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The Influence of Oxide on the Electrochemical Processes in K$_2$NbF$_7$-NaCl-KCl Melts

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ABSTRACT

Transient electrochemical techniques showed that in NaCl-KCl melts the reduction of K$_2$NbF$_7$ occurs through a two-step reaction Nb(V) → Nb(IV) → Nb. When oxide ions were introduced, cyclic voltammetry indicated that the waves corresponding to reduction of the complex NbF$_7^{2-}$ progressively disappeared. Oxo complexes, such as NbOF$_n^{(n-3)-}$, are reduced at a potential close to that of the Nb(IV) fluoro complexes. Niobium metal deposition was perturbed by the formation of niobium suboxides like NbO or Nb$_4$O$_5$. For molar ratios of oxide to Nb greater than one, a black layer of niobium oxide, NbO$_2$, appeared at the electrode surface. The present study confirms the high oxygen affinity of niobium and shows that a careful purification of the electrolyte and feeding materials is required for producing niobium with a low oxygen content.

Thermal reduction is the major processing route to produce metallic niobium. However, it is generally necessary to refine the metal considerably to satisfy industrial demands. This has motivated research on alternative processes that involve high temperature electrolysis in molten salts such as alkali metal fluorides or chlorides. The preferred electrolytes are the alkali chlorides which are cheaper and less toxic than fluorides. It has been shown that the mechanism of the electrodeposition process depended on temperature and the nature of the electrolyte.[1-4] At temperatures lower than 650°C, the formation of niobium subhalides perturbs the deposition.[5,6] In chloride melts, such as LiCl-KCl, NaCl-KCl, NaCl-AlCl$_3$, the oxidation states Nb(V), Nb(IV), and Nb(III) are stable.[5-8] A recent study[1] has shown that the presence of small amounts of fluoride ions modify the equilibrium conditions. In NaCl-KCl, at 720°C, for molar ratios of F/Nb, greater than two, the Nb(III) species are not stable anymore and direct reduction of Nb(IV) to metallic niobium is observed. This result explains the differences in the electrochemical behavior between niobium solutions prepared from K$_2$NbF$_7$ and from NbCl$_5$.

The presence of oxide ions has a considerable influence on the deposition process. These ions are a common impurity of the melts, and ignoring their presence may lead to erroneous interpretations. Moreover, there have been a few attempts to recover niobium from oxides dissolved in fused salts. It has been shown that niobium oxofluoro complexes in alkali fluoride melts reduced to niobium metal. The presence of a certain amount of oxide actually improved the current efficiency.[9] However, with NaCl-KCl as solvent, K$_2$NbF$_7$ reduced to NbO when oxide ions were present in the melt.[10] This result is in agreement with recent experiments,[11] which indicate that niobium is the only refractory metal which reacts with its oxides giving rise to suboxides such as NbO and Nb$_4$O$_5$. The aim of the present work is to study the mechanism of the electroreduction of K$_2$NbF$_7$ in NaCl-KCl melts as a function of the oxide ion content.

Experimental

The electrochemical cell consisted of an outer Hastelloy® (Cabot Corporation) shell (a cylinder closed at the bottom end). The glassy carbon vessel containing the molten salt was placed inside this envelope.[12] The experiments were carried out under on argon atmosphere. The NaCl-KCl mixture was purified according to a procedure involving high vacuum drying, chlorine bubbling, argon flushing, electrolysis, and finally filtering in a separate silica cell.[13] Anhydrous potassium heptafluoroniobate (Alpha Products) was purified by recrystallization from an aqueous hydrogen fluoride solution. Sodium oxide was obtained from Aldrich (98%) and was used without further purification. A few experiments were carried out using barium oxide or niobium pentoxide from Merck.

The reference electrode was a Ni^{2+}/Ni electrode (1 mole percent (m/o) NiCl$_2$ in NaCl-KCl); this electrode was standardized by the use of an internal reference system.[14] The counterelectrode was a graphite rod (No. 208 Le Carbone Lorraine). Platinum or tungsten (Matthey reagent, diameter 1 mm) wires were used as working electrodes. The generation of the potential sweep was performed with a Tacussel GSTP4 programmer and a Tacussel PRT 20/10
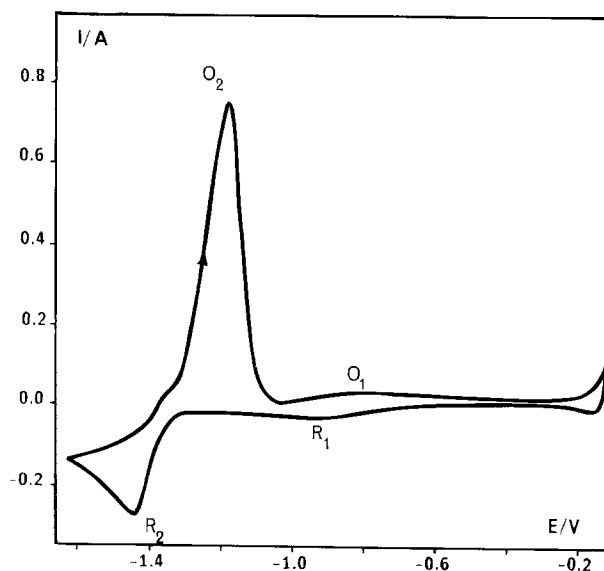
Fig. 1. Cyclic voltammogram of K$_2$NbF$_7$ (0.085 M) dissolved in NaCl-KCl-(0.1 M) NaF melt at 715°C. Working and reference electrode were platinum (0.5 cm^2) and Pt^{2+} (molar)/Pt, respectively. Scan rate, 1 V s^{-1}.
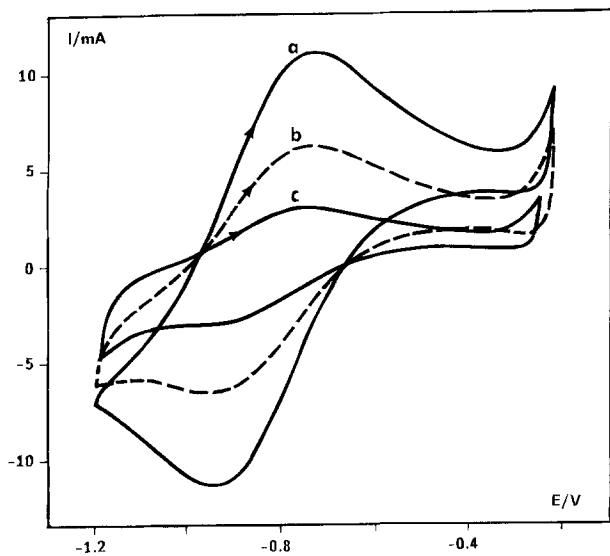
* Electrochemical Society Active Member.
[a] Unité de Recherche Associée au CNRS No. 430.

Fig. 2. Cyclic voltammograms for the reaction Nb(V) + e^- ↔ Nb(IV) at 720°C as a function of oxide additions to a melt containing K_2NbF_7 (0.143 M) dissolved in NaCl-KCl-(0.1 M) NaF. Oxide contents were: (a) 0, (b) 0.064 M, (c) 0.1 M. Working and reference electrodes were platinum (0.33 cm²) and Pt^{2+}(molar)/Pt, respectively. Scan rate, 0.2 V s^{-1}.

Fig. 3. Cyclic voltammograms at 720°C of K_2NbF_7 (0.143 M) dissolved in NaCl-KCl-(0.1 M) NaF melt with added oxide: (a) 0, (b) 0.028 M, (c) 0.064 M, (d) 0.86 M, (e) 0.1 M, (f) 0.122 M. Working and reference electrodes were platinum (0.33 cm) and Pt^{2+} (molar)/ Pt, respectively. Scan rate, 0.2 V s^{-1}.

potentiostat. The voltammograms were recorded on a Sefram X-Y recorder. A Nicolet 310 digital oscilloscope was sometimes used as an intermediate storage device.

Results

In the following, the notation Nb(V), Nb(V)O, and $Nb(V)O_2$ is used to symbolize niobium fluoro, niobium mono oxo fluoro, and niobium dioxo fluoro complexes in the oxidation state +5. Similarly Nb(IV) and Nb(IV)O denote niobium fluoro and oxo fluoro species in oxidation state +4, respectively. Standard potentials for the redox reactions of niobium occurring in the melts are given as $E^0_{x/y}$, x and y correspond to the higher and lower oxidation state of niobium for the redox reaction in question. The symbol Nb,O(ss) refers to a solid solution of oxygen in metallic niobium.

Molar ratio, O/Nb, less than one.—In Fig. 1, a voltammogram obtained with a platinum electrode in a solution of K_2NbF_7 in NaCl-KCl is shown. The R_1/O_1 peaks can be related to the reversible Nb(V)/Nb(IV) system. The reduction Nb(IV) + $4e^- \to$ Nb gives rise to the R_2 peak, and the steep anodic peak, O_2, corresponds to the oxidation of deposited metallic niobium. This demonstrates that the introduction of fluoride destabilizes the Nb(III) oxidation state in accordance with the results from previous work.[1]

From Fig. 2 it is obvious that the peak currents for the reaction Nb(V)/Nb(IV) rapidly decrease upon oxide addition and the R_1/O_1 peaks disappeared totally when the O/Nb ratio approached one (Fig. 3f). It should be noted that no change in the R_1/O_1 peak potentials can be seen during oxide addition. A similar behavior has been reported for the Nb(V)/Nb(IV) couple in LiCl-KCl melts[6] without added fluoride.

Figure 3 shows the evolution of the voltammograms with oxide additions using a wider potential window than in Fig. 2. It can be seen that the decrease in the R_1/O_1 peaks is associated with the appearance of a peak, R_3, at a potential more negative than for the R_2 peak (Fig. 3b and c). As the concentration of oxide ions is increased, the R_3 peak increases, and R_2 now appears as a shoulder on the R_3 peak (Fig. 3d, e, and f). In the investigated concentration range (0.05 to 0.3 M K_2NbF_7) similar results were obtained, for melts with molar ratios, O/Nb < 1. X-ray diffraction analysis (XRD) showed that the reaction giving rise to the R_2/O_2

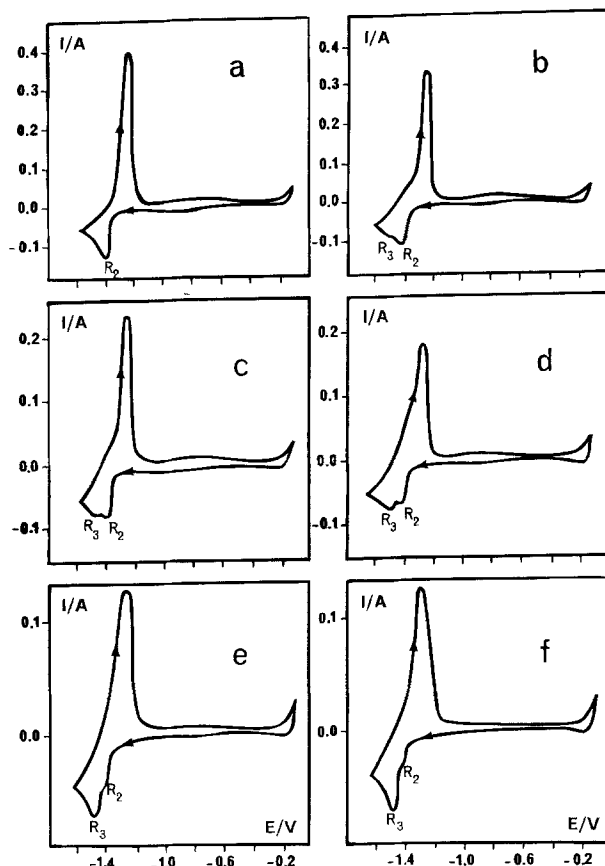peaks involved niobium deposition. Since the R_2 reduction peak diminishes with the addition of oxide to the melt, it is reasonable to suggest that it is caused by reduction of a Nb(IV) fluoro complex. The R_3 peak (Fig. 3) is believed to have connection with the presence of oxo halogeno complexes, as is discussed later.
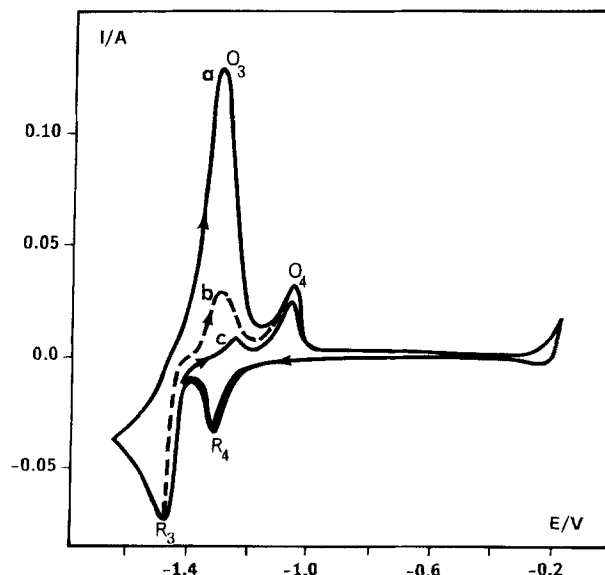
Fig. 4. Cyclic voltammogram of K_2NbF_7 (0.144 M) in NaCl-KCl with added Na_2O (0.17 M). Temperature: 720°C. Scan rate: 0.2 V s^{-1}. Cathodic switching potential, (a) −1.65 V, (b) −1.48 V, (c) −1.43 V. Working electrode, platinum (0.33 cm²). Reference electrode, Pt^{2+} (molar)/Pt.
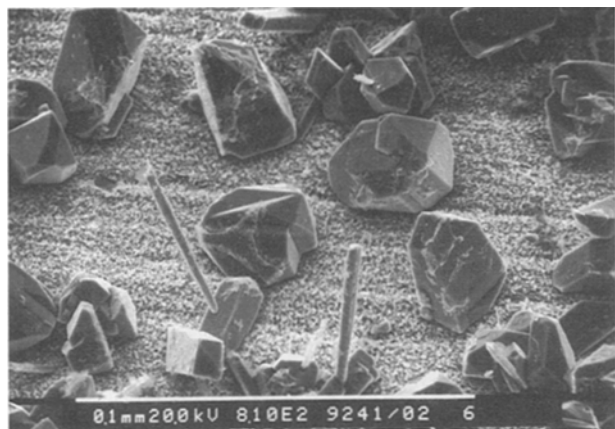
Fig. 5. Scanning electron micrograph (SEM) of a cathodic deposit on a molybdenum substrate. Electrolyte: K_2NbF_7 (0.48 *M*) dissolved in NaCl-KCl with added Nb_2O_5 (0.047 *M*). Electrode potential, *E* = −1.35 V *vs.* Pt (molar)/Pt. Temperature, 720°C.

Molar ratio O/Nb greater than one.—When more oxide is added (O/Nb > 1), a new reaction appears, giving rise to an oxidation peak, O_4, at −1.1 V, associated with a reduction peak, R_4 (Fig. 4). The steep shape of the peaks suggests that the reaction is probably not controlled by diffusion. Moreover, as pointed out in a previous paper,[15] the R_4 peak is not seen during the first potential sweep, it only appears once the O_4 peak has been obtained. For even higher oxide contents, O/Nb > 1.5, the R_3/O_3 peaks decreased and the R_4/O_4 peaks became very broad. A black precipitate, mainly consisting of NbO_2, formed at the electrode surface and on the wall of the crucible.

Discussion

Formation of oxo complexes; molar ratio, O/Nb, less than one.—The reduction of K_2NbF_7 in NaCl-KCl involves a two step reaction[1]

$$Nb(V) + e^- \leftrightarrow Nb(IV) \text{ and } Nb(IV) + 4e^- \leftrightarrow Nb \qquad [1]$$
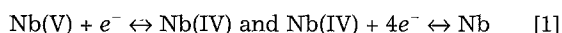
The present work confirms this scheme. The standard potentials (molar scale) of the redox couples, Nb(V)/Nb(IV) and Nb(IV)/Nb, are −0.85 and −1.31 V, respectively.

It has been shown[15] that, when oxide ions are added to the melt, oxo halogeno complexes are involved in the electrochemical reaction. Their reduction gives rise to the formation of metallic niobium and niobium suboxides with compositions ranging from NbO to Nb_4O_5. In the present work deposits of pure niobium could be obtained from a melt with O/Nb = 0.2. When a potential of −0.470 V *vs.* Ni^{2+}/Ni was applied, energy dispersive analysis by x-ray (EDAX) and x-ray diffraction (XRD) analysis of the surface only showed the presence of metallic niobium (no XRD lines due to niobium suboxides was observed). When the O/Nb ratio was increased to 0.4 most of the deposit consisted of metallic niobium, but a few long needles, that had a shape very similar to that of Nb_4O_5[16] also appeared (Fig. 5). In contrast to the experiments of Christensen *et al.,*[9] it was not possible to obtain oxygen-free niobium metal for O/Nb molar ratios approaching one. Our results are in agreement with the conclusions of Grinevich *et al.,*[11] who claimed that niobium is the only refractory metal that can reduce its oxides and oxo complexes. They showed that in the presence of metallic niobium, Nb_2O_5, added to a NaCl-KCl bath, was reduced according to the sequence

$$Nb_2O_5 \rightarrow NbO_2 \rightarrow Nb_4O_5 \rightarrow Nb_4O_5 + NbO \rightarrow Nb,O(ss) \quad [2]$$
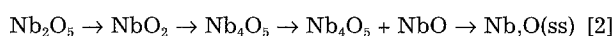
The exact nature of the various complexes occurring during reduction of oxygen ion containing K_2NbF_7 solution in NaCl-KCl melts is not yet fully elucidated. However, the complexes NbF_7^{2-} and $NbOF_5^{2-}$ have been identified by Raman spectroscopy in NaCl-KCl[15] and FLINAK melts.[17] Concerning the complex formation of niobium in oxidation states less than +5, the situation is less certain, but it is

likely that the NbF_7^{3-} complex exists in NaCl-KCl melts as in solidified CsCl-KCl-NaCl samples.[18] The high stability of the oxo fluoro complexes of niobium has recently been confirmed using molecular modeling techniques.[19] Complexes such as $NbO_2F_x^{(x-1)-}$ have been reported[17] and the existence of Nb(IV)O complexes cannot be excluded.

Recently, potentiometric titration (zirconia indicator electrodes) of K_2NbF_7 with oxide in NaCl-KCl melts[20] has shown that the concentration of oxide ions, O^{2-}, remains very low in the region 0 < O/Nb < 2. The reaction

$$NbF_7^{2-} + O^{2-} \leftrightarrow NbOF_5^{2-} + 2F^- \qquad [3]$$
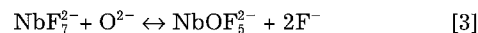
is shifted to the far right, the equilibrium constant being about $10^{8.2}$ (mol kg^{-1}).[20] In the present work, a small excess of fluoride was used to maintain the concentration of fluoride at a constant value. Further, this implies that no mixed chloride-fluoride complexes are likely to form and that the mono oxo fluoro complex with the oxidation state five is $NbOF_5^{2-}$.[15]

At a niobium electrode, the oxo complex, Nb(V)O could be reduced, resulting in a dissolution of oxygen in the metal

$$Nb(V)O + 5e^- \xrightarrow{Nb} Nb,O(ss) \qquad [4]$$
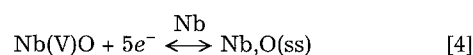
The solubility limit of oxygen in solid niobium has been measured to be 1.4 m/o at 720°C.[21,22] According to the Nb-O phase diagram, this value is the limit of the Nb-O solid solution, for a greater oxygen content a two-phase region appears: Nb-O solid solution + NbO. The oxygen atoms diffuse into the bulk of the metal. At 720°C the diffusion coefficient is 1.4×10^{-8} cm^2 s^{-1}.[22] When the metal surface is saturated with oxygen, niobium suboxide is precipitated together with the niobium metal according to the general equation

$$(1 + x)Nb(V)O + 3(1 + x)e^- \leftrightarrow NbO_{1+x} + xNb \qquad [5]$$
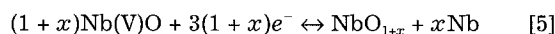
with 0 < x < 0.32.[11]

On the basis of these assumptions the decrease in the R_1/O_1 peaks is due to the depletion of Nb(V) and Nb(IV) fluoro complexes when oxide ions are added. In agreement with recent results from square wave voltammetry,[23] our study shows that the reduction of the Nb(V)O oxo fluoro species occurs at a potential more cathodic than for the reaction Nb(V) ↔ Nb(IV). Accordingly, the R_2 peak is due to the reduction of Nb(IV) to Nb, and the reduction of the Nb(V)O complexes gives rise to the peak R_3. In contrast to Kuznetsov *et al.,*[24] we find that the reduction of the Nb(V)O species takes place at a potential more negative than for the Nb(IV) fluoro complexes. However, in our experiments, an excess of fluorides has been added (molar ratio F/Nb ≥ 7). Whereas, in the case of Kuznetsov et al., the ratio, F/Nb, when oxide was added, became around four, *i.e.,* oxo complexes like $NbOF_4^-$ or $NbOF_xCl_y^{(x+y-3)-}$ were formed.

Modeling.—The electrochemical reactions are complex and involve multistep processes. For these conditions, conventional equations of cyclic voltammetry are not applicable. Digital simulation is then the only way to treat the phenomena comprehensively. Electron transfer is generally assumed to be rapid.[1,25] The concentrations, c_i, of the various electroactive species, must obey the Nernst equation

$$c_{NbV} = c_{NbIV} \exp \{f[E(t) - E^0_{NbV/NbIV}]\} \qquad [6]$$

and

$$c_{NbVO} = c_{NbIVO} \exp \{f[E(t) - E^o_{NbVO/NbIVO}]\} \qquad [7]$$

where *f* = F/RT. When niobium metal is present at the electrode surface the following equations are valid

$$c_{NbIV} = \exp \{4f[E(t) - E^o_{NbIV/Nb}]\} \qquad [8]$$

If the bath contains oxo complexes, the activity of oxygen in solid solution Nb,O(ss) is given by

$$a_{O(Nb)} = c_{NbVO} \exp \{-3f[E(t) - E^o_{NbVO/NbIIO}]\} \qquad [9]$$

Table I. Standard potentials for the redox reactions of niobium complexes in a solution of K_2NbF_7 in NaCl-KCl (0.1 M NaF) containing oxide ions at 720°C. For the reaction involving deposition of solid phase, Nb or NbO, the coverage factors, Q_M and QO_M, and the nucleation overpotentials, η_{Nb} and η_{NbO} are given. Pt^{2+} (molar)/Pt reference electrode.

$E^\circ_{NbV/NbIV}$ (V)	$E^\circ_{NbIV/Nb}$ (V)	$E^\circ_{NbVO/NbIIO}$ (V)	$E^{\circ*}_{NbVO/NbIVO}$ (V)	$Q_M \times 10^5$ (mol cm^{-2})	η_{Nb} (mV)	$QO_M \times 10^5$ (mol cm^{-2})	η_{NbO} (mV)
-0.85 ± 0.01	-1.31 ± 0.01	-1.32 ± 0.04	-1.3	5	50	3	90

* Estimated.

When the activity, $a_{O(Nb)}$, reaches unity, saturation occurs, and suboxides appear at the niobium surface, Eq. 5. In that case, the following equation is used instead of Eq. 9

$$c_{NbVO} = \exp\{3f[E(t) - E^\circ_{NbVO/NbIIO}]\} \quad [10]$$

Here, as a simplifying assumption, the formula for suboxides is taken as NbO. The model also accounts for the presence of platinum(II) ions arising from oxidation of the working electrode

$$c_{PtII} = \exp\{2f[E(t) - E^\circ_{PtII/Pt}]\} \quad [11]$$

$E^\circ_{PtII/Pt}$ is the standard potential for the couple Pt^{2+}/Pt.

Some specific features of the niobium electrolysis must be considered. For example, the separation of the R_2-O_2, or R_3-O_3, peak potentials (Fig. 1 and 4) is about 50 mV larger than expected for a fast reaction. It was shown that this departure actually originates from a potential-dependent nucleation growth process.[26] Indeed, during metal deposition or dissolution, the electrode surface may be only partly covered by the metal. If the amount of metal needed to obtain complete coverage of the electrode is denoted Q_M, and the actual amount of metal deposited at the electrode is q, then for q less than Q_M a coverage factor, $\theta = q/Q_M$, must be introduced in the calculation.[27] Introducing such a factor has two consequences: (i) a broadening of the anodic stripping peak accompanied by a decrease in the peak current (since the peak area must be constant) and (ii) a positive shift in the peak potential.

Another factor, which must be taken into account, is the nucleation overpotential.[26] Indeed, at the end of the anodic sweep, no crystals remain at the electrode surface. During the cathodic sweep an additional potential is needed to initiate the formation of new metal nucleii. As a consequence, a negative shift in the cathodic peak potential occurs.

The concentration profile of the soluble species is obtained by numerical integration of the diffusion equation. The current density, i, is calculated from the charge balance of the charged species at the electrode surface. More details concerning the digital simulation of the electrochemical reaction and the role of the coverage factor have been given in Ref. 27 and 28.

The parameters involved in the calculation (standard potentials, diffusion coefficients, coverage factors, and crystallization overpotentials) were varied to obtain the best fit to the experimental curves. Within the uncertainty of the measurements ($\pm 10\%$), it can be shown that the diffusion coefficients do not vary when oxides are added to the melt. The following values were obtained at 720°C, $D_{NbV} = D_{NbVO} = D_{NbIVO} = 1.8 \times 10^{-5}$ cm^2 s^{-1}, and $D_{NbIV} = 2.3 \times 10^{-5}$ cm^2 s^{-1}. As usual,[29] the diffusion coefficient of ionic species at a lower oxidation state seems to be slightly greater than those at higher oxidation state. However this trend is at the limit of the accuracy of the measurements.

The values of the standard potentials are reported in Table I. When oxide is added to a K_2NbF_7 solution, the concentration of fluoro complexes, Nb(V), decreases and Nb(V)O complexes form according to Eq. 3. The reduction of these oxo complexes occurs at a more cathodic potential than of the pure Nb(V) fluoro complexes. The reduction potential of the former is close to the reduction potential of Nb(IV). The values of the standard potentials and equilibrium constants K_V and K_{IV}

$$K_V = c_{NbIV}c_{O2}/c_{NbVO} \quad [12]$$

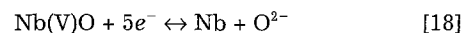$$K_{IV} = c_{NbIV}c_{O2}/c_{NbIVO} \quad [13]$$

for the reactions

$$Nb(V) + O^{2-} \leftrightarrow Nb(V)O \quad [14]$$

$$Nb(IV) + O^{2-} \leftrightarrow Nb(IV)O \quad [15]$$
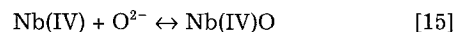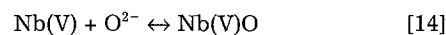
are linked by the relationships

$$K_V/K_{IV} = \exp[f(E^\circ_{NbVO/NbIVO} - E^\circ_{NbV/NbIV})] \quad [16]$$

and

$$K_V = \exp[5f(E^\circ_{NbVO/Nb} - 4/5E^\circ_{NbIV/Nb} - 1/5E^\circ_{NbV/NbIV})] \quad [17]$$

$E^\circ_{NbVO/Nb}$ is the standard potential for the reaction

$$Nb(V)O + 5e^- \leftrightarrow Nb + O^{2-} \quad [18]$$

Under the present experimental conditions an estimated value of K_V is $10^{-8.5}$ mol l^{-1}.[20] From Eq. 17 and the standard potentials given in Table I, a value of -1.55 V can be obtained for $E^\circ_{NbVO/Nb}$. The voltammograms in Fig. 6 and 7 show that the proposed reaction mechanism represents the experimental results correctly. The influence of the oxide ions is underscored, the R_2 peak that is associated with the direct reduction of oxygen-free fluoro complexes decreases in height when more oxide is added. Simultaneously, an increase in R_3 occurs since this peak belongs to the reduction of oxo fluoro complexes. The model also explains the shape of the anodic peak which results from the superimposition of the currents due to the formation of oxo fluoro and fluoro complexes.

Molar ratio O/Nb greater than one.—As mentioned earlier, the concentration of free oxide ions, c_{OII}, is low,[20] even for large amounts of oxide added (O/Nb $\simeq$ 1.5). This implies that the formation of dioxo fluoro complexes according to the reaction
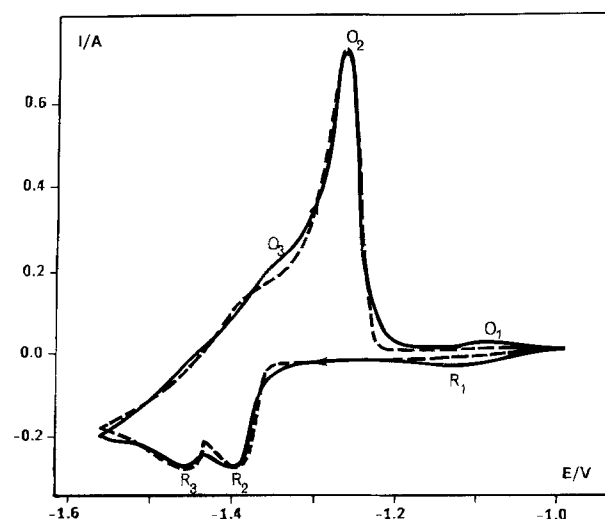
Fig. 6. Comparison between experimental and calculated cyclic voltammograms of K_2NbF_7 (0.225 M) in NaCl-KCl with added Na_2O (0.115 M). Working electrode, platinum (0.31 cm^2); reference electrode, Pt^{2+}(molar)/Pt. Temperature, 720°C. Scan rate, 1 V s^{-1}. Solid line, experimental; dashed line, simulated.
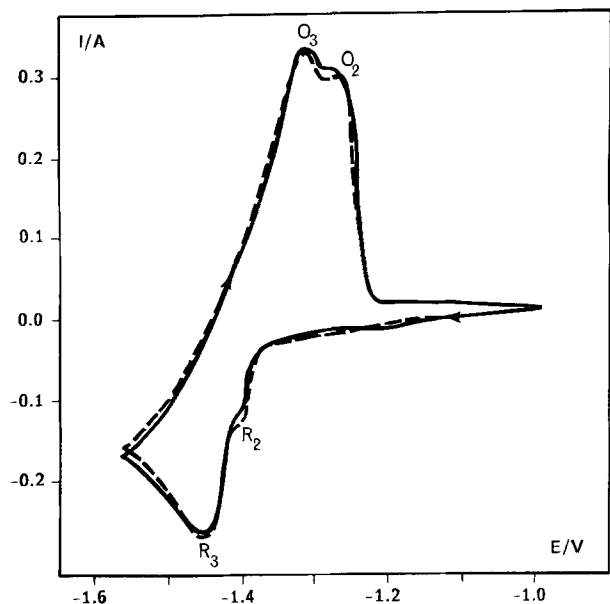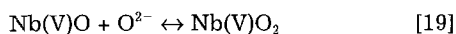
Fig. 7. Comparison between experimental and calculated cyclic voltammograms of K_2NbF_7 (0.225 M) in NaCl-KCl-(0.1 M) NaF with added Na_2O (0.18 M). Temperature, 720°C. Scan rate, 1 V s^{-1}. Solid line, experimental; dashed line, simulated. Working electrode, platinum (0.31 cm^2). Reference electrode, Pt^{2+} (molar)/Pt.

$$Nb(V)O + O^{2-} \leftrightarrow Nb(V)O_2 \qquad [19]$$

probably takes place. Niobium dioxo fluoro complexes are known to exist in the LiF-NaF-KF eutectic melt (FLINAK).[17] Because the complex formation in K_2NbF_7-NaCl-KCl seems to be similar in all other respects, it is reasonable to assume that dioxo fluoro complexes also exist in these melts. The standard potential, $E^o_{NbVO/Nb,NbVO_2}$ for niobium deposition via the reaction

$$2Nb(V)O + 5e^- \leftrightarrow Nb + Nb(V)O_2 \qquad [20]$$
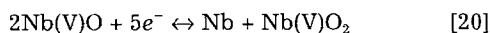
obeys the equation

$$E^o_{NbVO/Nb,NbVO_2} = E^o_{NbVO/Nb} - 1/5f \ln (KO_V) \qquad [21]$$

with

$$KO_V = c_{NbVO}c_{OII}/c_{NbVO_2} \qquad [22]$$

Preliminary results indicate that the dissociation constant for equilibrium, Eq. 19, can be estimated to $KO_5 = 10^{-7.5}$ mol $\cdot$ l^{-1}.[20] When the electrode is maintained at the equilibrium potential (approximately -1.2 V $vs.$ Pt^{2+}/Pt) in a melt with a O/Nb molar ratio of 1.25, a black precipitate, which is identified by XRD as NbO_2, appears at the electrode surface. If the electrode potential is maintained at -1.05 V, the XRD analysis of the deposit at the electrode surface is difficult to explain, but the presence of $KNbO_2$ has been detected. It is known that various compounds exist in the composition range Nb_2O_5, $(Alk_2O)_x$ where Alk = Na or K, when x varies from 0.33 to 5.[30] The assumption of the existence of a redox reaction involving NbO_2, and niobates in the solid state is supported by the potential-p_{O_2} diagram determined by Picard and Bocage[7] in LiCl-KCl. The reaction is written as

$$Nb(IV)O_2 \leftrightarrow Nb(V)O_2 + e^- \qquad [23]$$
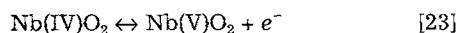
The reaction is probably controlled by a phase transformation in the solid state. The mechanism of this transformation is not yet known. The cyclic voltammograms show that the current density of this reaction obeys the following equation

$$i_s = kF\{q_{IV} \exp [(E(t) - E^o_{Nb(V)O_2/Nb(IV)O_2})/\eta_{s+}]$$
$$- q_V \exp [- (E(t) - E^o_{Nb(V)O_2/Nb(IV)O_2})/\eta_{s-}]\} \qquad [24]$$

where k is a kinetic constant, η_{s+} and η_{s-} represent the overpotentials of the phase transformations, and q_{IV} and q_V are the surface densities of $Nb(IV)O_2$ and $Nb(V)O_2$. The contribution from this reaction step was introduced in the simulation process, assuming that $\eta_{s+} = \eta_{s-} = \eta_s$. Experimental and calculated voltammograms are compared in Fig. 8. The peaks R_3/O_3 belong to the reduction and oxidation of the mono oxo fluoro complex in the melt. The two peaks R_4 and O_4 are related to products formed at the electrode surface. Digital simulation shows that the empirical Eq. 24 is convenient for representing the electrochemical reaction. This model is probably valid only for small concentrations of oxo complexes at the electrode surface; in the present experiments, the values of q_{IV} and q_V were 10^{-6} mol cm^{-2}, at most. The large separation of the peak potential, about 0.4 V, is mainly due to the low value of the kinetic constant. The different factors applied in the calculation are: $E^o_{Nb(V)O_2/Nb(IV)O_2} = -1.17 \pm 0.03$ V, $k = 0.07$ s^{-1} and $\eta_s = 30$ mV.

Conclusion

It has been shown that niobium oxo complexes form when oxide ions are introduced to solutions of K_2NbF_7 in NaCl-KCl melts. The proportion of the various complexes depends primarily on the molar ratio O/Nb. In agreement with the works of Chemla and Grinewich,[10] and Konstantinov et al.[31] we find that the electrochemical reduction of niobium oxo halogenides gives rise to the formation of niobium suboxides, NbO_{1+x} ($0 \le x \le 0.32$), together with niobium metal. The reduction of the niobium oxo complexes occurs at potentials more cathodic than those for the pure halogeno complexes.

Introducing more fluoride ions moves the equilibrium, Eq. 3, to the left. An increase in the value of the equilibrium constant K_V, Eq. 12, is obtained. The result of this is that the reduction of the oxo complexes to niobium metal is now possible as found in FLINAK melts.[9] In contrast to electrolysis in NaCl-KCl, no crystals of niobium suboxide appear during the metal deposition when FLINAK melts are used, provided that the molar ratio O/Nb is less than one. The activity of oxygen in the metal obeys Eq. 9. The dependence of oxygen activity in the metal on the concentration of oxo complexes in the melt may explain why electrorefined niobium contains more oxygen (540 ppm) than the crude metal (42 ppm), as shown by Robin et al.[32]

This result is of crucial importance since the mechanical properties of niobium are strongly dependent on the oxygen content.[21,22] The presence of oxygen decreases the toughness and plasticity of the metal and may cause brittleness.[21] The present study confirms the high oxygen affin-
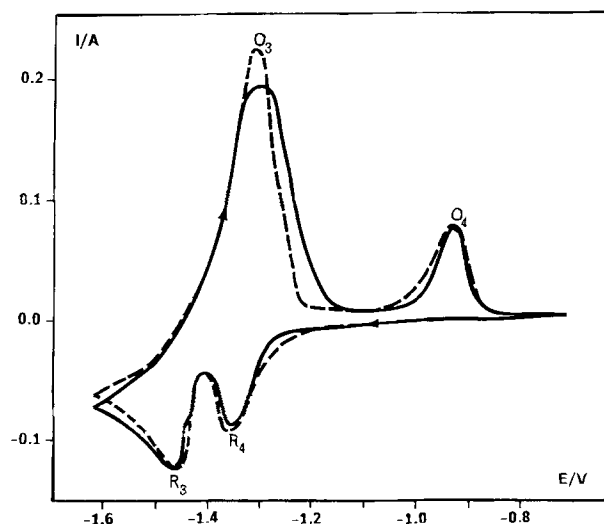

Fig. 8. Cyclic voltammogram of K_2NbF_7 (0.225 M) in NaCl-KCl (0.1 M NaF) with added Na_2O (0.28 M). Temperature: 720°C. Scan rate, 1 V s^{-1}. Solid line, experimental; dashed line, simulated. Working electrode, platinum (0.15 cm^2). Reference electrode, Pt^{2+} (molar)/Pt.

ity of niobium. Electrowinning of oxygen-free niobium requires electrolytes without dissolved oxygen ions. In order to obtain niobium with a low oxygen concentration (<10 ppm) from a solution 0.1 M K_2NbF_7 in NaCl-KCl melt, the oxygen content of the electrolyte must be less than 15 ppm. This demand requires strict purification of both the molten salt solvent and the solute salts together with a careful control of the cell atmosphere.

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