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Electrochemistry of Titanium(IV) in Basic *n*-Butylpyridinium Chloride–Aluminum Chloride in the Presence of Oxide

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Abstract: The electrochemistry of Ti(IV) has been studied in basic aluminum chloride–*n*-butylpyridinium chloride (Bu(py)Cl). Ti(IV) has been found to exist as two electrochemically reducible species, one an oxide complex, which are in slow equilibrium; both are diffusion controlled as determined by normal pulse voltammetry. The $E_{1/2}$ value for the first wave, where the species is assumed to be $TiCl_6^{2-}$, is −0.343 V vs. an Al reference electrode and is independent of the melt acidity. The second reduction, where the species is assumed as $TiOCl_4^{2-}$, occurs at ca. −0.77 V and shows a half-wave potential variation with melt acidity, indicating the involvement of two chloride ions per Ti(IV). Only one oxidation wave, presumably that of a Ti(III) chloro complex, is found. The equilibrium constant for the reaction $TiCl_6^{2-} + AlOCl_2^- \rightleftarrows AlCl_4^- + TiOCl_4^{2-}$ has been determined as 900 at 40 °C and, within experimental error, appears independent of melt acidity in the region of 0.7:1 to 0.9:1 $AlCl_3$–Bu(py)Cl. Titanium metal may be anodized to yield Ti(III) but appears to passivate in the melt.

Molten mixtures of n-butylpyridinium chloride and aluminum chloride have interest as solvents for electrochemical and spectroscopic studies. This results from their low melting point, which is below 40 °C in the composition range 2:1–0.75:1 mole ratio of $AlCl_3$–*n*-butylpyridinium chloride (Bu(py)Cl), the huge change in acid–base properties in going from acid (excess $AlCl_3$) to basic (excess Bu(py)Cl) composition,[1,2] and their aprotic and anhydrous properties. The melts start to decompose around 140 °C, and the maximum temperature where they can usefully be employed as solvents without significant decomposition is approximately 100 °C. The activity of free $AlCl_3$ in acid melts appears lower than systems of alkali halide and aluminum chloride.[2] Composition changes due to evaporation of Al_2Cl_6(g) are minimal in these melts even at temperatures as high as 140 °C.

The practical application of these melts has thus far been limited. One area, however, where these melts may be useful is as media for photoelectrochemistry at semiconductor electrodes. An oxide, such as TiO_2, may be used as the semiconductor.[3] This present study was undertaken in part as an outgrowth of semiconductor electrode studies to obtain information on electrochemistry of titanium in these melts.

No investigations on the electrochemistry of titanium in $AlCl_3$–Bu(py)Cl melts are reported in the literature. Fung and Mamantov[4] have investigated the electrochemistry of Ti(II) in acid mixtures of NaCl–$AlCl_3$ in the temperature range 150–300 °C. Ti(II) was oxidized reversibly in two steps to Ti(III) and Ti(IV). The stability of Ti(II) increased with increasing acidity and lower temperatures.

Ti is a very active metal with a standard potential close to Al.[5] The reaction between Ti(s) and pure $AlCl_3$(l) has been used to prepare $Ti(AlCl_4)_2$.[4,6] Fung and Mamanotov found no reduction of Ti^{2+} to Ti metal in NaCl–$AlCl_3$; a reduction to pure titanium metal is unlikely in a melt containing an appreciable activity of $AlCl_3$.

The determination of the oxide content and the identification of oxide containing species in a chloroaluminate melts is complex and has been the subject of a number of investigations.[7-10] The reaction of oxide with the melt can be separated, from a stoichiometric point of view, into two parts, depending on the composition of the melt

$$O^{2-} + AlCl_4^- \rightleftarrows AlOCl + 3Cl^- \qquad (1)$$

$$O^{2-} + AlCl_4^- \rightleftarrows AlOCl_2^- + 2Cl^- \qquad (2)$$

where (1) is the dominant reaction in the acid composition range, leading to the formation of AlOCl, and (2) is the dominant reaction in the basic composition range, leading to the formation of $AlOCl_2^-$. Equilibrium 2 does not exclude formation of AlO_2^- as equilibrium 3 is independent of the Cl^- concentration.

$$2AlOCl_2^- \rightleftarrows AlO_2^- + AlCl_4^- \qquad (3)$$

Mamantov and Osteryoung[11] have surveyed proposed methods for determination of oxide in these melts and concluded that no viable method for the determination of oxide has been reported thus far.

Experimental Section

Chemicals. Titanium(IV) chloride (Fisher Scientific) was obtained as a liquid with a slight yellowish color and was purified by distillation to give a colorless product.

$TiCl_4$ was introduced into the melt by a syringe. The density of $TiCl_4$ is 1.726 g cm^{-3} compared to 1.231 g cm^{-3} for a 0.8:1 melt at 40 °C. The $TiCl_4$ sank to the bottom but dissolved easily with stirring to yield a light yellow colored melt; it was stable in these melts for at least 1 week. Concentrations of approximately 5–30 mM were used for this study.

Aluminum chloride from Flúka A. G. was distilled twice under vacuum in a sealed Pyrex tube from a mixture containing a small amount of NaCl and Al metal. This technique, as well as the preparation of *n*-butylpyridinium chloride and preparation of melts, is described elsewhere.[1] Lithium carbonate (Fisher Scientific) was dried under vacuum for several hours at 200 °C before use. Chemicals were stored and all experiments performed, in a Vacuum Atmosphere drybox with an HE 193-2 drytrain, as described in prior publications.

Cells, Electrodes, and Instrumentation. The electrochemical cell was made of Pyrex and covered with a Teflon cap. The volume of the cell was approximately 20 mL. The cap was drilled with holes to facilitate mounting of thermocouple well, auxiliary, reference, and indicator electrodes. The indicator electrode was a 3-mm diameter vitreous carbon electrode (Tokai) sealed in a Pyrex tube and polished to a mirrorlike finish. The auxiliary and reference electrodes consisted of Al wire immersed in a 2:1 $AlCl_3$–Bu(py)Cl melt. These melts were contained in glass tubes, and the melts were separated from the melt in the bulk phase by fine porosity glass frits. The melt level in the reference and secondary

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[1] Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.

[2] Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.

[3] Gale, R. J.; Nozik, A. J.; Osteryoung, R. A., paper presented at the Mile High Symposium, The Electrochemical Society, Ft. Collins, CO, June 1979.

[4] Fung, K. W.; Mamantov, G. *J. Electroanal. Chem.* **1972**, *35*, 27.

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[8] Tremillon, B.; Bermond, A.; Molina, R. *J. Electroanal. Chem.* **1976**, *74*, 53.

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[10] Picard, G.; Sean, F.; Tremillon, B. *J. Electroanal. Chem.* **1979**, *102*, 65.

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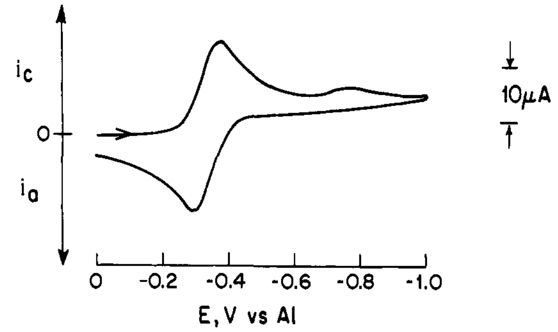

Figure 1. Cyclic voltammogram in a 0.8:1 $AlCl_3$–Bu(py)Cl melt at 40 °C: concentration of $TiCl_4$, 13.65 mM; sweep rate, 50 mV s^{-1}; electrode area, 0.0706 cm^2.

compartments was kept slightly higher than the bulk melt. The aluminum wire was cleaned in a mixture of H_2SO_4–H_3PO_4–HNO_3, rinsed with distilled water and dried in vacuo prior to use. A simple furnace was made by winding a heating element around a 150-mL beaker. The electrochemical cell was placed in this furnace, and the temperature was controlled to ±0.5 °C by a temperature controller (Thermo Electric 400) connected to a Chromel-Alumel thermocouple. Coulometric experiments were carried out in a glassy carbon crucible which was also used as the working electrode. Experiments were performed with a PARC Model 174 polarographic analyzer and with a Tacussel model UAP4 Research Polarograph.

Results and Discussion

Calculation of Activities. The equilibrium constant at 30 °C for anions in a melt of Bu(py)Cl and $AlCl_3$ may be described by using expression 4.[2] Raman spectra of these melts[12] have shown

$$K = \frac{(a_{\mathrm{Al_2Cl_7}})(a_{\mathrm{Cl^-}})}{(a_{\mathrm{AlCl_4^-}})^2} \leq 3.83 \times 10^{-13} \qquad (4)$$

that they contain no significant amount of molecular aluminum chloride, which may explain the apparently low vapor pressure of these melts compared to systems of alkali metal chlorides–$AlCl_3$. The observed aluminum chloride containing species for neutral (1:1) and basic melts was exclusively $AlCl_4^-$, and for the purpose of calculation it is therefore safe to neglect the mole fraction of any other aluminum containing species. Mixing of Z mol of $AlCl_3$ ($Z \leq 1.0$) with 1.0 mol of Bu(py)Cl therefore leads to formation of Z mol of $AlCl_4^-$ and $(1 - Z)$ mol of Cl^-. The following expression for the activity (a) of $AlCl_4^-$ and Cl^- is then obtained by assuming an ideal mixture.

$$a_{\mathrm{AlCl_4^-}} = \frac{Z}{(1 - Z) + Z} = Z \qquad (5)$$

$$a_{\mathrm{Cl^-}} = \frac{1 - Z}{(1 - Z) + Z} = 1 - Z \qquad (6)$$

An ideal mixture has been shown to be a useful approximation for these melts.[2] Consideration of the melt as an ionic or molecular mixture causes no difference in the calculation of activities or concentrations in moles per liter as long as there is a common cation $(Bu(py))^+$.

A. Electrochemistry of Ti(IV) in "Absence" of Oxide. Figure 1 shows a cyclic voltammogram of 13 mM $TiCl_4$ in a basic melt. The rest potential is −0.03 V vs. the Al(0) reference electrode. There is a reduction peak at $E_{p,c}{}^1 = -0.375$ V and a second, smaller reduction peak at $E_{p,c}{}^2 = -0.77$ V. The second peak results from oxide impurity (see below). One reoxidation wave is observed at $E_{p,a} = -0.30$ V. Table I shows the sweep rate dependence of the function $i_{p,c}/\nu^{1/2}$, where $i_{p,c}$ is the height of the first, most positive reduction wave. $i_{p,c}/i_{p,a}$ is the ratio of this reduction peak to the oxidation peak, and ΔE_p is the peak separation.

For a diffusion-controlled process, $i_p/\nu^{1/2}$ should be constant and independent of scan rate. In the present case the value of $i_p/\nu^{1/2}$ decreases slightly with increasing scan rate. The peak separation ΔE_p increases slightly with scan rate, about a 25-mV increase for 1 order of magnitude increase in scan rate. A similar effect was found for the couple Fe^{3+}/Fe^{2+} in a 1:1 $AlCl_3$–Bu(py)Cl by Hussey et al.,[13] who attributed this effect to filming of the surface of the electrode. The small decrease in the $i_p/\nu^{1/2}$ value may therefore be caused by a distortion of the curves due to filming or uncompensated IR drop.

Table I. Reduction of $TiCl_4$[a]

ν, V s^{-1}	$i_p/\nu^{1/2}$, mA, cm^{-2} $V^{-1/2}$ $s^{1/2}$	$E_{p,c}$, V	$i_{p,c}/i_{p,a}$	ΔE_p, V
0.02	1.19	−0.375	1.01	0.075
0.05	1.13	−0.375	1.00	0.080
0.10	1.12	−0.380	1.00	0.085
0.20	1.11	−0.385	1.02	0.100

[a] Cyclic voltammetric data at 40 °C and melt composition 0.8:1 $AlCl_3$-Bu(py)Cl. Concentration of Ti^{4+} is 13.65 mM.

Table II. Cyclic Voltammetric Data for Ti^{3+} in a 0.8:1 Melt[a]

ν, V s^{-1}	$i_{p,a}/\nu^{1/2}$, mA cm^{-2} $V^{-1/2}$ $s^{1/2}$	$E_{p,a}$, V	$i_{p,c}/i_{p,a}$	ΔE, V
0.01	0.601	−0.290	0.97	0.070
0.02	0.600	−0.290	0.98	0.070
0.05	0.608	−0.280	1.01	0.080
0.10	0.626	−0.280	1.02	0.080
0.20	0.577	−0.275	1.02	0.085
0.50	0.600	−0.270	1.03	0.100

[a] Temperature is 60 °C and Ti^{3+} concentration 5.62 mM. Theoretical peak separation, ΔE_p, is 66 mV at 60 °C.

We were unable to obtain a melt completely free of oxide. As will be discussed, $TiCl_4$ forms two species in the melt where the concentration of one of them—an oxychloride complex—is dependent on the oxide concentration in the melt. "Absence" of oxide means that the oxide concentration, and the amount of titaniumoxychloride species formed, is negligible compared to the concentration of $TiCl_4$ added.

Constant potential coulometric experiments performed at −0.5 V vs. the reference electrode (diffusion plateau for the first wave) show that the reduction of Ti^{4+} is a one-electron process ($n = 1.00 \pm 0.01$); both reduction waves were then absent, indicating an equilibrium between two Ti(IV) species (see below).

A red color is given by Ti^{3+} in these melts and appears to be stable for weeks. Table II shows cyclic voltammetric data for a 5.62 mM molar Ti^{3+} solution in a 0.8:1 melt at 60 °C. $i_p/\nu^{1/2}$ is independent of scan rate. The oxidation thus is diffusion controlled. The half-wave potential, $E_{1/2} = (E_{p,a} + E_{p,c})/2$ is -0.322 ± 0.002 V and is independent of the scan rate. The peak separation increases slightly with increasing scan rate but not as much as Ti(IV)—see Table I.

Normal pulse voltammetric experiments were used to determine the diffusion coefficients for the Ti(IV) species as a function of acidity. The diffusion-controlled limiting current produced by the electroreducible species is given by the Cottrell equation[14]

$$i_{\mathrm{lim}} = nFAc(D/\pi t_{\mathrm{m}})^{1/2} \qquad (7)$$

where n is the number of electrons transferred, F Faradays constant, A the area of the electrode, c the concentration of the reducible species, D the diffusion coefficient, and t_m the measurement time, i.e., the time after pulse application when i is measured. Figure 2 shows a normal pulse voltammogram obtained for Ti(IV) reduction. The concentration of Ti(IV) is 15.3 mM. Pulse widths were varied from 75.0 to 400 ms, and a delay time between pulses was 10 times the pulse width. There are two reduction waves, where the first (most anodic) accounts for ap-

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(12) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728.

(13) Hussey, C. L.; King, L. A.; Wilkes, J. S. *J. Electrochem. Chem.* **1979**, *102*, 321.

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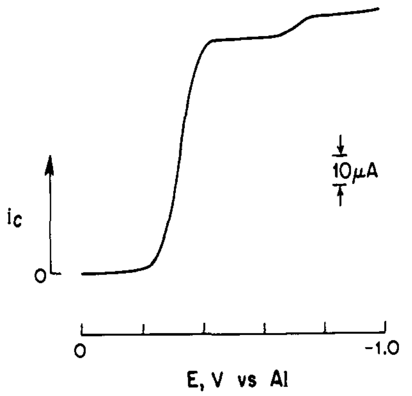

Figure 2. Normal pulse voltammogram for Ti^{4+}: concentration of $TiCl_4$, 15.3 mM; melt composition, 0.95:1; temperature, 40 °C; the pulse width, 100 ms.

proximately 90% of the total limiting current. The second (most cathodic) is due to titanium(IV) oxychloride and is discussed later. Analysis of the limiting current as function of pulse width can also be used to substantiate that as the reduction process is diffusion controlled. Equation 7 can be rewritten as eq 7a. The

$$i_{\text{lim}} = \text{constant} \times t_m^{-1/2} \qquad (7a)$$

pulse width was varied, and the slope of a log i vs. log t_m plot obtained. The more anodic limiting current may be expressed as eq 8, whereas the total limiting current may be expressed as

$$i_{\text{lim}} = 912 t_m^{-0.52} \qquad (8)$$

eq 9, where i_{lim} is given in microamperes and t_m in milliseconds.

$$i_{\text{lim}} = 955 t_m^{-0.51} \qquad (9)$$

The exponent for t_m was found to vary from −0.49 to −0.53 for both waves. The reduction of both species therefore appears to be diffusion controlled.

The diffusion coefficient for the major species can be obtained by using the total concentration of titanium added and the total limiting current in eq 7, and results are shown in Figure 3. This is a reasonable approximation as long as the limiting current for the major species contributes more than 80% to the total current. Figure 3 also includes the diffusion coefficient for Ti^{3+} at 40 °C.

The changes in diffusion coefficient as a function of melt composition can be attributed to changes in viscosity of the melt. The relationship between the viscosity η and diffusion coefficient as given by the Stokes–Einstein equation[15] predicts D is inversely proportional to the viscosity. Measurement of viscosity in these melts is a separate project, but if we assume the Stokes–Einstein equation to be valid, it seems as if the viscosity of the melt is inversely proportional to the $AlCl_4^-$ activity in this composition range.

The equation for a reversible current–voltage curve employing normal pulse voltammetry is

$$E = E_{1/2} + (2.3RT/nF) \log \frac{i_d - i}{i} \qquad (10)$$

where i and i_d are the current and limiting current, respectively, $2.3RT/F$ is 62 mV for $n = 1$ at 40 °C, and $E_{1/2}$ is the half-wave potential. Analysis of the first wave in Figure 2 gives $E_{1/2} = -0.320$ V and a slope of 62.8 mV. This half-wave potential is very close to what was found from cyclic voltammetry ($E_{1/2} = -0.322 \pm 0.002$ V). Similar wave shape analysis for a 0.85:1 melt at 60 °C gave $E_{1/2} = -0.343$ V and a slope of 64.5 mV, compared to the theoretical value of 65.9 mV.

The mean value for $E_{1/2}$ for 11 different melt compositions between 0.60:1 and 0.95:1 at 60 °C is $E_{1/2} = -0.343 \pm 0.008$ V, independent of melt acidity. A basic melt contains $AlCl_4^-$ and Cl^- as anions. Their activities change as the composition of the melt is varied; see eq 5 and 6. The activity of Cl^- is increased by a factor of 8 as the composition of the melt varies from 0.95:1 to 0.6:1. Since the half-wave potential of the first wave for the reduction of Ti^{4+} to Ti^{3+} is independent of melt composition over this range and the reduction is reversible, it appears that neither $AlCl_4^-$ nor Cl^- is involved in the reduction process. This further suggests that the coordination number for Ti^{4+} and Ti^{3+} must be the same.

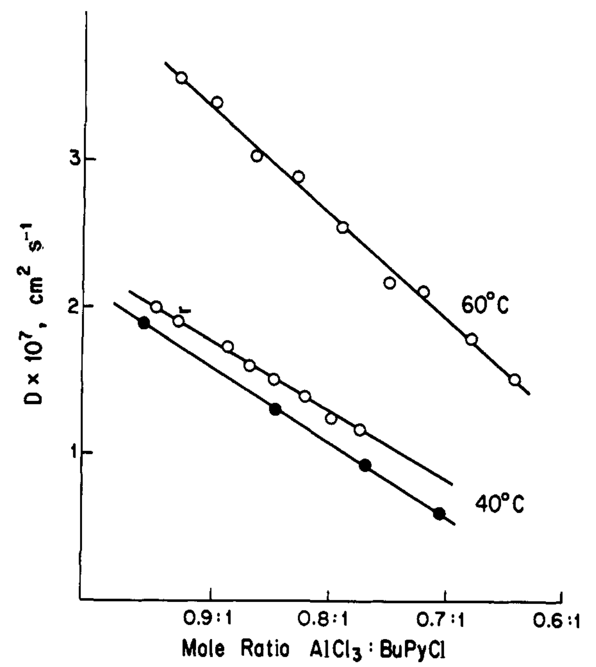

Figure 3. Diffusion coefficients for Ti^{4+} (open circles) at 40 and 60 °C as function of melt composition. Filled circles: diffusion coefficient for Ti^{3+} at 40 °C as function of melt composition.

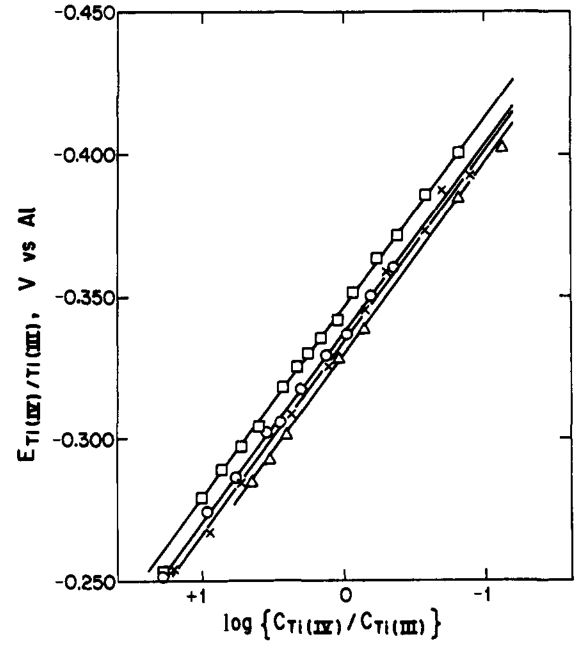

Figure 4. Potential for the couple Ti^{4+}–Ti^{3+} at 60 °C as function of log $c_{Ti^{4+}}/c_{Ti^{3+}}$: △, melt composition 0.93:1, $E = -0.329 + 0.067 \log (c_{Ti^{4+}}/c_{Ti^{3+}}$; +, melt composition 0.90:1, $E = -0.334 + 0.067 \log (c_{Ti^{4+}}/c_{Ti^{3+}})$; ○, melt composition 0.80:1, $E = -0.337 + 0.066 \log (c_{Ti^{4+}}/c_{Ti^{3+}})$; □, melt composition 0.7:1, $E = -0.345 + 0.067 \log (c_{Ti^{4+}}/c_{Ti^{3+}})$.

In additional experiments, Ti^{4+} was reduced coulometrically at constant potential to Ti^{3+} and the potential measured as a function of the ratio of Ti^{4+}:Ti^{3+} (Figure 4). The slopes of these lines correspond to the theoretical 66 mV for 60 °C. There is a shift in the formal potential of 16 mV from −0.329 V for a 0.93:1

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[15] Sundheim, B. R. In "Fused Salts"; Sundheim, B. R., Ed.; McGraw-Hill: New York, 1964; p 165.

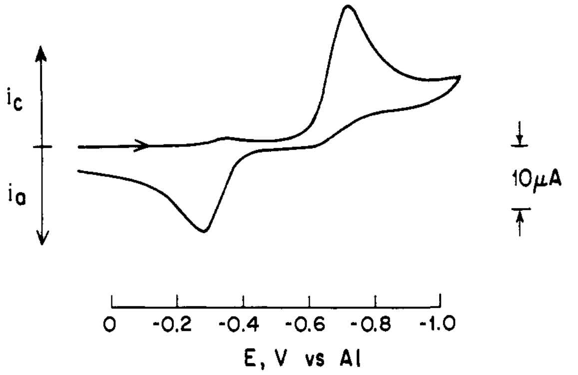

Figure 5. Cyclic voltammogram of a melt (0.8:1) containing ~50 mM oxide and 9.1 mM $TiCl_4$: scan rate, 100 mV s^{-1}; temperature, 60 °C; the area of the electrode, 0.0706 cm^{-2}.

to −0.344 for a melt with composition 0.70:1. The theoretical shift for each Cl^- involved in the reaction, for a change in chloride activity of 0.07 to 0.3 (see eq 5), is 42 mV. No systematic shifts are found in the half-wave potential from the normal pulse experiments; the shift of 16 mV may be due to change in liquid junction potentials. The magnitude of such potentials have not been investigated, however. These potentiometric experiments are in accord with the normal pulse voltammetric experiments.

B. Electrochemistry of Titanium in Oxide-Containing Melts. Titanium(IV) shows two well-defined one-electron reduction waves in basic melts. The results of the coulometric and normal pulse voltammetric experiments (see above) indicate the presence of two Ti(IV) species in slow equilibrium. Initially, the height of the second, more cathodic wave varied randomly with the temperature and melt composition and for melts with the same composition prepared at different times. The apparently random behavior suggested, however, that this wave might be due to complexation between added $TiCl_4$ and an impurity of unknown quantity in the melt. (Impurity in the water-clear distilled $TiCl_4$ seemed unlikely).

Oxygen in the form of oxide is expected to exist as an impurity in chloroaluminate melts. To investigate if the second wave was due to a Ti–O–Cl complex in the melt, we had to introduce oxide ions deliberately and quantitatively. Sodium oxide was found to be insoluble in the melt. Sodium carbonate and barium carbonate have been used as oxide sources,[8,9] but these carbonates have low solubility in the melt at 100 °C. Lithium carbonate on the other hand was easily dissolved. The carbonate was dissolved with gas evoluation.

$$CO_3^{2-} \rightarrow CO_2(g) + O^{2-} \qquad (11)$$

Although free O^{2-} has been suggested in melts of $NaCl-AlCl_3$,[9] the reaction of O^{2-} with the basic melt is assumed to be described by eq 2.

A cyclic voltammogram of a melt containing around 50 mM added oxide and 9.1 mM Ti^{4+} is shown in Figure 5. The rest potential is −0.05 V. It is thus possible to convert the titanium chloride almost entirely to a complex whose concentration depends on the amount of the aluminum oxychloride species in the melt, leaving only traces of the more easily reducible Ti(IV) species which is dominant in melts of negligible oxide content. Adding $TiCl_4$ to the melt causes the first peak to increase, and this indicates an equilibrium involving two Ti(IV) species, $AlCl_4$, $AlOCl_2^-$, and eventually Cl^-.

Controlled potential coulometry at $E = -0.9$ (plateau for the second wave, Figure 2 or 5) showed the total number of electrons in the reduction was 1.0 and that all the Ti(IV) was reduced to Ti(III).

Evidence for the formation of the complex ion $TiOCl_4^{2-}$ in a KCl-NaCl melt with added TiO_2 has been reported by Gruevich and Bezukladnikov.[16] Existence of a titanium–oxygen complex is aluminum chloride containing melts and the existence of a equilibrium between these can be considered from an acid–base equilibrium point of view. This equilibrium is described by the Lux–Flood theory.

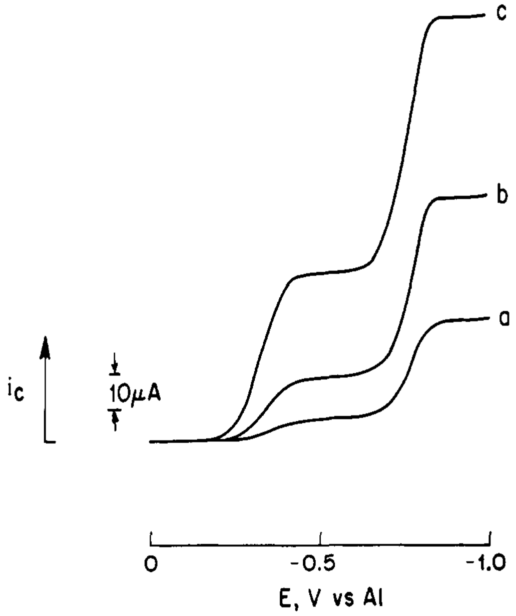

Figure 6. Normal pulse voltammogram of a 0.6:1 melt at 60 °C, 22.2 mM carbonate, and (a) 9.1 mM, (b) 18.2 mM, and (c) 31.8 mM $TiCl_4$. Pulse width is 150 ms.

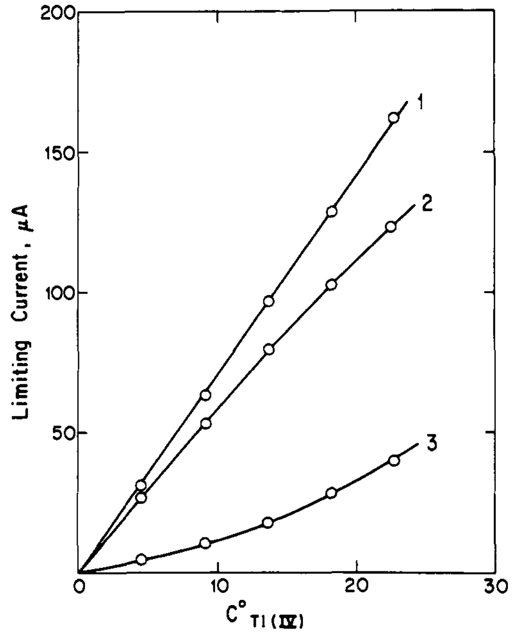

Figure 7. Normal pulse limiting current of $TiOCl_4^{2-}$ (2) and $TiCl_6^{2-}$ (3) and total limiting current (1) in a 0.9:1 melt containing 30.45 mM $AlOCl_2^-$ at 60 °C. Pulse width is 100 ms.

$$\text{acid} + O^{2-} \rightleftarrows \text{base}$$

Reaction between pure Al_2Cl_6(l, g) and TiO_2(s) leads to the formation of $TiCl_4$(l, g) and Al_2O_3(s). The acidity of pure $AlCl_3$ is therefore much higher than for pure $TiCl_4$. The acidic character of $AlCl_3$ is changed as a result of the formation of $AlCl_4^-$ and the formation of aluminum oxychloride. An oxygen-containing Ti species in equilibrium with an aluminum oxychloride species suggests that the acidity of Ti^{4+} and Al^{3+} is comparable in our medium.

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(16) Gurevich, L. M.; Bezukladnikov, A. B. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1973**, *18* (*1*), 54.

(17) Nicholson, R.; Shain, I. *Anal. Chem.* **1964**, *36* (4), 706.

(18) Reference 5, p 366.

Table III. Example of Calculation of Equilibrium Constant for Eq 18[a]

added $TiCl_4$, μL	calcd values for K' with the following initial amounts of oxide, $c_{AlOCl_2^-}$, mM					
	0	1	2	3	4	5
15	1159	1034	963	901	904	798
20	1220	1112	1022	946	880	822
25	1255	1122	1014	926	851	788
30	1314	1143	1011	907	823	753
35	1428	1201	1035	910	811	733
40	1536	1233	1030	885	775	690
45	1821	1363	1090	907	777	680
50	2157	1475	1121	904	757	652
55	2560	1565	1127	880	722	613
$\overline{K}$	1605	1250	1046	907	804	725
std dev in K, %	30.00	14.32	5.24	2.16	6.29	9.86

[a] z is zero. Melt composition is 0.7:1 and temperature 40 °C. Concentration of added carbonate is 19.81 mM.

A normal pulse voltammogram in a 0.6:1 melt at 60 °C, initially 22.2 mM in oxide to which were made successive additions of $TiCl_4$, is shown in Figure 6. Both limiting current plateaus are diffusion controlled, as determined from $t^{-1/2}$ behavior in pulse voltammetry experiments and the total limiting current is directly proportional to the added $TiCl_4$ (Figure 7). (The limiting current of the first plateau is also linearly dependent on added $TiCl_4$ if oxide is "absent".) This suggests that both species are monomeric with respect to titanium and that their concentrations are additive. The following mass balances are assumed to describe the system given in eq 12, 12a, and 13, where c^0_{oxide} is the total analytical

$$\text{added carbonate} = c_{AlOCl_2^-} + c_{Ti-O-Cl_y^{2-y}} \tag{12}$$

$$c^0_{oxide} = c_{AlOCl_2^-} + c'_{AlOCl_2^-} + c_{Ti-O-Cl_y^{2-y}} \tag{12a}$$

$$c^0_{Ti(IV)} = c_{TiCl_x^{4-x}} + c_{Ti-O-Cl_y^{2-y}} \tag{13}$$

concentration of oxide in all species in the melt and $c^0_{Ti(IV)}$ the analytical concentration of all Ti(IV) species in the melt, which corresponds to the amount of $TiCl_4$ added. $c'_{AlOCl_2^-}$ is the concentration of the unknown, initial oxide impurity, whereas $c_{AlOCl_2^-}$ is the difference between added carbonate and $c_{Ti-O-Cl_y^{2-y}}$. The concentration of the $TiCl_x^{4-x}$ complex is calculated from the limiting current of the first plateau, the diffusion coefficient for this species determined as previously described. The concentration of the $Ti-O-Cl_y^{2-y}$ complex is then calculated from eq 13.

An equilibrium of the form

$$TiCl_x^{4-x} + AlOCl_2^- \rightleftarrows AlCl_4^- + TiOCl_y^{2-y} + zCl^- \tag{14}$$

is therefore suggested in the melt and the equilibrium constant expressed as

$$K = \frac{c_{AlCl_4^-}c_{TiOCl_y^{2-y}}c_{Cl^-}{}^z}{c_{TiCl_x^{4-x}}(c_{AlOCl_2^-} + c'_{AlOCl_2^-})} \tag{15}$$

This chloride balance gives

$$z = x - 2 - y \tag{16}$$

The concentrations of $AlCl_4^-$ and Cl^- are generally between 1 and 2 orders of magnitude greater than the added titanium chloride and are therefore determined by the melt composition.

The determination of K is as follows. The melt, containing a known amount of added oxide (as Li_2CO_3), is titrated with $TiCl_4$. The cooncentration of $TiCl_x^{4-x}$ and $Ti-O-Cl_y^{2-y}$ is determined from the pulse voltammetry experiments, as described above, after each addition of $TiCl_4$. The concentration of the impurity, $c'_{AlOCl_2^-}$, is unknown and as a first approximation is set equal to zero. An apparent equilibrium constant, K', is calculated. A series of equilibrium constants is then calculated for various assumed values of $c'_{AlOCl_2^-}$. This sequence is repeated for each addition of $TiCl_4$. The best value of K, together with an estimation of $c'_{AlOCl_2^-}$, the oxide impurity initially present, is then taken where the standard deviation of K', for a series of such determinations, has its minimum value. An example of this calculation is shown in Table III. The equilibrium constants obtained from experiments at various mole ratios of Bu(py)Cl–$AlCl_3$, and two different temperatures, and the estimates of oxide impurity in the melt are given in Table IV.

Table IV. Calculated Equilibrium Constant for Equilibrium 14 + Calculated Concentrations of Oxide Impurity

Bu(py)Cl–$AlCl_3$	c_{Cl^-}, mol L^{-1}	t, °C	$c_{AlOCl_2^-}$, mM	$\overline{K}$
0.7:1	1.39	40	3	907
0.8:1	0.88	40	3	942
0.85:1	0.65	40	2	888
0.6:1	1.92	60	3	805
0.8:1	0.87	60	5	753
0.9:1	0.42	60	2	792

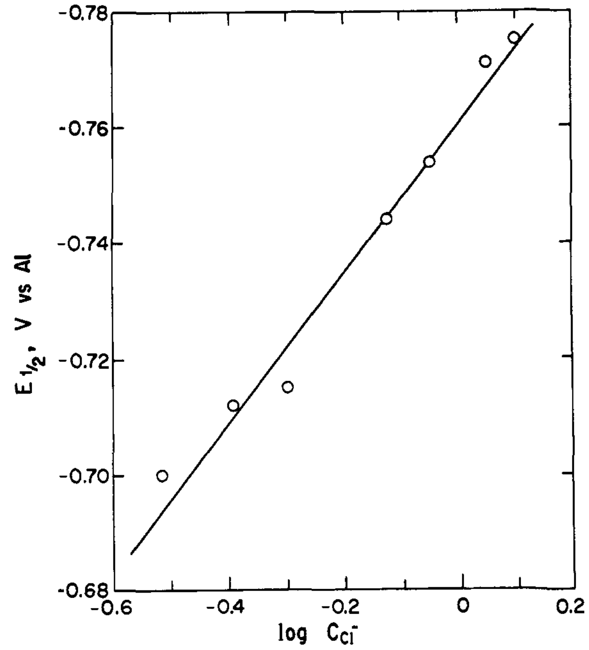

Figure 8. Half-wave potential, $E_{1/2}$, for reduction of the $TiOCl_{x-2}^{4-x}$ complex as function of log c_{Cl^-} at 40 °C.

Calculations indicate that K is independent of c_{Cl^-}, in accord with the potentiometric data. These data indicate that the $E°$ of the Ti(IV)–Ti(III) couple is independent of melt acidity, indicating no change in the coordination number. This gives $z = 0$ and combined with eq 15 yields $y = x - 2$. The equilibrium is therefore

$$TiCl_x^{4-x} + AlOCl_2^- \rightleftarrows TiOCl_{x-2}^{4-x} + AlCl_4^- \tag{17}$$

An alternate method of handling this data for direct determination of oxide will be presented elsewhere.[19]

By analogy to the situation in the $AlCl_3$–NaCl melt, we have assumed that the dominant O^{2-}-containing chloroaluminate species would be $AlOCl_2^-$; no experimental evidence on this matter exists, but the experiment certainly suggests that there is one dominant oxide-containing species.[9,20]

Equilibrium 17 explains why controlled potential coulometric experiments given $n = 1$ at a potential of both –0.5 and –0.9 V. As $TiCl_x^{4-x}$ is reduced to $TiCl_x^{3-x}$ at –0.5 V, the equilibrium is shifted toward the left. At –0.9 V the $TiOCl_{x-2}^{4-x}$ complex is reduced, and the equilibrium is shifted toward the right.

While the half-wave potential for the reduction of $TiCl_x^{4-x}$ was found to be independent of the melt composition, the half-wave

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(19) Stojek, Z.; Linga, H.; Osteryoung, R. A. *J. Electroanal. Chem.*, **1981**, *119*, 365.

(20) Robinson, J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1977**, *16*, 3040.

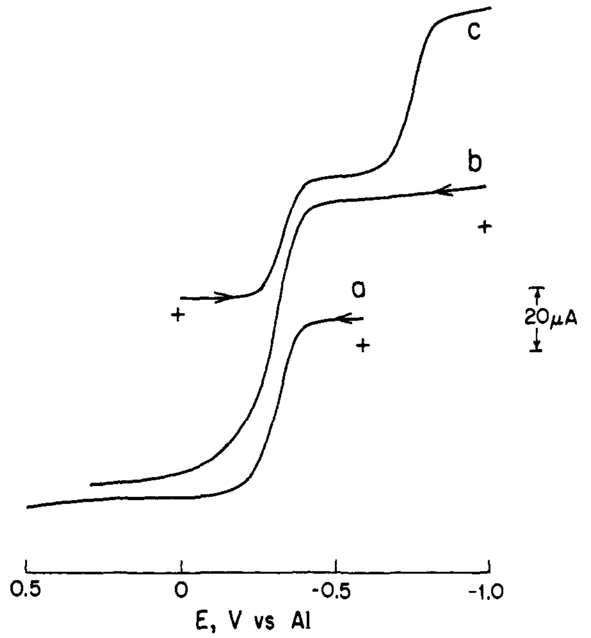

Figure 9. Normal pulse (c) and reverse pulse (a, b) voltammograms of 14.7 mM TiCl$_4$ in a 0.9:1 melt containing 14.1 mM carbonate: pulse width, 100 ms; delay time, 1 s; temperature, 40 °C.

potential for reduction of the TiOCl$_{x-2}{}^{4-x}$ complex shifted anodically with increasing acidity. For a fixed acidity this half-wave potential was constant for pulse widths between 75 and 250 ms. Figure 8 shows $E_{1/2}$ for the TiOCl$_y{}^{2-y}$ as a function of log c_{Cl^-}, for melts at 40 °C where the titanium chloride is converted into the oxychloride complex. The slope of the line is −0.122 V, suggesting two Cl$^-$ are involved. (The theoretical slope expected for two Cl$^-$ is −0.136 V, where changes in both c_{Cl^-} and $c_{\mathrm{AlCl_4}^-}$ are taken into account.) The reduction of the TiOCl$_{x-2}{}^{4-x}$ complex is therefore proposed as

$$\mathrm{TiOCl}_{x-2}{}^{4-x} + e^- \rightleftarrows \mathrm{TiOCl}_{x-2}{}^{3-x} \quad (18)$$

with a fast following chemical reaction

$$\mathrm{TiOCl}_{x-2}{}^{3-x} + \mathrm{AlCl_4}^- \rightleftarrows \mathrm{TiCl}_{x-2}{}^{5-x} + \mathrm{AlOCl_2}^- + 2\mathrm{Cl}^- \quad (19)$$

or, overall

$$\mathrm{TiOCl}_{x-2}{}^{4-x} + \mathrm{AlCl_4}^- + e^- \rightleftarrows \mathrm{TiCl}_{x-2}{}^{5-x} + \mathrm{AlOCl_2}^- + 2\mathrm{Cl}^- \quad (20)$$

The half-wave potential shifts anodically with pulse widths greater than 500 ms and becomes constant at −0.64 V independent of melt composition. This suggests an additional slow following chemical reaction

$$\mathrm{TiCl}_{x-2}{}^{5-x} + 2\mathrm{Cl}^- \rightleftarrows \mathrm{TiCl}_x{}^{3-x} \quad (21)$$

since the potentiometric measurements on the Ti(IV)–Ti(III) species indicate no dependence on the Cl$^-$ activity; i.e., x, the number of chlorides coordinated with the oxide-free Ti(IV) species, must be the same as that coordinated with the Ti(III) species. The following chemical reaction (19) must be very fast since only one peak for a single Ti^{3+} species is observed on a cyclic voltammogram and no trace of an anodic wave could be seen on reverse pulse voltammograms—Figure 9. The overall process for the reduction of the Ti–O–Cl complex is therefore

$$\mathrm{TiOCl}_{x-2}{}^{4-x} + \mathrm{AlCl_4}^- + e^- \rightleftarrows \mathrm{TiCl}_x{}^{3-x} + \mathrm{AlOCl_2}^- \quad (22)$$

The rate of formation of the TiOCl$_{x-2}{}^{4-x}$ complex can be estimated from the cyclic voltammogram of a solution containing TiCl$_x{}^{3-x}$ and AlOCl$_2{}^-$. TiCl$_x{}^{3-x}$ is oxidized to TiCl$_x{}^{4-x}$ which then reacts with AlOCl$_2{}^-$ according to eq 17. The ratio between the cathodic and anodic peaks for the TiCl$_x{}^{4-x}$–TiCl$_x{}^{3-x}$ couple increases with increasing scan rate. The variation of the ratio of anodic and cathodic current of oxidation of Ti(III) and the variation of the ratio of the cathodic peaks for different scan rates in CV is presented in Figure 10. Following the procedure described by Nicholson,[17] the value of the rate of formation of TiOCl$_{x-2}{}^{4-x}$, is 3.5 10^{-1} s^{-1} in a 0.8:1 melt at 60 °C and in the presence of 50 mM AlOCl$_2{}^-$ ions. No electrochemical evidence for a Ti^{3+} oxy complex is found in this work, which indicates that Al^{3+} is much more acid than Ti^{3+} in these melts.

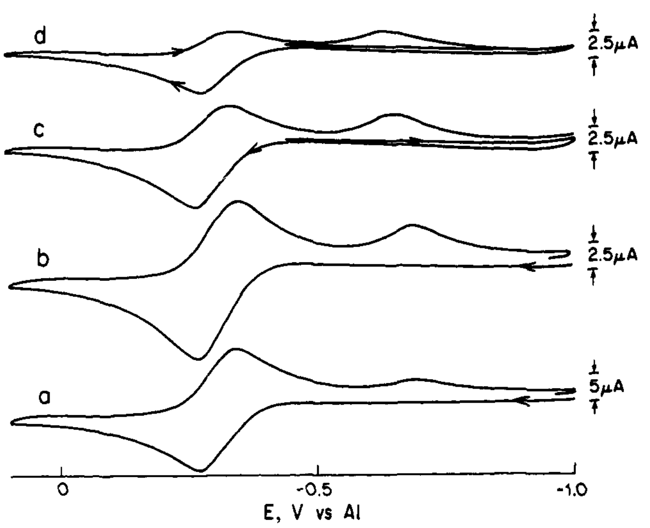

Figure 10. Cyclic voltammetric curves of 5 mM Ti(III) in a 0.8:1 melt containing 50 mM AlOCl$_2{}^-$: temperature, 60 °C; scan rates, 100 (a), 50 (b), 20 (c), 10 (d) mV/s.

The coordination number x for the TiCl$_x{}^{3-x}$ complex can, in principle, be obtained by measuring the potential between Ti metal and the TiCl$_x{}^{3-x}$ complex in the melt. This potential is given by eq 23, where the activity of Ti(s) = 1 and $E°$ is the standard

$$E = E^\circ + (2.303RT/3F) \log \frac{c_{\mathrm{TiCl}_x{}^{3-x}}}{c_{\mathrm{Ti(s)}}c_{\mathrm{Cl}^-}{}^{x}} \quad (23)$$

potential. The concentration of TiCl$_x{}^{3-x}$ may be kept constant (only adjusted for dilution effect), and the measured potential as function of c_{Cl^-} gives at 40 °C

$$E = E^\circ + \text{constant} - x0.0207 \log c_{\mathrm{Cl}^-} \quad (24)$$

In an effort to determine x, Ti(III) was generated by oxidation of a titanium wire electrode at constant current (see below, however). At fixed Ti(III) concentration F as a function of log c_{Cl^-} gave a straight line with slope = 134 mV, which gave a value of x of ca 6.5 and an apparent $E°$ value of −0.50 V. This suggests that both Ti^{3+} and the Ti^{4+} complexes are six coordinated, that the Ti(IV) chlorocomplex is TiCl$_6{}^{-2}$, and that the Ti–O–Cl complex is TiOCl$_4{}^{2-}$, which is in accord with the proposed species in other chloride melts.[16]

However, these results are not as "ideal" as one would like. The oxidation of titanium metal was not straightforward. Titanium metal could indeed be oxidized to yield Ti(III). The equilibrium potentials upon anodization of the metal were not terribly reproducible. The most striking feature was that the potential of the Ti–Ti(III) couple was shifted 300 mV or more in the cathodic direction, compared to the Ti(IV)–Ti(III) couple, and that this potential tended to drift anodically. Thus, the open circuit potential measured immediately after anodization at 1 mA was close to −1.0 V and drifted positive. However the potential at which Ti(0) was oxidized (−0.59 to −0.70 V, measured with respect to the Al reference electrode), under a 1-mA constant current, indicated, together with the color of the melt, that the titanium was oxidized to the +3 state. This was confirmed by coulometric oxidation of the titanium generated from the wire under these conditions, which usually indicated in excess of 95% Ti(III) had been formed. Experiments with lower currents, however, gave a mixture of Ti(III) and Ti(IV). The potential at which the Ti(0) was oxidized was more positive (−0.30 to −0.40 V) and resulted in some of the Ti(III) being oxidized to Ti(IV), since the half-wave

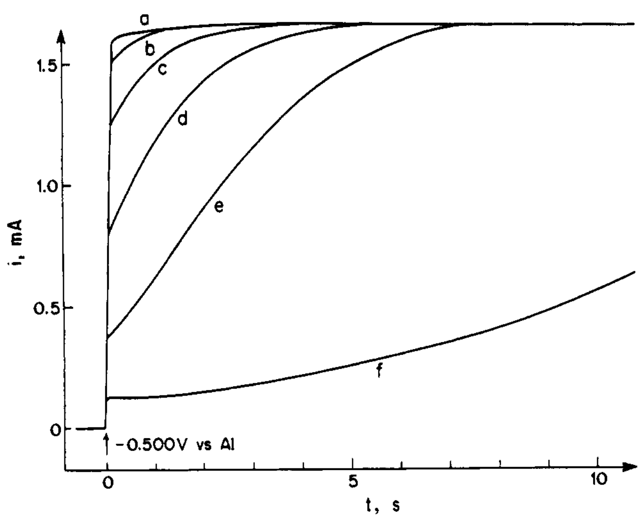

Figure 11. Chronoamperometric curves of oxidation of a titanium wire at −0.5 V in a 0.75:1 melt at 60 °C. The curves were obtained after the electrode circuit was disconnected for 2 s (a), 10 s (b), 20 s (c), 60 s (d), 5 min (e), and 120 min (f).

potential for the Ti(IV)–Ti(III) couple is −0.32 V.

The titanium wire apparently passivates in the melt, and this was briefly examined. A Ti wire was held at a constant potential of −0.5 V;after the current had achieved a value of about 1.6 mA, which corresponded to its "activated" state—i.e., to a condition where Ti(III) was generated under conditions similar to those in the constant current experiments—the electrode was disconnected and held at open circuit for varying periods of time time 2 s to 120 min. Figure 11 shows the current–time behavior after the potential of −0.5 V had been reimposed. One can see from these experimental chronoamperometric curves that it takes the electrode some considerable time to recover from a prolonged open-circuit condition. That is, when held at open-circuit for increasing periods of time, its ability to pass anodic current to generate Ti(III) is significantly altered.

An Al wire immersed in these basic melts reduces the butylpyridinium cation to give a blue color in the immediate vicinity of the electrode.[21] This, however, is not the case for a Ti wire even on long-term contact with the melt, allthough a slight bluish tinge of the metal electrode was once observed. Although Ti metal is extremely sensitive to air and a clean surface reacts immediately in contact with air to form an oxide layer,[18] the drift in potential of the metal in contact with the melt cannot be due to air. Slow alloy formation between Al and Ti on the surface or interaction of the Ti with oxide in the melt are possible explanations. The change in the potential measured as a function of acidity for the experiments in which the concentration of Ti(III) was held constant in an effort to determine x might yield the "correct value" for x (ca. 6.5) but an incorrect value for $E°$ (−0.5 V). A detailed examination of this problem was, however, beyond the scope of these studies.

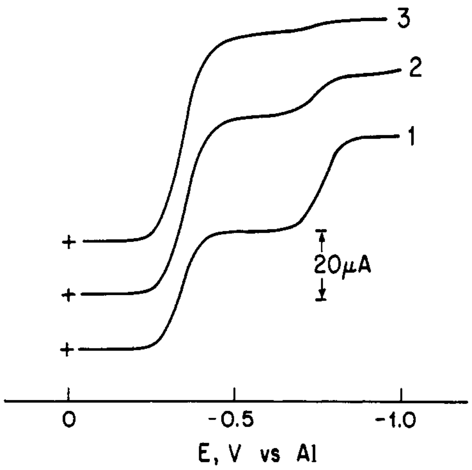

Figure 12. Normal pulse voltammograms of 18.2 mM Ti(IV) in presence of 11.4 mM $AlOCl_2^-$ and 0 (1), 93 (2), and 167 (3) mM water: 0.85:1 melt, temperature, 40 °C; pulse time, 200 ms.

No indication of the reduction of Ti(IV) or Ti(III) to the metal was found. While nucleation problems at the glassy carbon electrode may be the cause, we are unable to comment further on this puzzling phenomenon.

C. Addition of Water to the Melt. The reactivity between melt and water was found to be strongly dependent on the composition of the melt. In an acid melt, the addition of water leads to a spontaneous reaction giving off fumes (HCl).

Tremillon et. al.[8] have reported reaction 25 in the basic Na-Cl–$AlCl_3$ melts. Thus, the addition of water to these melts might be expected to have a similar effect as the addition of Li_2CO_3,

$$AlCl_4^- + H_2O \rightleftarrows 2HCl + AlOCl_2^- \qquad (25)$$

Introduction of $AlOCl_2^-$ (by adding Li_2CO_3) shifts equilibrium 17 to the right. However, normal pulse voltammetry experiments showed that addition of H_2O to the basic melt containing Ti(IV) did not have the same effect as introduction of carbonate—i.e., to give $AlOCl_2^-$—but of "removal". The equilibrium was shifted to the left, as indicated by the observation that the total limiting current was constant whereas the limiting current of the first plateau increased, as shown in Figure 12. Water in the melt must therefore react with $AlOCl_2^-$ to decrease its concentration. It is most likely that water reacts both with $AlCl_4^-$ (which is well buffered) and $AlOCl_2^-$ to form a reaction product ($Al(OH)_2Cl$?) which is not involved in an equilibrium with titanium.

Acknowledgment. H.L. wishes to express thanks for a grant from the Norwegian Council for Scientific and Industrial Research. This work was supported by the Air Force Office of Scientific Research.

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[21] Gale, R. J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1980**, *127*, 2167.