Technical University of Denmark

DTU

Electrochemical Study of Tantalum in Fluoride and Oxofluoride Melts

Polyakova, L.; Polyakov, E.; Matthiesen, F.; Christensen, Erik; Bjerrum, Niels J.

DTU Library
Technical Information Center of Denmark

Electrochemical Study of Tantalum in Fluoride and Oxofluoride Melts

L. P. Polyakova and E. G. Polyakov

Institute of Chemistry, KSC RAS, Apatity 184200, Russia

F. Matthiesen, E. Christensen, and N. J. Bjerrum*

Materials Science Group, Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark
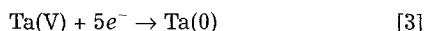
ABSTRACT

The electrochemical behavior of tantalum in the form of K_2TaF_7 in an LiF–NaF–KF eutectic melt has been studied by linear voltammetry in the temperature range of 560 to 815°C with and without additions of Na_2O. An amperometric titration has been performed by measuring the heights of the cathodic and the anodic peaks. It was shown that at a molar ratio $Na_2O/K_2TaF_7 = 1$ the predominating complex in the melt is $TaOF_5^{2-}$, whereas with an Na_2O/K_2TaF_7 molar ratio of 2 it is $TaO_2F_x^{(x-1)-}$, probably in the form of $TaO_2F_4^{3-}$. Increase in the Na_2O/K_2TaF_7 molar ratio in excess of two leads to a decrease of tantalum concentration in the melt, and precipitation of $KTaO_3$ occurs. Both the fluoro complex and the monooxofluoro complex were reduced to metal in a single five-electron step. The fluoro complexes, in the temperature range 625 to 815°C with potential scan rates <0.5 V · s^{-1}, discharge quasi-reversibly, but at potential scan rates >0.5 V · s^{-1} they discharge irreversibly. Monooxofluoro complexes discharge irreversibly at all temperatures and scan rates studied. The diffusion coefficient of the tantalum fluoro complex depends on the temperature as $\log D = -2.55 - 2044/T$ with an activation energy of 39.1 kJ · mol^{-1}. For the tantalum monooxofluoro complex the dependence is $\log D = -2.35 - 2293/T$ with an activation energy of 43.9 kJ · mol^{-1}.

From the time of Senderoff et al.[1] who studied the electroreduction of K_2TaF_7 in the LiF–NaF–KF [46.5, 11.5, 42.0 mole percent (m/o)] eutectic melt called FLINAK, extensive investigations of the mechanism of the reduction of tantalum ions in fluoride melts have been carried out,[2-7] with two distinct mechanisms being suggested: (*i*) that the process proceeds in two sequential steps[1,3]

$$Ta(V) + 3e^- \rightleftharpoons Ta(II) \qquad [1]$$

$$Ta(II) + 2e^- \rightarrow Ta(0) \qquad [2]$$
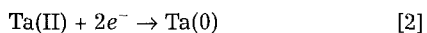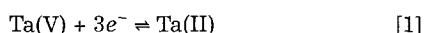
and (*ii*) that the process is one step[4,5,8]

$$Ta(V) + 5e^- \rightarrow Ta(0) \qquad [3]$$

A parallel investigation using the analogous chloride-fluoride melt (KCl–KF–K_2TaF_7), which was titrated with tantalum pentoxide, gave the stoichiometry of the ligand substitution reaction and the effect of the oxide ions on the mechanism of the cathodic process was demonstrated. Oxofluoride melts may be of considerable practical interest but the electrochemical behavior of tantalum oxofluoro complexes, formed in fluoride melts containing oxide ions,[9-11] is still unknown. However, tantalum reduction has been studied in molten Na_3AlF_6 containing Ta_2O_5 or $NaTaO_3$ using chronopotentiometry.[12] In both cases Ta(V) ions were reduced to metal in a single reversible five-electron step.

The aim of the present investigation was an understanding of the nature of the tantalum reduction process in FLINAK–K_2TaF_7 melts and of the effect of the oxide ions on the mechanism of this process.

Experimental

Alkali metal fluorides were purified either as described previously[13] or by zone-refining. The voltammetric characteristics of a zone-refined melt are given in Fig. 1. In both cases the voltammograms had anodic waves corresponding to the oxidation of oxide to oxygen, which is followed by the chemical oxidation of carbon to CO and CO_2.[14] The effect of this on the redox reactions of Ta(V) is discussed later.

K_2TaF_7 was prepared from high purity tantalum hydroxide by dissolving in hydrofluoric acid, precipitating with aqueous potassium chloride, followed by subsequent re-

crystallization from HF solution, washing with ethanol and drying in vacuum at 80 to 90°C. The transparent K_2TaF_7 crystals obtained were packed in hermetically sealed polyethylene containers. The product was sensitive to atmospheric moisture which caused hydrolysis and loss of transparency. Na_2O (Aldrich (98 weight percent (w/o)) was used without additional purification.

A Schlumberger potentiostat Model 1286 or a potentiostat PI-50-1.1. with PDA-1 potentiometer and S9-8 oscilloscope were used in the linear sweep voltammetry measurements. The electrochemical cells and the experimental technique have been described earlier.[13,15]

The experiments were carried out in three-electrode cells where glassy carbon served both as a container for the electrolyte and as a counterelectrode. The potentials were measured against platinum or glassy carbon quasi-reference electrodes. To obtain more reliable potential values an Ag/NaCl–KCl–AgCl (2 w/o) reference electrode was used. The Nernstian behavior of this electrode has been demon-
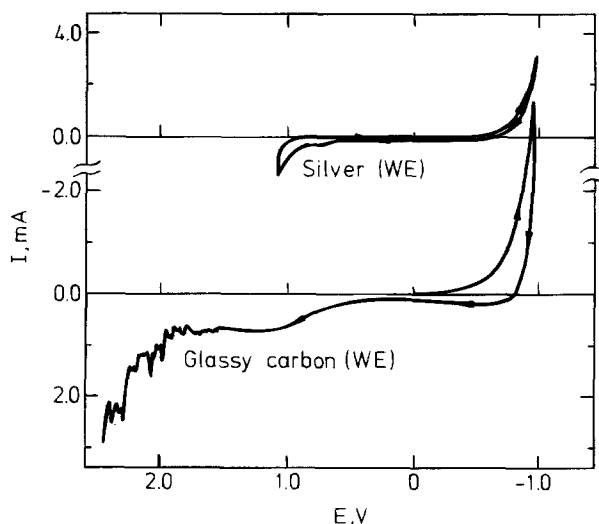

Fig. 1. Linear sweep voltammogram of a FLINAK background melt, temperature $T = 708$°C, scan rate 0.1 V · s^{-1}, platinum quasi-reference electrode. Working electrodes: silver electrode, $A_{Ag} = 0.57$ cm^2, and glassy carbon (GC) electrode, $A_{GC} = 0.22$ cm^2. Oxide concentration: $C_{O^{2-}} = 2.4 \cdot 10^{-3}$ m/o.
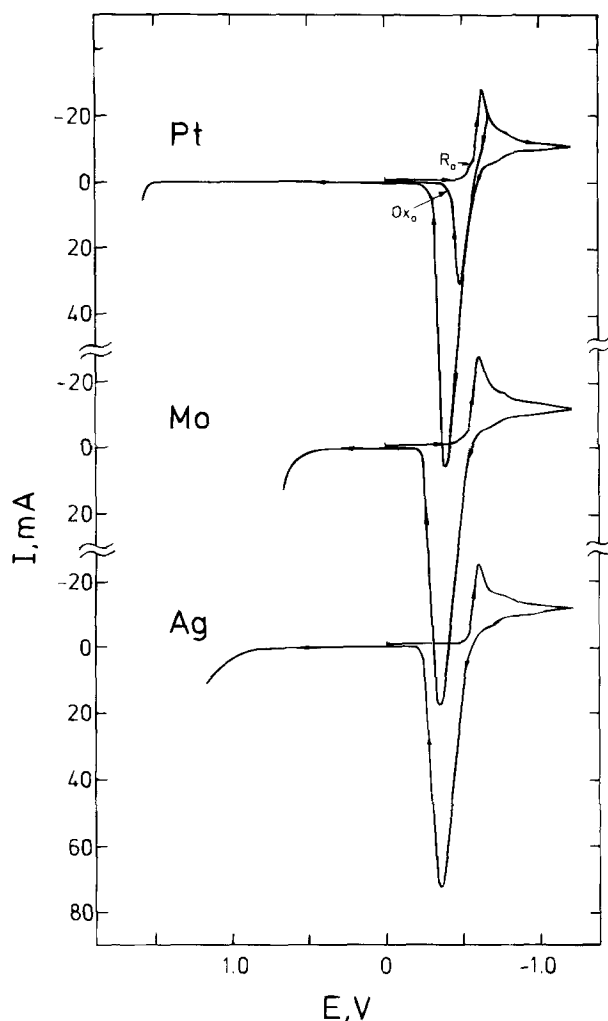
Fig. 2. Voltammograms of FLINAK-K_2TaF_7 melts, $T = 710°C$, scan rate 0.1 V · s^{-1}, platinum quasi-reference electrode. Various working electrodes: molybdenum, $A_{Mo} = 0.32$ cm²; platinum, $A_{Pt} = 0.35$ cm²; silver, $A_{Ag} = 0.30$ cm². $C_{K_2TaF_7} = 0.237$ m/o.

increase in temperature. These observations and the absence of the wave R_0 with Mo and Ag electrodes suggest intermetallic Pt-Ta compounds formation, cf. the Pt-Ta phase diagram.[16] Thus molybdenum and silver electrodes are preferable to platinum electrodes, because tantalum forms a continuous series of solid solutions with molybdenum, whereas it does not interact with silver in the solid state.[17] As a result only an insignificant distortion of the initial section was seen on the polarization curve with Mo, and voltammograms obtained on silver electrodes had no trace of interaction between silver and tantalum. Hence silver working electrodes were used exclusively in our study.

Results and Discussion

The cyclic voltammogram shape, with additions of less than 0.1 m/o of K_2TaF_7 to FLINAK, was not reproducible. This can be explained as the effect of oxide impurities in the melt, due either to nonreproducible purification of the salts or to contact of the melt with oxide ceramics. Use of insufficiently purified FLINAK and low K_2TaF_7 concentrations results in cyclic voltammograms with the shape as curve c in Fig. 4, where the cathodic peaks R_2 and R_3 on the voltammograms (with corresponding anodic Ox_2 and Ox_3 peaks) are seen but only increase of the K_2TaF_7 concentration increases the size of peak R_1 (curve b in Fig. 4). If K_2TaF_7 contains minimal amounts of oxide impurity it is possible, by increasing its concentration to 0.4 to 0.5 m/o, to obtain a voltammogram showing only the cathodic peak R_1 and the corresponding anodic peak Ox_1 (curve a Fig. 4). As was stated earlier,[15] this made complications for the interpretation of the cathodic peaks, since they could be assigned either to different steps in the reduction of one Ta(V) fluoro complex to metal, or to the reduction of two tantalum species (a fluoro complex and an oxofluoro complex). Here potentiostatic electrolysis at potentials corresponding to the first wave resulted in deposition of metallic tantalum on the cathode, just as in mixed chloride fluoride melts.[8,15]

Titration of tantalum in halide melts with tantalum pentoxide was reported by Konstantinov *et al.*[8] It explained the nature of the voltammogram peaks, the reduction mechanism and also determined the stoichiometry of the ligand displacement reactions of the fluoro complexes initially present. An alternative approach is to titrate with sodium monoxide where the complication of changes in tantalum concentration does not occur. Thus Raman spectroscopy has been used recently for investigation[11] of the

strated in KCl-KF-K_2TaF_7 chloride-fluoride melts[8] and in CsCl-KCl-NaCl-K_2TaF_7-melts.[15] When this reference electrode was used, the potentials measured were 460 to 470 mV more negative than when the platinum quasi-reference electrode was used. However, the Ag/AgCl reference electrode worked only in a limited region of the electrolytes studied here. When it was possible, the potentials were measured *vs.* all three reference electrodes.

Since interactions between tantalum species and the electrode materials,[4] (glassy carbon, platinum, molybdenum, and silver) are possible, preliminary experiments were carried out. Cathodic curves on glassy carbon electrodes had no clearly defined peaks in the potential range of Ta(V) reduction. Thus these electrodes were used only to record anodic curves of oxide oxidation during titration of the melt with sodium oxide, to determine the residual content of oxide in the background electrolyte concerning the residual content of oxide ions and the change in oxide concentration following K_2TaF_7 additions.

Typical voltammograms of FLINAK-K_2TaF_7 melts obtained with Pt, Mo, and Ag electrodes are given in Fig. 2. The cathodic part of the voltammograms obtained with the platinum electrode are shown in more detail in Fig. 3. Besides the main peaks discussed below, a shoulder (R_0) was seen only when a platinum electrode was used (Fig. 2). The wave R_0 was not well defined even at high K_2TaF_7 content and its limiting current did not depend on the K_2TaF_7 concentration (Fig. 3). However the height of this wave was affected by the temperature; it disappeared when the temperature was lower than 630°C, but appeared again with
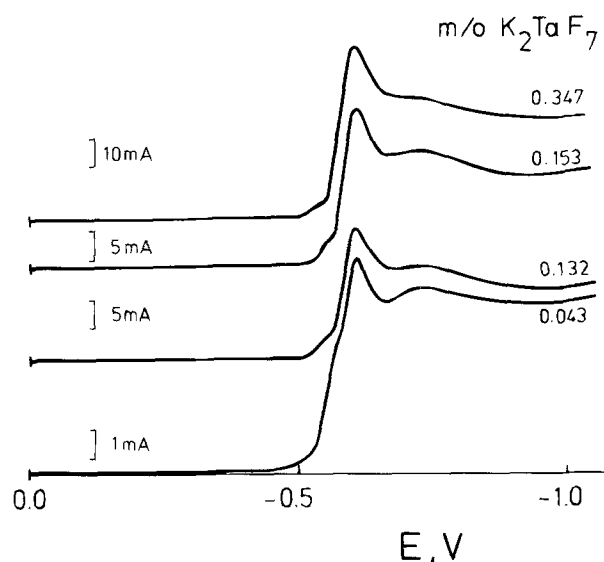

Fig. 3. Voltammograms of FLINAK-K_2TaF_7 melts, $T = 708°C$, scan rate 0.05 V · s^{-1}, platinum quasi-reference electrode. Platinum working electrode, $A_{Pt} = 0.31$ cm²; $C_{K_2TaF_7} = 0.043, 0.132, 0.153,$ and 0.347 m/o.
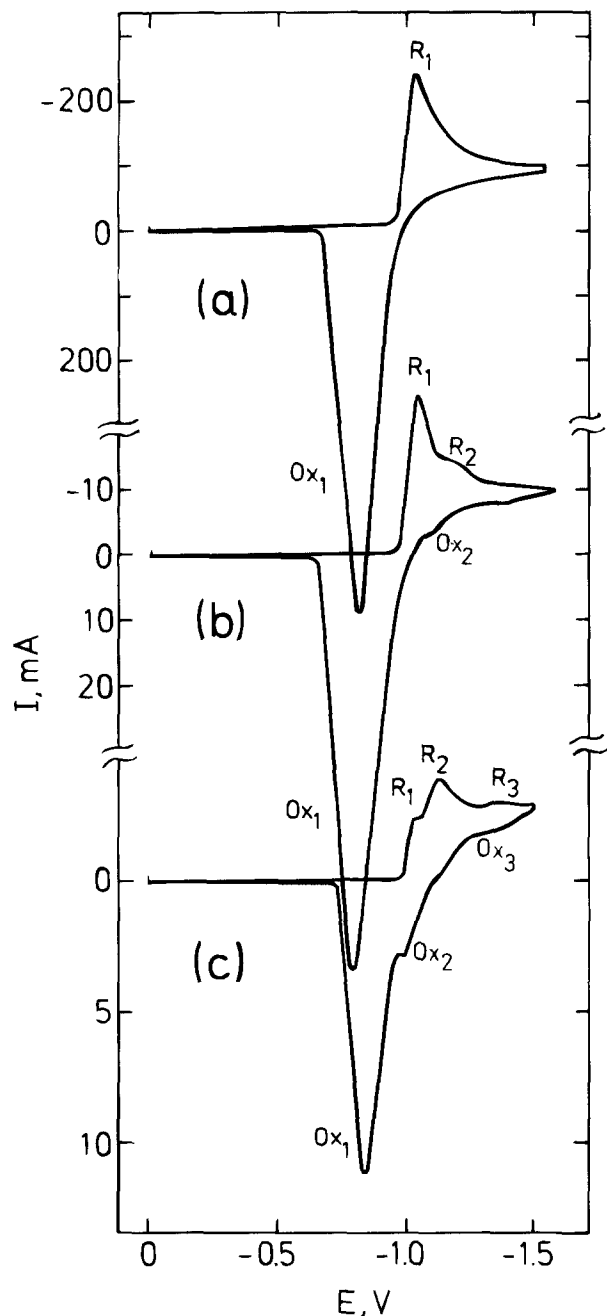
Fig. 4. Variation of cyclic voltammetric curves shape depending on the purity of the melt, $T = 708°C$, scan rate 0.1 V · s^{-1}, Ag/AgCl reference electrode. Silver working electrodes: (a) $A_{Ag} = 0.57$ cm^2, $C_{K_2TaF_7} = 0.526$ m/o; (b) $A_{Ag} = 0.31$ cm^2, $C_{K_2TaF_7} = 0.106$ m/o; (c) $A_{Ag} = 0.42$ cm^2, $C_{K_2TaF_7} = 0.0206$ m/o.

FLINAK-K$_2$TaF$_7$-melt structure during titration with sodium monoxide.

In the present work we also used sodium monoxide additions to follow the change in shape of the cathodic part of the voltammograms and the peak height. This work also involved estimation of the height of the oxidation peaks of oxide ions, using a glassy carbon indicator electrode, to determine the decomposition of the complexes formed in the oxofluorotantalate-containing melts. Earlier White[18] found that the height of these peaks was directly proportional to the amount of oxide added to the melt, and thus determined the oxide concentration.

It is apparent from Fig. 5 (curve a1) that the starting electrolyte with 0.406 m/o of K$_2$TaF$_7$ already contained a small quantity of oxide ions. This was confirmed by the shape of the cathodic part of the voltammograms obtained with a silver electrode, (Fig. 5, curve b1). Here, besides the

main reduction peak of the TaF$_7^{2-}$ complex[9-11] to metal, a second minor peak was present. The latter wave corresponding to discharge of oxofluoro complexes. Addition of small amounts of sodium oxide to the molten FLINAK-K$_2$TaF$_7$ melt (Fig. 5b 2-6) resulted in lowering the first peak, R_1, and the growth of the second and third peaks, R_2 and R_3. The anodic curves (Fig. 5a 2-6) showed a corresponding increase in the oxide oxidation wave. A plot of the peak current of oxide ion oxidation vs. the molar ratio Na$_2$O/K$_2$TaF$_7$ (Fig. 6) was used as a calibration curve to determine the initial oxide content in the melt. The concentration of oxide ions in this initial melt was 0.029 m/o by extrapolation. A plot of the first cathodic peak current against the Na$_2$O/K$_2$TaF$_7$ ratio (Fig. 7a) was linear and allowed estimation of the stoichiometry of ligand displacement, Eq. 4, (taking into account the initial oxide content)

$$K_2TaF_7 + Na_2O \rightleftharpoons K_2TaOF_5 + 2NaF \qquad [4]$$
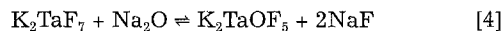
since the height of the first peak reached zero at a molar ratio of Na$_2$O/K$_2$TaF$_7$ close to unity.

When the sodium oxide concentration in the melt exceeded a molar ratio of Na$_2$O/K$_2$TaF$_7$ = 1, there was proportional growth of the anodic oxide oxidation waves (Fig. 5a 7-11). The corresponding cathodic curves (Fig. 5b 7-11) showed proportional lowering of the discharge wave of the monooxofluoro complexes and growth of the more negative third peak. This variation of anodic and cathodic waves stopped when the Na$_2$O/K$_2$TaF$_7$ molar ratio reached a value of 2.01 (including initial oxide content, Fig. 7b) suggesting Eq. 5

$$K_2TaF_7 + 2Na_2O \rightleftharpoons K_2TaO_2F_3 + 4NaF \qquad [5]$$
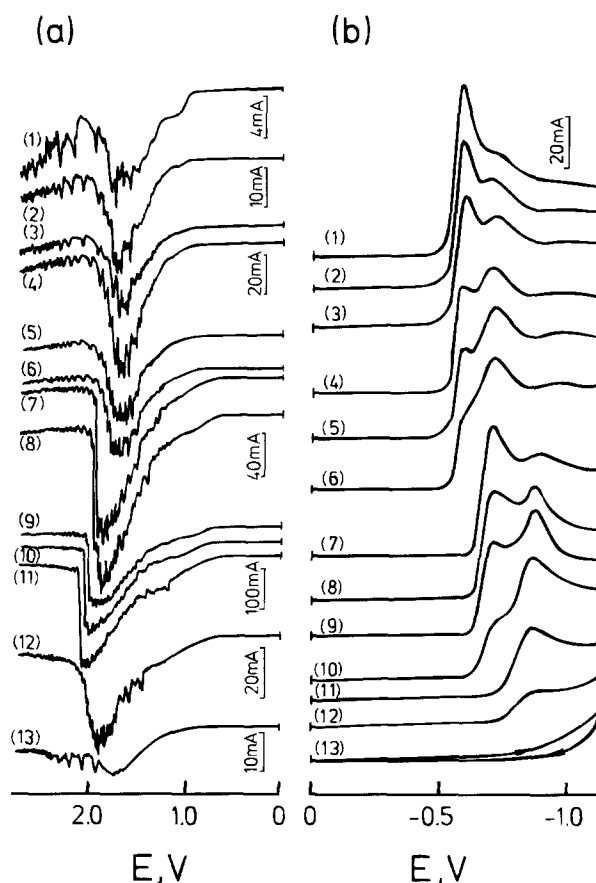
Fig. 5 (a) Variation of O^{2-} oxidation anode waves and (b) tantalum reduction cathode waves in FLINAK-K$_2$TaF$_7$-NaO$_2$ melts at $T = 710°C$, with scan rate in all cases 0.1 V · s^{-1}, and with Pt quasi-reference electrode. Working electrodes: (a) glassy carbon, $A_{GC} = 0.25$ cm^2; (b) silver, $A_{Ag} = 0.42$ cm^2. K$_2$TaF$_7$ initial concentration 0.406 m/o and different Na$_2$O/K$_2$TaF$_7$ ratio: (1) 0; (2) 0.135; (3) 0.214; (4) 0.373; (5) 0.470; (6) 0.518; (7) 0.942; (8) 1.140; (9) 1.250; (10) 1.545; (11) 1.947; (12) 2.581; (13) 3.034.

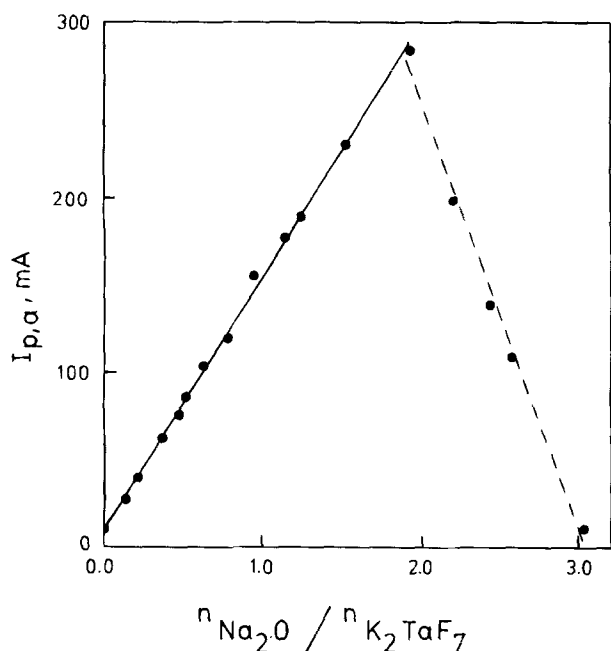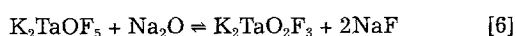Fig. 6. Anodic current of O^{2-} oxidation peak as a function of molar ratio Na_2O/K_2TaF_7 in FLINAK-K_2TaF_7-Na_2O melts, $T = 710°C$, $A_{GC} = 0.26$ cm^2; $C_{K_2TaF_7}^{init.} = 0.406$ m/o.

or, assuming the earlier formation of K_2TaOF_5 (Eq. 4)

$$K_2TaOF_5 + Na_2O \rightleftharpoons K_2TaO_2F_3 + 2NaF \qquad [6]$$

Unfortunately, voltammetry does not determine the accurate stoichiometry of the complexes participating in the electrode reactions. Thus the dioxofluoro complexes formed in the molten state as a result of the chemical interaction should be written as $TaO_2F_x^{(x-1)-}$, (x was proposed previously to be equal to 4,[11] the compounds $K_3TaO_2F_4$[19] and $KTaO_2F_2$[20] also have been reported).

Further addition of Na_2O in excess of a molar ratio Na_2O/K_2TaF_7 equal to 2 resulted in simultaneous lowering of both the anodic and the cathodic peaks (Fig. 5a 12, b 12), but no new peaks appeared. The plot of $I_{p,a}$ vs. Na_2O/K_2TaF_7 gave a line crossing the concentration axis in a point close to a value of 3 (Fig. 6). The voltammograms corresponding to this Na_2O/K_2TaF_7 ratio (Fig. 5a 13 and b 13) were similar to the background electrolyte voltammograms suggesting an absence of tantalum in the melt. The bottom of the solidified electrolyte after an experiment contained solid $KTaO_3$ (identified by XRD), *i.e.*

$$(x - 1)K^+ + TaO_2F_x^{(x-1)-} + O^{2-}$$

$$\rightarrow KTaO_3 + xF^- + (x - 2)K^+ \qquad [7]$$
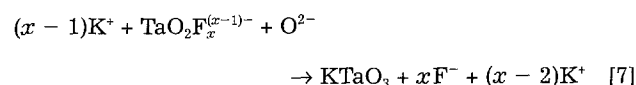
Na_2O addition in excess of a molar ratio Na_2O/K_2TaF_7 of 3 gave an increase in the anodic currents. This is probably due to oxidation of oxide ions formed by the dissolution of excess Na_2O.

As mentioned above, while the first cathodic peak on the voltammogram of K_2TaF_7 containing FLINAK melts corresponding to the reduction to the metal from TaF_7^{2-} fluoro complexes, the corresponding anodic peak for metal dissolution, Ox_1, is shown in Fig. 4a. The nature of this tantalum reduction process was studied using the dependence of the linear voltammogram parameters on the potential sweep rate (Fig. 8a, b) and the concentration of tantalum ions (Table I). The peak current ($I_{p,1}$) is linearly proportional to the K_2TaF_7 concentration in the melt. For temperatures from 625 to 815°C the peak potential $E_{p,1}$ depended on the logarithm of the scan rate (log v) (Fig. 8b), shifting to the negative potential region with increasing scan rate. At scan rates <0.5 V · s^{-1} this plot is nonlinear, whereas at $v \geq 0.5$ V · s^{-1} the peak potential is linearly dependent on log v.

Figure 8a also demonstrates the complex character of the peak current change at scan rates <0.5 V · s^{-1}, in that $I_{p,1}$ was not linearly dependent on the square root of the potential scan rate, but $I_{p,1}/v^{1/2}$ became smaller with the increase in log v. At rates of 0.5 to 2.0 V · s^{-1} the $I_{p,1}/v^{1/2}$ ratio became constant.

There is a convenient and simple criterion to determine process reversibility: the difference between peak and half-peak potentials which for reversible processes is described by the following expression

$$E_{p/2} - E_p = 2.20 \, RT/nF \qquad [8]$$

For potential scan rates <0.5 V · s^{-1} the number of electrons calculated using this equation from the voltammograms exceeded a value equal to 5. However for irre-

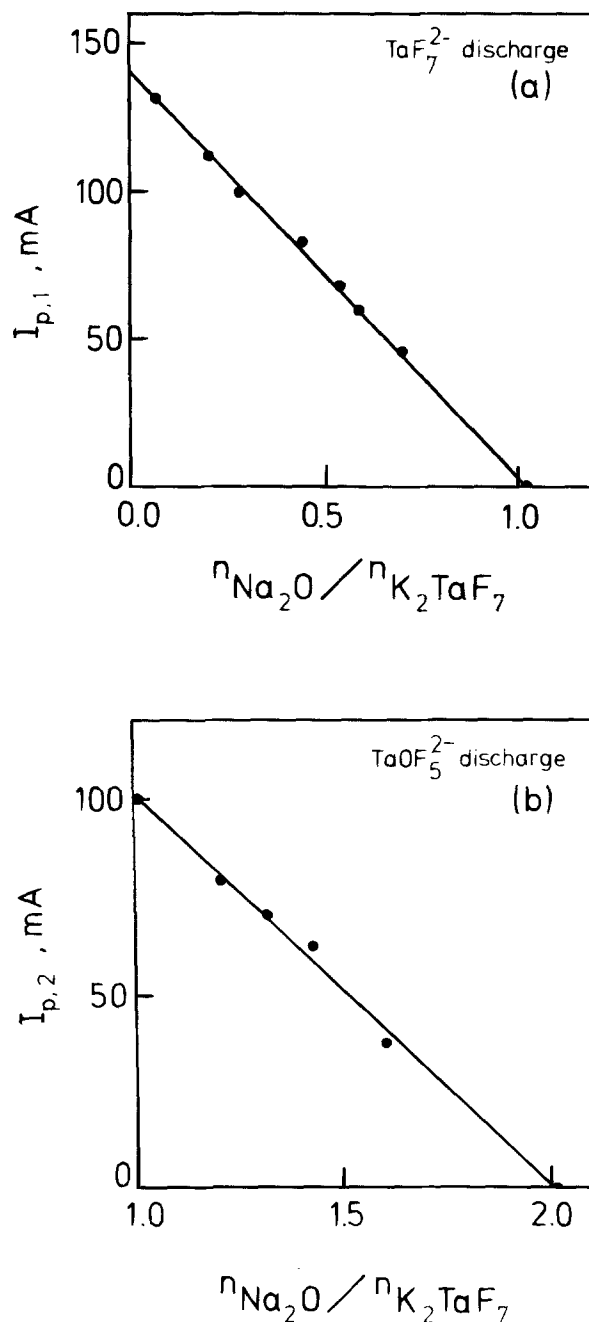Fig. 7. Tantalum reduction peak currents as a function of the Na_2O/K_2TaF_7 molar ratio in FLINAK-K_2TaF_7-Na_2O melt, $T = 710°C$, scan rate 0.1 V · s^{-1}. $A_{Ag} = 0.42$ cm^2; (a) TaF_7^{2-} discharge; (b) $TaOF_5^{2-}$ discharge; $C_{K_2TaF_7}^{init.} = 0.406$ m/o. The oxide contents have been corrected with an amount corresponding to 0.029 m/o on the basis of the measurements shown in Fig. 6.
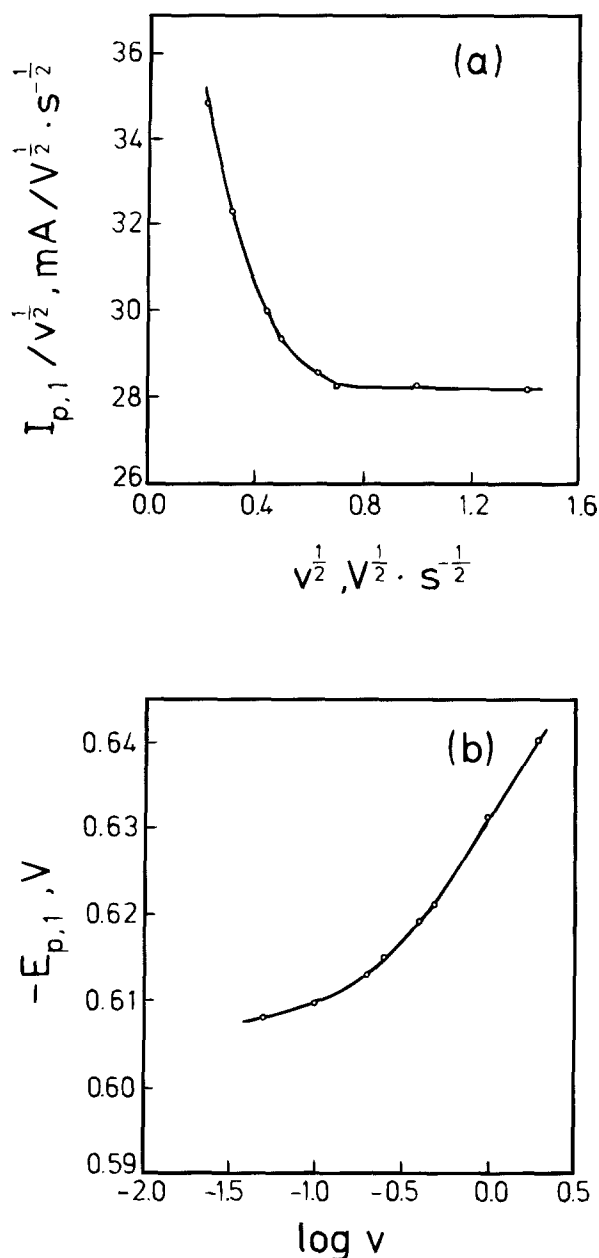
Table II. Kinetic parameters of $TaF_7^{2-} + 5e^- \rightarrow Ta + 7F^-$ process (FLINAK-K_2TaF_7 melt, scan rate = 0.5 V · s^{-1}, A_{Ag} = 0.42 cm².).

T (°C)	Peak current $I_{p,1}$ (mA)	$C \cdot 10^5$ K_2TaF_7 (mol · cm^{-3})	αn_α	$D \cdot 10^5$ ($cm^2 \cdot s^{-1}$)
815	226.0	7.90	3.87	3.70
725	192.0	8.36	3.50	2.57
672	170.2	8.49	3.36	1.93
625	147.5	8.61	3.19	1.41
572	132.7	8.74	2.97	1.12

0.4 V · s^{-1} was only quasi-reversible, (*i.e.*, the rate of the diffusion step approached the rate of the electron-transfer step). Further increase of scan rate above 0.5 V · s^{-1} resulted in the transformation of the quasi-reversible process into an irreversible one. Lowering of temperature effected the process in the same way; at temperatures lower than 580°C the process became irreversible at all scan rates studied. In contrast it has been found previously for mixed chloride/fluoride melts[8,22] that the reduction of TaF_7^{2-} to metal was reversible. Thus when the alkali fluoride content in the mixed systems is increased to very high values (such as in FLINAK) the kinetics of the process must be changed to irreversible.

The mathematical treatment of voltammograms of a quasi-reversible process is complicated,[23] thus only the data obtained at irreversible conditions (*i.e.*, at $v \geq 0.5$ V · s^{-1}) is considered here, the transfer coefficient α is calculated from the slope of the linear section of the E_p vs. log v plot (Fig. 8b) at 710°C using the following equation[24]

$$K = 2.303 \, RT/2\alpha n_\alpha F \qquad [10]$$

where K is a slope and n_α is number of electrons.[24] For 983 K αn_α equals 3.09, and since n must be 5 (electrolysis at poten-

Fig. 8. Scan rate effect on (a) peak current and (b) peak potential of the TaF_7^{2-} reduction process, T = 710°C, platinum quasi-reference electrode. (a) A_{Ag} = 0.31 cm²; (b) A_{Ag} = 0.036 cm²; $C_{K_2TaF_7}$ = 0.043 m/o.

versible electrode processes another equation should be used[21]

$$E_{p/2} - E_p = 1.857 \, RT/\alpha n_\alpha F \qquad [9]$$

but αn_α calculated for the rate range 0.05 to 0.4 V · s^{-1} was >5, though the transfer coefficient α was always smaller than unity.

These considerations, together with the peak current and the peak potential dependence on concentration and potential scan rate, show that the reduction of Ta(V) fluoro complexes to the metal in the scan rate interval 0.05 to

Fig. 9. Stationary voltammogram of tantalum reduction, T = 710°C, scan rate 0.0025 V · s^{-1}, platinum quasi-reference electrode. (a) TaF_7^{2-} discharge, A_{Ag} = 0.57 cm², $C_{K_2TaF_7}$ = 0.056 m/o; (b) $TaOF_5^{2-}$, A_{Ag} = 0.31 cm², $C_{K_2TaF_7}$ = 0.071 m/o.

Table I. TaF_7^{2-} reduction peak current related to concentration of K_2TaF_7. (T = 710°C, scan rate 0.1 V · s^{-1}, A_{Ag} = 0.57 m².).

C K_2TaF_7 (m/o)	0.06	0.11	0.19	0.25	0.33	0.42	0.53	0.63
I_{p1} (mA)	21	45	88	114	147	194	242	290
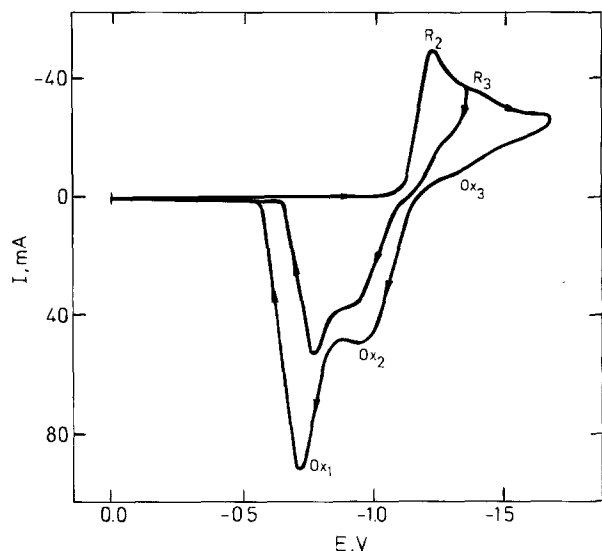
Fig. 10. Cyclic voltammogram of FLINAK-K_2TaF_7-Na_2O melt, T = 710°C, scan rate 0.5 V · s^{-1}, Ag/AgCl reference. A_{Ag} = 0.31 cm^2. $C_{K_2TaF_7}$ = 0.139 m/o. Molar ratio Na_2O/K_2TaF_7 = 1. The oxide content has been corrected with an amount corresponding to 0.029 m/o on the basis of the measurements shown in Fig. 6.

tials corresponding to this wave resulting in tantalum deposition), α is equal to 0.62. αn_α values for temperatures from 572 to 815°C, calculated from the difference of the peak and half-peak potentials (Eq. 9), are summarized in Table II.

With a knowledge of the αn_α values, it is possible to calculate the diffusion coefficient of the Ta(V) fluoro complexes. The equation[24] for an irreversible electrochemical process with deposition of an insoluble layer at the cathode is

$$I_p = 0.496 nFCAD^{1/2}(\alpha n_\alpha Fv/RT)^{1/2} \qquad [11]$$

The tantalum concentration was corrected both for the initial oxide ion content in the melt, and assuming that the peak current value of the Ta(V) → Ta(0) reduction of fluoro complexes was diminished by the amount of tantalum ions converted into monooxofluoro complexes. The temperature dependence of the logarithm of the diffusion coefficient of TaF_7^{2-} ions can then be expressed by the empirical equation

$$\log D = -2.55 - 2044/T \qquad [12]$$

The activation energy of diffusion determined from the slope of log D vs. $1/T$ was 39.1 kJ · mol^{-1}. All the kinetic parameters of the tantalum reduction process in fluoride melts are summarized in Table II.

Plots of log $(I_\ell - I)$ vs. E and log $[(I_\ell - I)/I]$ vs. E (Fig. 9a) have shown that in the temperature range 600 to 815°C, both curves are nonlinear. This also indicates that the process is quasi-reversible. In this case it is possible to calculate the coefficient α, from a plot of log $[(I_\ell - I)/I]$ vs. E, by measuring the asymptotic slope at more negative potentials where the forward reaction is much faster than the reverse reaction.[21,25] The α value at 710°C calculated in this way is equal to 0.77, which is similar to, but somewhat larger than, the value obtained using Eq. 10.

When a 1:1 composition of sodium monoxide:K_2TaF_7 in FLINAK, taking into account the initial content of oxide ions, was studied, the peak due to tantalum reduction from the TaF_7^{2-} complex, R_1 seen in Fig. 4, was completely suppressed (Fig. 10). Further, x-ray diffraction (XRD) showed that the deposit obtained during potentiostatic electrolysis at this half-wave potential consisted of metallic tantalum. Thus metallic tantalum was deposited by reduction of $TaOF_5^{2-}$ as well as by reduction of TaF_7^{2-}.

To clarify the mechanism of tantalum reduction from the $TaOF_5^{2-}$ complex, we studied plots of the peak current ($I_{p,2}$) and of peak potential against scan rate (Fig. 11a, b). The
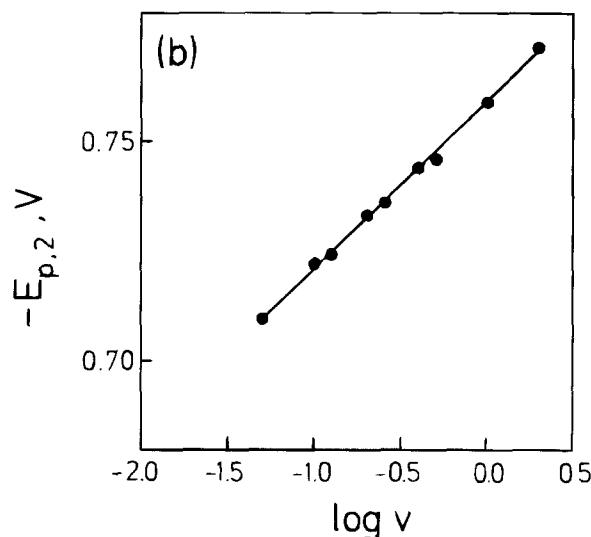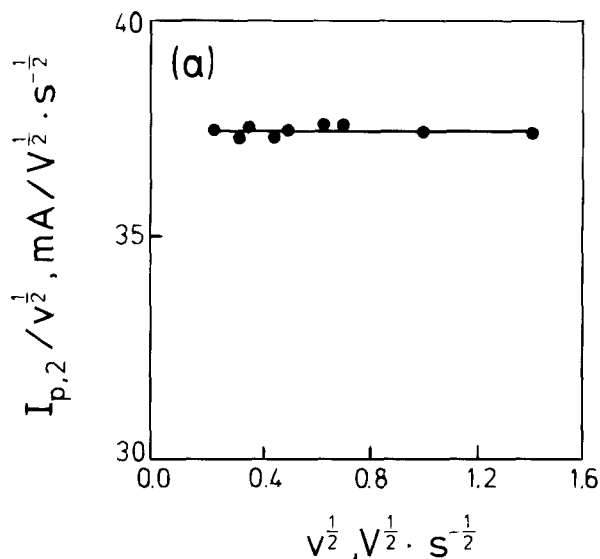
Fig. 11. Scan rate effect on (a) peak current and (b) peak potential of the $TaOF_5^{2-}$ reduction process, T = 709°C, Pt quasi-reference electrode. (a) A_{Ag} = 0.31 cm^2; (b) A_{Ag} = 0.036 cm^2. $C_{K_2TaF_7}$ = 0.071 m/o. Molar ratio Na_2O/K_2TaF_7 = 1.

parameter $I_{p,2}/v^{1/2}$ was independent of $v^{1/2}$ in the scan rate range of 0.05 to 2.0 V · s^{-1}, but the $E_{p,2}$ potential showed linear dependence on log v and shifted to the negative region with the increase in scan rate. This, as well as the fact that the peak current was proportional to the concentration, and that the peak potential was independent of concentration, allowed us to conclude that this process was irreversible in the temperature range 580 to 800°C. The

Table III. Kinetic parameters of $TaOF_5^{2-}$ + $5e^-$ → Ta + $5F^-$ + O^{2-} process (FLINAK-K_2TaF_7-Na_2O melt, molar ratio Na_2O/K_2TaF_7 = 1, scan rate = 0.5 V · s^{-1}, A_{Ag} = 0.31 cm^2).

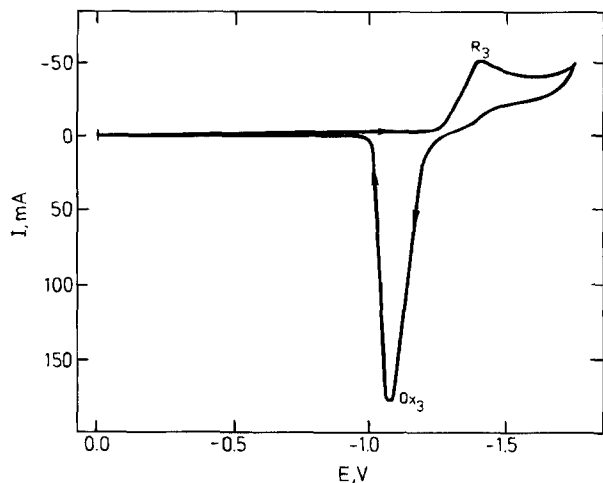| T (°C)	Peak current $I_{p,1}$ (mA)	$C \cdot 10^5$ K_2TaF_7 (mol · cm^{-3})	αn_α	$D \cdot 10^5$ (cm^2 · s^{-1})
813	25.0	1.468	2.896	3.40
768	23.0	1.488	2.776	2.80
718	20.5	1.511	2.643	2.16
708	19.9	1.515	2.617	2.02
658	17.5	1.537	2.483	1.52
649	17.2	1.541	2.464	1.46
597	5.0	1.558	2.320	1.09

Fig. 12. Cyclic voltammogram of FLINAK-K$_2$TaF$_7$-Na$_2$O melts, $T = 710°C$, scan rate 0.1 V · s^{-1}, Ag/AgCl reference electrode. $A_{Ag} = 0.42$ cm^2. $C_{K_2TaF_7} = 0.406$ m/o. Molar ratio Na$_2$O/K$_2$TaF$_7 = 2.01$. The oxide content has been corrected with an amount corresponding to 0.029 m/o on the basis of the measurements shown in Fig. 6.

product of the transfer coefficient (α) and the number of electrons (n_α) characterizing the irreversibility of the electrochemical process was calculated using Eq. 9 and its values are given in Table III.

Further, αn_α values were calculated from the slope of $E_{p,2}$ vs. log v (Fig. 11b) using Eq. 10. The slope was $K = 0.0385$; therefore at 710°C the αn_α was equal to 2.53.

Using these αn_α values (Table III) the diffusion coefficient for the Ta(V) monooxofluoro complex was obtained from Eq. 11. The values of the diffusion coefficient for the Ta(V) monooxofluoro complex calculated from $I_{p,2}$ are lower than the real value because of tantalum reduction from dioxofluoro complexes ($I_{p,3}$) which always occurs to a small extent.

The plot of the logarithm of the TaOF$_5^{2-}$ diffusion coefficient vs. $1/T$ is a straight line, which can be expressed by the following empirical equation

$$\log D = -2.35 - 2293/T \qquad [13]$$

the activation energy of diffusion determined from its slope being 43.9 kJ/mol.

The results from linear voltammetry have been confirmed by polarographic data. From these latter measurements it has been found that the limiting current of the reduction wave was directly propotional to the TaOF$_5^{2-}$ concentration, and that the half-peak potentials were not dependent on Ta(V) concentration.

Analysis of the stationary wave corresponding to the TaOF$_5^{2-}$ + 5e^- → Ta + 5F$^-$ + O^{2-} reduction process (Fig. 9b) shows that the plot of log $[(I_\ell - I)/I]$ vs. E is linear with a slope larger than 2.3 $RT/n_\alpha F$, indicating an irreversible process. Assuming that Eq. 14 is valid in this case[21,25]

$$E = E_{1/2} + \frac{2.303 \, RT}{\alpha n_\alpha F} \log \frac{I_\ell - I}{I} \qquad [14]$$

an α value of 0.58 was obtained for n_α equal to 5.

Use of a molar ratio (Na$_2$O/K$_2$TaF$_7$) close to two showed the absence of peaks associated with tantalum reduction from TaF$_7^{2-}$ and TaOF$_5^{2-}$ species (Fig. 12). Hence the dioxofluoro complex is formed exclusively and the voltammogram, which exhibits a near cathodic peak and an anodic dissolution peak corresponding to it, is that of the dioxofluoro complex alone. As can be seen from the cyclic voltammogram, the dissolution of the solid product de-

posited on the electrode occurs at a marked overvoltage. Electrolysis under potentiostatic conditions with a potential corresponding to this limiting current value gave a reduction product, which XRD data showed to be only KTaO$_3$. Apparently the primary electrochemical step proceeds a chemical reaction involving KTaO$_3$ formation.

Conclusion

Titration of TaF$_7^{2-}$ ions (dissolved in FLINAK) with oxide ions leads to the stepwise formation of TaOF$_5^{2-}$ and TaO$_2$F$_x^{(x-1)-}$ complexes.

Electrochemically TaF$_7^{2-}$ is reduced to tantalum metal in a single quasi-reversible five-electron step. TaOF$_5^{2-}$ is also reduced to metal in a five-electron step but this process is irreversible. Electrochemical reduction of TaO$_2$F$_x^{(x-1)-}$ leads to the formation of an insoluble product, KTaO$_3$.

Acknowledgment

REFERENCES

1. S. Senderoff, G. W. Mellors, and W. I. Reinhart, *This Journal,* **112,** 840 (1965).
2. D. Inman, R. P. Sethi, and R. Spencer, *J. Electroanal. Chem.,* **29,** 137 (1971).
3. P. Taxil and J. Mahenc, *Corros. Sci.,* **21,** 31 (1981).
4. P. Taxil, *J. Less-Common Met.,* **113,** 89 (1985).
5. P. Taxil and J. Mahenc, *J. Appl. Electrochem.,* **17,** 261 (1987).
6. K. H. Stern and D. R. Rolison, *This Journal,* **136,** 3760 (1989).
7. A. Espinola, A. J. B. Dutra, and F. T. Silva, *Anal. Chim. Acta,* **251,** 53 (1991).
8. V. I. Konstantinov, E. G. Polyakov, and P. T. Stangrit, *Electrochim. Acta,* **23,** 713 (1978).
9. J. S. Fordyce and R. L. Baum, *J. Phys. Chem.,* **69,** 4335 (1965).
10. J. S. Fordyce and R. L. Baum, *J. Chem. Phys.,* **44,** 1166 (1966).
11. J. H. von Barner, R. W. Berg, N. J. Bjerrum, E. Christensen, and F. Rasmussen, *Mater. Sci. Forum,* **73-75,** 279 (1991).
12. J. Hinden, J. Augustynski, and R. Monnier, *Electrochim. Acta,* **21,** 459 (1976).
13. E. Christensen, X. Wang, J. H. von Barner, T. Østvold, and N. J. Bjerrum, *This Journal,* **141,** 1212 (1994).
14. A. J. Calandra, C. E. Castellano, and C. M. Ferro, *Electrochim. Acta,* **24,** 425 (1979).
15. L. P. Polyakova, E. G. Polyakov, A. I. Sorokin, and P. T. Stangrit, *J. Appl. Electrochem.,* **22,** 628 (1992).
16. R. P. Elliot, *Constitution of Binary Alloys,* 1st Suppl., M. Metallurgia, Vol. 2 (1970).
17. M. Hansen and K. Anderko, *Constitution of Binary Alloys,* McGraw-Hill, New York (1958).
18. S. H. White, in *Molten Salt Techniques,* D. Lovering and R. Gale, Editors, Vol. 1, p. L, Plenum Press, New York (1983).
19. J. P. Chaminade, V. Vlasse, M. Pouchard, and P. Hagenmuller, *Bull. Soc. Chim. Fr.,* **9/10,** 1791 (1974).
20. J. P. Chaminade, M. Pouchard, and P. Hagenmuller, *Rev. Chim. Miner.,* **9,** 381 (1972).
21. Z. Galus, *Fundamentals of Electrochemical Analysis,* Ellis Harwood Ltd., Chichester (1976).
22. F. Lantelme, A. Barhoun, and G. Li, *This Journal,* **139,** 1249 (1992).
23. H. Matsuda and Y. Ayabe, *Z. Electrochem.,* **59,** 494 (1955).
24. P. Delahay, *New Instrumental Methods in Electrochemistry,* Interscience, New York (1954).
25. J. Heyrovsky and J. Kuta, *Principles of Polarography,* Academic Press, New York (1966).