TiCl_4 solubility in the IL influences significantly the reduction mechanism, re-

sulting in a very complicated reduction pattern. Theoretical explanation of the electrochemical processes in such a heterogeneous system is still to be found.

Acknowledgements

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