Chemistry of Niobium Chlorides in the CsCl–NaCl Eutectic Melt. 2. Voltammetric Studies of Niobium Chlorides and Oxochlorides in the CsCl–NaCl Eutectic Melt

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Cyclic voltammetry has been used to study the reduction mechanisms of niobium chlorides and oxochlorides in the CsCl–NaCl eutectic melt at temperatures between 823 and 973 K. Nb(V) in the melt is reduced in two steps to Nb(III): NbCl₅⁻ + e⁻ = NbCl₄²⁻ with E₁/₂ = −0.31 V versus the standard chlorine electrode, and NbCl₄²⁻ + e⁻ = NbCl₃⁽x⁻³⁾⁻ + (6 − x)Cl⁻, (x = 4, 5 or 6), with E₁/₂ = −1.14 V. NbCl₃⁽x⁻³⁾⁻ is reduced to the metal in several unidentified steps occurring at potentials from −1.6 to −2.0 V. In oxide-containing melts NbOCl₄²⁻ ions are reduced in two steps: NbOCl₄²⁻ + e⁻ = NbOCl₃⁽x⁻²⁾⁻ + (5 − x)Cl⁻, (x = 3, 4 or 5) with E₁/₂ = −1.19 V and NbOCl₃⁽x⁻²⁾⁻ to a solid, probably NbO(s) at −1.8 V. NbOCl₃⁽x⁻¹⁾⁻ (x = 3 or 4) ions probably also exist in NbCl₃-containing melts saturated with Nb₂O₅. This ion is probably reduced to NbO(s) at −1.39 V. In melts containing Cs₂NbOCl₄, Nb₂O₅(s) and Nb metal, Nb(V) oxochlorides with a molar ratio O/Nb = 1 are the main niobium-containing ions in the solution. These ions may oxidise to NbOCl₄²⁻, and when reduced a solid, probably NbO(s), at about −1.6 V is formed. Moreover, Nb(V) oxochloride ions react with glassy carbon, forming niobium carbide. The electrodeposition of niobium on steel has also been studied, and to obtain pure, dense and coherent niobium metal deposits it is important to establish equilibrium between the niobium-containing ions in solution and niobium metal. Moreover, the temperature during deposition should be higher than about 920 K. In melts where O/Nb ≥ 1, metallic deposits were not obtained.

Previously, Raman spectroscopic studies¹ in the system CsCl–NbCl₃–NbOCl₃, absorption spectroscopic studies² of niobium chlorides and oxochlorides in molten alkali chloride melts, and EMF measurements³ of NbCl₃ in the CsCl–NaCl eutectic melt have been presented. In this paper we focus on the reduction mechanism of niobium chlorides and oxochlorides in the CsCl–NaCl eutectic melt. Mellors and Sendoroff,⁴ using an alkali fluoride melt, were the first to report successful electrodeposition of niobium on steel. A number of other investigations on the electrochemistry of niobium in both alkali fluoride, alkali chloride and mixed chloride fluoride melts have also been presented⁵−²¹ throughout the last three decades. So far, high-quality electrodeposits of niobium on steel from alkali chloride melts have not been reported. However, from both an economical and environmental point of view, such melts are better solvents for the deposition process than alkali fluoride melts. Moreover, in spite of the amount of results reported, there is still disagreement concerning the reduction mechanism of niobium chlorides. We therefore feel that it is worthwhile to study these matters further. Mellors and Sendoroff⁴ concluded that melts used for the electrodeposition of high-quality niobium deposits should be free from oxides. However, recently Christensen et al.¹⁸ found that a small amount of oxide in LiF–NaF–KF eutectic melts containing niobium ions in equilibrium with niobium metal improved the current efficiency of the deposition reaction. Only a few studies on the electrochemistry of niobium oxochlorides have been published¹⁵,²² and the results of these studies do not agree. Because the influence of oxide ions on the deposition process of niobium seems to be important, and since there are some discrepancies in the previous work reported in this area, we have also investigated the reduction mechanism of niobium oxochlorides in alkali chloride melts.

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Experimental

**Chemicals and equipment.** Since niobium chlorides have a very high affinity for $\text{O}^{2-}$ ions in melts, a base melt practically free from oxides was needed for our investigations. The experiments and handling of the purified salts were therefore carried out in a glove box with water content $< 1$ ppm and oxygen content $< 5$ ppm. A sample of the pure CsCl–NaCl eutectic melt was analysed as previously described.\(^3\) The oxide content in the eutectic was below $10^{-6}$ mol%. The chemicals used and purification procedures are given in Table 1. NbOCl\(_3\) was added as Cs\(_2\)NbOCl\(_5\).\(^1\) To obtain a 0.5 mol% NbOCl\(_3\) solution, 0.8549 g Cs\(_2\)NbOCl\(_5\) was added to 40.00 g of the CsCl–NaCl eutectic. To saturate the melt with Nb\(_3\)O\(_5\), 0.650 g Nb\(_2\)O\(_5\) was added. Finally, to study the reduced niobium oxochlorides, 2.2 g niobium metal were added.

The electrochemical cell has been described previously.\(^7\) However, room for an additional electrode was provided in the cell. The reference electrode was a nullite tube closed in one end ($\Omega$ 10 x 6 mm Morgan Impervious Mullite, UK) with a silver wire dipping into a CsCl–NaCl eutectic containing 5 mol% AgCl.\(^3\) Since oxide-free melts containing niobium in valence states five and four can dissolve both Al\(_2\)O\(_3\) and SiO\(_2\), the reference electrode was dipped into the melt only during the voltammetric measurements. The reference electrode was raised above the melt when it was not in use, and no signs of corrosion on the electrode could be observed after the experiments. The working and counter-electrodes were glassy carbon rods (Carbone V25, 3 x 70 mm) connected to nickel rods by graphite connection pieces. The crucible was also made of glassy carbon (Carbone V25, 45 mm). The temperature was measured with a calibrated thermocouple (Pt/Pt, 10% Rh). Since Nb(V) chloride melts are known to oxidise gold,\(^25\) and therefore probably also platinum, the wires of the thermocouple were only immersed into the melt for the time needed to read the stable temperature and were lifted well above the melt between measurements. A PAR M273A Potentiostat/Galvanostat was used to record the voltammograms. IR compensation was always employed to assure correct potential readings.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Producer and purification</th>
</tr>
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<tbody>
<tr>
<td>CsCl</td>
<td>Fluka &gt; 99.9%, dried with HCl and recrystallised</td>
</tr>
<tr>
<td>NaCl</td>
<td>Merck p.a., recrystallised</td>
</tr>
<tr>
<td>NbCl(_6)</td>
<td>Alfa grade 1, resublimed under vacuum</td>
</tr>
<tr>
<td>Nb(_2)O(_5)</td>
<td>Alfa 88-291 &gt; 99.9%, dried under vacuum</td>
</tr>
<tr>
<td>NbCl(_3)</td>
<td>Made from sublimed NbCl(_6) (Alfa grade 1) and Nb (Alfa &gt; 99.9%), according to Schäfer and Dohmann(^23)</td>
</tr>
<tr>
<td>Nb</td>
<td>Alfa &gt; 99.9%</td>
</tr>
<tr>
<td>AgCl</td>
<td>Fluka &gt; 99%, dried under vacuum at 420 K</td>
</tr>
</tbody>
</table>

Electrodeposition experiments were performed in the same cell, but with a stainless-steel rod replacing the working electrode. In experiments where equilibrium between the dissolved niobium chlorides and niobium metal was established, a niobium metal rod was used as an anode. Otherwise, the glassy carbon counter-electrode was used. In the latter cases, care was taken not to deplete the melt of the niobium-containing species, and relatively low charges were transferred. Platinum, fused silica or glassy carbon crucibles were used in various deposition experiments. The depositions were performed galvanostatically, and a reference electrode was not employed. The stainless steel substrates were cleaned in nitric acid and dried before use. The furnace used was a Kanthal wound vertical and tubular furnace controlled with an Eurotherm controller. The furnace was mounted under the glove box in such a way that the experimental cell could be handled from inside the box. The temperature in the cell was stable within $\pm 2$ K.

**Modelling.** The LSV models used in this work are based on the discrete point method described by Britz\(^26\) and a third-order Runge–Kutta integration to solve the diffusion equations. To allow modelling of voltammograms with low sweep rates under limiting current conditions, a maximum Nernst diffusion layer has been introduced, defined by the equation

$$\delta_{\text{max}} = nFDe^{1/2}/i_{\text{lim}}$$  \hspace{1cm} (1)

where $i_{\text{lim}}$ is the limiting current density, $D$ is the diffusion coefficient, $c^*$ is the bulk concentration of the electroactive species, $F$ is Faraday's constant, and $n$ is the number of electrons transferred in the electrode reaction. The thickness of this diffusion layer was fitted to the time required to reach limiting-current conditions in potential-step experiments, typically 15 s, from the Cottrell equation:

$$|i| = nFD^{1/2}c^*/\pi^{1/2}t^{1/2}$$  \hspace{1cm} (2)

yielding $\delta_{\text{max}} \text{cm} = 3.9(\pi D/c^*m^2 s^{-1})^{1/2}$. In eqn. (2) $i$ is the time, $i$ is the current density, and the other symbols have the same meaning as in eqn. (1). The introduction of this $\delta_{\text{max}}$ term modelled voltammograms similar to the experimental ones, also at sweep rates of 50 mV s$^{-1}$ and lower. In a number of the experimentally recorded voltammograms, the initial potential of the sweep was kept for several seconds before starting the actual sweep, and in some cases oxidation of the niobium-containing species in the melt took place during this time. A potential step simulation was therefore included in the computer model to calculate the changes in concentration profiles due to this oxidation. The computer models were fitted to the experimental data by introducing the following parameters: (i) a reduction mechanism including the number of electrons transferred in each step and the potentials for the reduction steps obtained from the experimental voltammograms, (ii) bulk concentrations of the electroactive species, (iii) temperature, (iv) sweep rate
and (v) time at the initial potential before starting the sweep. 

The computer model calculates the concentration gradient of the electroactive species at the electrode surface multiplied by \((nFv/RT)^{1/2}\) as a function of the potential (v is the sweep rate). To fit these raw data to the voltammogram, they were simply multiplied by a factor containing information about the diffusion coefficients for the electroactive species. Calculated diffusion coefficients values were close to \(3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\), a value typical for complex ions in alkali halide melts.

**Results**

_Voltammograms and models._ All potentials presented in this work are referred to the standard chlorine electrode in the CsCl–NaCl eutectic melt. Figure 1 shows a voltammogram of a CsCl–NaCl eutectic melt at 823 K containing 0.4 mol% CsNbCl₆ recorded with a sweep rate of 0.2 V s⁻¹. The voltammogram shows three reduction steps and five oxidation steps. The reduction steps R₁ and R₂ correspond to the oxidation steps Ox₁ and Ox₂, respectively, while the third reduction step, R₃, corresponds to the three oxidation steps Ox₃, Ox₄, and Ox₅. 

The cathodic current at potentials positive of −1 V decreased during the first hours after addition of CsNbCl₆. To study the electrochemistry of Nb(IV) in the melt, 0.4 mol% silver was added to the melt to reduce the Nb(V) to Nb(IV).²⁵ Fig. 2 shows a voltammogram of this melt recorded with a sweep rate of 0.2 V s⁻¹. The voltammogram shows six reduction steps and six corresponding oxidation steps: R₁ corresponds to Ox₁ etc. Increasing the temperature from 823 to 963 K resulted in slightly steeper deposition peaks, but otherwise the voltammogram did not change in appearance. In Fig. 3 four voltammograms of 0.5 mol% Cs₅NbOCl₆ in the CsCl–NaCl eutectic melt at 823 K are presented. The voltammograms are recorded using a constant initial anodic po-

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**Fig. 1.** Cyclic voltammogram of a CsCl–NaCl eutectic melt containing 0.4 mol% CsNbCl₆ at 823 K. Sweep rate 0.2 V s⁻¹.

**Fig. 2.** Cyclic voltammogram of a CsCl–NaCl eutectic melt containing 0.4 mol% CsNbCl₆ and 0.4 mol Ag at 823 K. Sweep rate 0.2 V s⁻¹.

**Fig. 3.** Four cyclic voltammograms of a CsCl–NaCl eutectic melt containing 0.5 mol% Cs₅NbOCl₆ at 823 K. Sweep rates 0.2 V s⁻¹. An LSV model is also included in the figure. The parameters for the model were: Mechanism: \(A + e^- \rightarrow B\), \(E^0 = -1.19 \text{ V}\), \(B + 2e^- \rightarrow C(s)\), \(E^0 = -1.8 \text{ V}\); only A is present in the bulk; temperature 823 K, sweep rate 0.2 V s⁻¹; rest time at initial potential 0 s. (——) Experimental voltammograms; (-----) LSV model.
Fig. 4. Quasi-steady-state voltammogram of a CsCl–NaCl eutectic melt containing 0.5 mol% Cs$_2$NbOCl$_6$ at 823 K. Sweep rate 0.001 V s$^{-1}$. An LSV model is also included in the figure. The parameters for the model were: Mechanism: A$+\text{e}^-\rightarrow\text{B}$, $E^\circ = -1.19$ V, B$+2\text{e}^-\rightarrow\text{C(s)}$, $E^\circ = -1.8$ V; only A is present in the bulk; temperature 823 K, sweep rate 0.001 V s$^{-1}$, rest time at initial potential 0 s. (-----) Experimental voltammogram; (---) LSV model.

Fig. 5. Cyclic voltammogram of a CsCl–NaCl eutectic melt containing 0.5 mol% Cs$_2$NbOCl$_6$ and excess Nb$_2$O$_3$(s) at 883 K. Sweep rate 0.2 V s$^{-1}$.

Fig. 6. Six cyclic voltammograms of a CsCl–NaCl eutectic melt containing 0.5 mol% Cs$_2$NbOCl$_6$, Nb$_2$O$_3$(s) and Nb(s) at 923 K. Sweep rates 0.2 V s$^{-1}$. An LSV model is also included in the figure. The parameters for the model were: Mechanism: A$+\text{e}^-\rightarrow\text{B}$, $E^\circ = -1.14$ V, B$+2\text{e}^-\rightarrow\text{C(s)}$, $E^\circ = -1.63$ V; only B is present in the bulk; temperature 923 K; sweep rate 0.2 V s$^{-1}$; rest time at initial potential 3 s. (-----) Experimental voltammogram; (---) LSV model.

Fig. 7. Quasi-steady-state voltammogram of a CsCl–NaCl eutectic melt containing 0.5 mol% Cs$_2$NbOCl$_6$, Nb$_2$O$_3$(s) and Nb(s) at 923 K. Sweep rate 0.001 V s$^{-1}$. An LSV model is also included in the figure. The parameters for the model were: Mechanism: A$+\text{e}^-\rightarrow\text{B}$, $E^\circ = -1.14$ V, B$+2\text{e}^-\rightarrow\text{C(s)}$, $E^\circ = -1.63$ V; only B is present in the bulk; temperature 923 K, sweep rate 0.001 V s$^{-1}$, rest time at initial potential 3 s. (-----) Experimental voltammogram; (---) LSV model.
Table 2. Half-wave potentials, $E_{1/2}$, and deposition potentials for the observed reduction reactions. All potentials are referred to the standard chloride electrode.

<table>
<thead>
<tr>
<th>Melt/concentrations in mol %</th>
<th>T/K</th>
<th>Red. step</th>
<th>$E_{1/2}$/V</th>
<th>$E_{dep}$/V</th>
<th>Reduction reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CsCl-NaCl)$_{euc}$ + 0.4% CsNbCl$_6$ + 0.4% Ag</td>
<td>823</td>
<td>R$_1$</td>
<td>-0.31</td>
<td></td>
<td>NbCl$_6^{2-}$ + e$^-$ = NbCl$_5^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_2$</td>
<td>-1.14</td>
<td></td>
<td>NbCl$_5^{2-}$ + e$^-$ = NbCl$<em>4^{(x-3)</em>-}$ + (6 - x)Cl$^-$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_3$</td>
<td>-1.53</td>
<td></td>
<td>Ag$^{+}$ + e$^-$ = Ag(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_4$</td>
<td>-1.6</td>
<td>See text</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>R$_5$</td>
<td>-1.8</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_6$</td>
<td>-2.0</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td>(CsCl-NaCl)$_{euc}$ + 0.5% Cs$_2$NbOCl$_6$</td>
<td>823</td>
<td>R$_1$</td>
<td>-1.19</td>
<td></td>
<td>NbOCl$<em>5^{2-}$ + e$^-$ = NbOCl$</em>{(x-2)_-}$ + (5 - x)Cl$^-$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_2$</td>
<td>-1.8</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td>(CsCl-NaCl)$_{euc}$ + 0.5% Cs$_2$NbOCl$_6$ + Nb$_2$O$_5$(s)</td>
<td>883</td>
<td>R$_1$</td>
<td>-1.15</td>
<td></td>
<td>NbOCl$<em>5^{2-}$ + e$^-$ = NbOCl$</em>{(x-2)_-}$ + (5 - x)Cl$^-$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_2$</td>
<td>-1.38</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_3$</td>
<td>-1.43</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_4$</td>
<td>-1.65</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td>(CsCl-NaCl)$_{euc}$ + 0.5% Cs$_2$NbOCl$_6$ + Nb$_2$O$_5$(s) + Nb(s)</td>
<td>923</td>
<td>R$_1$</td>
<td>-1.14</td>
<td></td>
<td>NbOCl$<em>5^{2-}$ + e$^-$ = NbOCl$</em>{(x-2)_-}$ + (5 - x)Cl$^-$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_2$</td>
<td>-1.48</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R$_3$</td>
<td>-1.60</td>
<td>See text</td>
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</tbody>
</table>

ever, being 0.001 V s$^{-1}$. The currents in such a voltam- mogram will be close to the limiting currents for all po- tentials, and it is therefore called a quasi-steady-state voltamogram. An LSV model is also included in this figure. To the 0.5 mol% Cs$_2$NbOCl$_6$ melt, Nb$_2$O$_5$(s) was added in excess, and in Fig. 5 a voltamogram of this melt at 883 K is shown. The voltamogram is recorded with a sweep rate of 0.2 V s$^{-1}$ and shows four reduction steps and five oxidation steps. When the temperature was raised to 973 K, R$_5$ became a little steeper, and only one corresponding oxidation step was present. To the CsCl-NaCl eutectic melt containing 0.5 mol% Cs$_2$NbOCl$_6$ and an excess of Nb$_2$O$_5$(s), niobium metal was added, and six voltamograms with sweep rates of 0.2 V s$^{-1}$ at 923 K are shown in Fig. 6. Three reduction peaks and three corresponding oxidation peaks are observed. The only change observed in the voltamograms when changing the temperature between 823 and 973 K was that R$_5$ became more pronounced. An LSV model is also shown in Fig. 6. Figure 7 shows a quasi-steady-state voltam- mogram and an LSV model of the same melt as above. A summary of the different reduction steps and the various reduction potentials is given in Table 2.

Electrodeposition experiments. Electrodeposition experiments have been performed at 823, 873, 923, 973 and 1073 K. In melts containing 1–2.5 mol% oxide-free niobium chlorides in equilibrium with Nb metal, dense and coherent niobium metal deposits were obtained at temperatures above 920 K and current densities from 15 to 100 mA cm$^{-2}$. At lower temperatures, however, black and incoherent non-metallic deposits were produced. Electrolysis from melts contained in platinum, glassy-carbon and fused-silica crucibles gave dense and coherent deposits when the melt was equilibrated with niobium metal. The surfaces of the dense and coherent niobium metal deposits were quite rough with varying thickness, especially for thicknesses above 0.2 mm. X-Ray analysis of the deposited metal showed only peaks belonging to niobium. The current efficiencies ranged between 30 and 60% assuming that niobium was deposited in a three- electron transfer reaction. When the dissolved niobium chlorides were not equilibrated with niobium metal, metallic deposits were obtained above 920 K, but they were powder-like and adhered poorly to the electrode. At temperatures below 920 K, black and non-metallic deposits were obtained. In a melt with O/Nb(V) = 1 at 823 K, only black, dendritic and non-metallic deposits were obtained. Similar deposits were obtained from a melt containing Nb(S) saturated with Nb$_2$O$_5$(s) at 923 K. In melts containing both Nb$_2$O$_5$(s) and Nb metal, only thin black non-metallic deposits were obtained in the temperature range 823–1023 K.

Discussion

Reduction mechanisms

Reduction mechanism of CsNbCl$_6$. The voltamogram of 0.4 mol% CsNbCl$_6$ in the CsCl-NaCl eutectic melt at 823 K (Fig. 1) shows three peaks, and the behaviour is quite different from a reversible and diffusion-controlled three-step reaction. A survey of the reduction steps is given in Table 2. Only the most anodic couple, R$_1$/O$_1$, with $E_{1/2} = -0.31$ V, shows reversible and diffusion-controlled behaviour. The peak current is proportional to the square root of the sweep rate, and the peak potential is independent of the sweep rate. The relation$^{28}$

$$|E_p - E_{p/2}| = 2.2 \frac{RT}{nF}$$

(3)

gives n-values close to one for different sweep rates. In eqn. (3) $E_p$ and $E_{p/2}$ are the potential at the peak and halfway up the peak, respectively, R is the gas constant,
and $T$, $n$ and $F$ have their usual meaning. Other diagnostic methods to check reversibility are difficult to apply to this reduction couple, because the standard potential for the reaction is close to the chlorine evolution potential. Because the reduction potential of Nb(V) in alkalichloride melts is close to that of the chlorine evolution,\textsuperscript{13} it seems reasonable to suggest that the redox couple R$_2$/O$_x$ is due to Nb(V)/Nb(IV). These results agree with the work of Lantelme et al.\textsuperscript{15} and Picard and Bocage,\textsuperscript{14} who found that Nb(V) is reduced reversibly and diffusion-controlled to Nb(IV) in a LiCl–KCl eutectic melt at 723 K, and that the standard potential for the reaction was $-0.32$ V. Elizarova et al.\textsuperscript{12} and Kuznetsov et al.\textsuperscript{5} reported a reduction potential of Nb(V) at ca. 0 V vs. an Ag/AgCl electrode. This is about $-1.1$ V referred to the standard chlorine electrode, and in view of the oxidising power of Nb(V) in alkalichloride melts,\textsuperscript{13,25} the conclusion of these authors is probably wrong. Schäfer and Dohmann\textsuperscript{23} observed that NbCl$_6^{2-}$ disproportionate to NbCl$_4^{2-}$ and NbCl$_2$, at temperatures above 573 K. However, Nb(IV) is repeatedly reported to be stable in alkalichloride melts.\textsuperscript{24,14,15,25} indicating that NbCl$_6^{2-}$ is considerably stabilised by the alkalichloride melts. Voyiatzis et al.\textsuperscript{26} found that Nb(IV) is present as NbCl$_6^{2-}$ in alkalichloride melts. The stabilising effect of the alkalichloride melt may explain the very large difference between the observed potential for the reduction of NbCl$_6^{2-}$ to NbCl$_2$ in the melt and the potential for reaction (1) in Table 3. The small difference in the potential between the redox couple Nb(V)/Nb(IV) and the chlorine evolution can explain the observed reduction of cathodic currents at potentials positive of $-1$ V in voltammograms recorded during the first hours after addition of Cs$_2$NbCl$_6$. Considering the reaction

$$\text{NbCl}_6^{2-} + \text{Cl}^- \rightarrow \text{NbCl}_4^{2-} + 1/2\text{Cl}_2$$

and approximating $E^\circ$ with $E_{1/2}$ and using Nernst’s law, we obtain

$$\frac{a_{\text{NbCl}_6^{2-}}}{a_{\text{NbCl}_4^{2-}}} = \exp \left( \frac{E_{1/2}F}{RT} \right) = 0.015$$

(5)

where $E^\circ$ and $E_{1/2}$ are, respectively, the standard potential and the potential at which the concentrations of the reduced and oxidised species at the surface of the electrode are the same. At low chlorine pressures ($p_{\text{Cl}_2} \approx 2.3 \times 10^{-4}$ atm) comparable amounts of Nb(V) and Nb(IV) will exist at equilibrium. A reduction in the amount of Nb(V) will result in lower cathodic currents, as observed. The peak current for R$_2$ could not be evaluated, since R$_1$ is a shoulder on R$_3$. However, the anodic peak corresponding to R$_2$, O$_x$, has the broad shape typical of oxidation of a dissolved species, showing that the redox couple R$_2$/O$_x$ only involve dissolved species. When the maximum current at $-1.63$ V for the shoulder is plotted versus the square root of the sweep rate, a non-linear plot is obtained with decreasing slope at increasing sweep rates. Moreover, applying the reversibility condition\textsuperscript{28}

$$|E^C - E^A| = 2.2 \frac{RT}{nF} = | -1.63 - 0.83 V |$$

(6)

to R$_2$/O$_x$ gives $n = 0.2$. $E^C$ and $E^A$ are the potentials at the cathodic and anodic peak, respectively. When considering the large current value for R$_2$ compared to R$_1$, more than 0.2 electrons were obviously transferred at R$_2$. The second reduction step is therefore not of the reversible and diffusion-controlled type, and the number electrons transferred at R$_3$ can not be determined.

The third reaction step, R$_3$, has the characteristic shape of a deposition reaction (a sharp reduction peak and a corresponding sharp oxidation peak). The reduction step does not satisfy reversible and diffusion controlled conditions. A well defined peak did not form even when the voltamogram was swept to potentials negative of $-2.18$ V. However, careful examination of the voltammograms revealed that there were three oxidation steps, O$_x$, O$_x$, and O$_x$, corresponding to R$_3$, of which O$_x$ shows a quite irreversible behaviour (large potential difference between reduction and oxidation).

Reduction mechanism of Cs$_2$NbCl$_6$ + Ag. When an amount of silver equal to the amount of Cs$_2$NbCl$_6$ (0.4 mol%) is added to the melt, the shape of the voltammogram changes. This is seen when comparing Figs. 1 and 2. The second reduction step, R$_2$, changes from a shoulder to a peak, and deposition occurs at a more anodic potential. The peak potentials of steps R$_1$ and R$_2$ and the corresponding O$_x$ and O$_x$, are independent of the sweep rate, and the peak currents are proportional to the square root of the sweep rate, indicating diffusion control. Equation (3) gives one electron transferred in each step, leading to the following reduction scheme for the first two steps shown in Fig. 2; Nb(V)→Nb(IV)→Nb(III) occurring at $E_{1/2}$ values of $-0.31$ and $-1.14$ V, respectively, in good agreement with the results of Lantelme et al.\textsuperscript{15} and Picard and Bocage.\textsuperscript{14} At the potential of R$_2$, Elizarova et al.\textsuperscript{12}

| Table 3. Electrochemical reactions referred to the standard chlorine electrode at 900 K. Data from Barin.\textsuperscript{27} |
| --- | --- | --- |
| Reaction | $n$ | $E_{1/2}^{900}$/V | $E_{1/2}^{933}$/V |
| 1 | NbCl$_6$(g) = NbCl$_4$(g) + 1/2Cl$_2$(g) | 1 | $-0.90$ | $-0.95$ |
| 2 | MbCl$_4$(g) = NbCl$_2$(s) + 1/2Cl$_2$(g) | 1 | $-0.64$ | $-0.57$ |
| 3 | NbCl$_4$(s) = Nb(s) + 3/2Cl$_2$(g) | 3 | $-1.30$ | $-1.39$ |
| 4 | NbO(s) + 2NaCl(l) = Nb(s) + 2Na$_2$O(s) + Cl$_2$(g) | 2 | $-3.57$ | $-3.61$ |
| 5 | 2NaCl(l) + NbCl$_3$(s) = Nb(s) + 2Na$_2$O(s) + 2Cl$_2$(g) | 4 | $-2.38$ | $-2.36$ |

Standard states: NbCl$_6$(g), NbCl$_4$(g), NbCl$_2$(s), NbOCl$_2$(s), NbO(s), Nb(s)Na$_2$O(s), NaCl(l), all at 1 atm.
and Kutznetsov et al.\textsuperscript{5} report that Nb(V) is reduced to Nb(IV). They have probably missed the first reduction step, since this is close to the chlorine evolution, and believed that the second step was the reduction of Nb(V). The observed standard potential for the reduction of Nb(IV) to Nb(III) is much more negative than the potential for reaction (2) in Table 3, and again we see that NbCl\textsubscript{5}\textsuperscript{−} is stabilised by the melt. Estimates for the activity coefficients for NbCl\textsubscript{5}\textsuperscript{−} and NbCl\textsubscript{6}\textsuperscript{2−} (g and l) are given later. The equation\textsuperscript{28}

\[ E_p - E_{p/2} = 0.77 RT/nF \]  

(7)

is valid for a reversible electrodeposition reaction. By applying this equation to R\textsubscript{1}, n = 1 is obtained, and R\textsubscript{1} is therefore attributed to the reduction of Ag\textsuperscript{+}. Ox\textsubscript{4}, is attributed to oxidation of silver deposited at R\textsubscript{1}. The reduction steps R\textsubscript{4}, R\textsubscript{5}, R\textsubscript{6} and the corresponding Ox\textsubscript{4}, Ox\textsubscript{5}, and Ox\textsubscript{6} have shapes typical of deposition and stripping reactions, indicating that several deposition reactions are taking place in addition to the deposition of silver.

There are some disagreements concerning the stability of NbCl\textsubscript{5} in molten alkaline chlorides.\textsuperscript{5,10,11,12,13} EMF measurements,\textsuperscript{1} together with UV−VIS−IR studies, show that Nb(III) is stable in a CsCl−NaCl eutectic containing Nb metal. A disproportionation of NbCl\textsubscript{5} to NbCl\textsubscript{4} and an insoluble species will therefore probably take place when NbCl\textsubscript{5} is added to an alkali-chloride melt.

Different reduction products of the final reduction steps of Nb(V) in alkali-chloride melts\textsuperscript{10,5,11,12,13} have been proposed. The potential for the deposition reactions R\textsubscript{4} and R\textsubscript{5} compares reasonably well with the potential for reaction (3) in Table 3 when the activity of NbCl\textsubscript{5} in the melt, being ca. 0.002,\textsuperscript{2} is taken into account. The deposition products are therefore substances with chemical potentials similar to niobium metal. Lantelme et al.\textsuperscript{15} and Kuznetsov et al.\textsuperscript{5} claim that the first deposition products of niobium chlorides dissolved in the LiCl−KCl eutectic at 723 K are clusters containing niobium chloride. Such clusters have a considerable degree of niobium−niobium bonds. Absorption spectroscopic investigations of the cluster compound Na\textsubscript{4}Nb\textsubscript{x}Cl\textsubscript{12} in the LiCl−KCl eutectic melt do, however, show that these clusters are unstable in melts with excess alkali chlorides and that they disproportionate to Nb(III) and a solid.\textsuperscript{5} It therefore seems improbable that the observed non-metallic reduction products are clusters. More likely they are subvalent alkali−niobium chlorides formed due to local supersaturation at the electrode. Alkali−niobium chloride compounds precipitated in melts with more than 0.2 mol% NbCl\textsubscript{5} when NbCl\textsubscript{4} was in equilibrium with Nb metal.\textsuperscript{1}

Another matter of discussion is the relatively large differences in the voltammograms shown in Figs. 1 and 2. Addition of silver to the melt will reduce NbCl\textsubscript{5}\textsuperscript{−} to NbCl\textsubscript{6}\textsuperscript{2−} according to the reaction\textsuperscript{25}

\[ \text{NbCl}_5^{-} + \text{Ag} + \text{Cl}^{-} = \text{NbCl}_6^{2-} + \text{AgCl}. \]  

(8)

Adding silver to the melt should therefore give a shift of the current towards more anodic values since the bulk concentration of NbCl\textsubscript{5}\textsuperscript{−} decreases. Moreover, an extra deposition and stripping peak due to deposition and stripping of silver would be expected. These changes are observed experimentally; however, in addition to the expected changes, the current in the second reduction step decreases and R\textsubscript{5} takes the shape typical of a reversible and diffusion-controlled reduction. We have not been able to find a reasonable explanation for this change in the reduction mechanism. A summary of the reduction steps in the melt with NbCl\textsubscript{5} and Ag is given in Table 2.

**Reduction mechanism of Cs\textsubscript{5}NbOCl\textsubscript{5}**. When the molar ratio O/Nb is changed from zero to one, several important changes take place in the reduction mechanism, as can be seen from Fig. 3. There are no reductions taking place at potentials positive of −0.8 V in the cathodic sweep, and only two reduction peaks, R\textsubscript{1} and R\textsubscript{2}, are present in the voltammogram. This observation agrees with the work of Lantelme et al.,\textsuperscript{15} while Elizarova et al.\textsuperscript{22} only observed one reduction peak. The oxidation peak belonging to R\textsubscript{1} is Ox\textsubscript{4}, and the peaks belonging to R\textsubscript{2} and Ox\textsubscript{2} and Ox\textsubscript{3}. Both R\textsubscript{1} and R\textsubscript{2} show peak currents proportional to the square root of the sweep rate and peak potentials independent of the sweep rate, indicating diffusion-controlled reaction rates. Raman spectroscopic investigations\textsuperscript{1} show that NbOCl\textsubscript{5}\textsuperscript{2−} is present in CsCl−NaCl eutectic melts with O/Nb = 1. Using eqn. (3) on the first reduction step gives n ≈ 1, and it is reasonable to assume that NbOCl\textsubscript{5}\textsuperscript{2−} is reduced at R\textsubscript{1} to either a simple tetravalent niobium chloride or oxochloride. Oxide solubility measurements\textsuperscript{28} have shown that NbOCl\textsubscript{5}\textsuperscript{(x−2)−} ions are stable in the CsCl−NaCl eutectic melt. It is therefore reasonable to assume that NbOCl\textsubscript{5}\textsuperscript{(x−2)−} is reduced to NbOCl\textsubscript{5}\textsuperscript{(x−2)−}. The number of chlorides, x, in the Nb(IV) oxochloride is probably three, four or five. R\textsubscript{2} may be the sum of two reduction steps, since there is a double oxidation peak corresponding to R\textsubscript{2}. The quasi-steady-state voltammogram in Fig. 4 supports this view, since it shows a shoulder and a sharp deposition peak at the potential of R\textsubscript{2}. The final currents in the voltammogram in Fig. 4 are very high, and they are probably caused by an increasing area of the electrode due to dendritic growth of a conductive deposit. Deposition experiments from melts with O/Nb(V) = 1 gave black non-metallic and dendritic deposits. Electrochemical investigations show that NbO(s) is deposited on a glassy carbon electrode during electrolysis of niobium oxofluorides from a mixture of chloride−fluoride melts,\textsuperscript{29} and NbO(s) is formed in the LiCl−KCl eutectic melt when niobium oxochlorides are reduced.\textsuperscript{14,15} The deposition product is therefore probably NbO(s), and because NbO(s) is a metallic conductor,\textsuperscript{30} the electrode will not be passivated. However, Christensen et al.\textsuperscript{39} who studied the electrodeposition of niobium from LiF−NaF−KF eutectic melts with various O/Nb ratios, obtained metallic niobium deposits from melts with O/Nb below 0.8, and Elizarova et al.\textsuperscript{22} although presenting a reduction mechanism different from the one proposed in this work, observed niobium metal deposits at −1.8 V from a KCl−
CsCl–NaCl melt at 888 K containing NbCl₅ and Nb₂O₃ in a molar ratio 5/1, i.e. an O/Nb ratio equal to 0.7. Moreover, von Barner et al. studied the reduction of NbOF₄²⁻ in KCl–NaCl and found that NbOF₄⁺ was reduced to Nb(s) in a single step. Metallic niobium deposits from the melt with O/Nb = 1 would therefore not be surprising. Visual inspection of the deposit, however, showed no metal.

The LSV model data shown in Fig. 3 are in reasonable agreement with Rₒ, but R₅ is not as steep as predicted by the model, and the peak current is somewhat lower. The deposition reaction is therefore not completely described by a simple reduction of NbOClₓ⁺⁺⁻ to NbO(s), in agreement with the double oxidation peak corresponding to R₂. The LSV model shown in Fig. 4 also represents the first reduction step well, but there is a large deviation between the model and the recorded quasi-steady-state voltammogram for the deposition step. This is probably mainly due to the dendritic growth of the deposit. The reduction scheme for melts with O/Nb = 1 is given in Table 2.

Reduction mechanism of Cs₂NbOClₓ + Nb₂O₃(s). In melts saturated with Nb₂O₃(s) the reduction mechanism is more complex. The voltammogram of a Nb(V) melt saturated with Nb₂O₃(s) in Fig. 5 shows two additional reduction peaks, R₂ and R₄, at −1.38 and −1.43 V, respectively. R₃ and R₅ were also present when a platinum working electrode was used. The currents for these peaks increased relative to R₁ with increasing temperature. The oxidation corresponding to R₂ and R₄, Oₓ and Oₓ₅, takes place at a potential slightly anodic of Oₓ. R₁ has the typical shape of a deposition reaction. Solubility measurements of Nb₂O₃ in a CsCl–NaCl eutectic melt containing from 0.5 to 10 mol% NbCl₅ at 923 K showed that O/Nb was 1.2. A melt containing Nb(V) saturated with Nb₂O₃(s) will therefore probably contain niobium oxochlorides with molar ratios O/Nb = 1 and 2. NbOClₓ⁺⁺⁺⁺⁺⁺ (x = 8) ions have been found in alkali fluoride melts and in mixed alkali fluoride-chloride melts. A molar ratio O/Nb = 1.2 gives a ratio NbOClₓ⁺⁺⁺⁺⁺⁺ / Nb₂O₃(s) = 4. It therefore seems reasonable to assume that NbOClₓ⁺⁺⁺⁺⁺⁺ is reduced to NbO(s), which deposits at R₃, and that Nb₂O₃(s) is oxidised to NbOClₓ⁺⁺⁺⁺⁺⁺ at Oₓ. The number of chloride ions, x, in NbOClₓ⁺⁺⁺⁺⁺⁺ is probably three or four. The origin for the reduction step R₂ has not been found. An increasing solubility of Nb₂O₃ with increasing temperature can explain the observed larger current for R₁ at higher temperatures. NbO(s) is an n-type semiconductor with electrical conductivity equal 0.01 Ω⁻¹ at 823 K, and will therefore not passivate the electrode. Picard and Bocage claim that Nb₂O₃(s) has a stability range of 0.25 V in the LiCl–KCl eutectic melt at 723 K, in reason-
mental voltammograms allows us to assume that the stable valence state of niobium oxochlorides in equilibrium with Nb metal in melts saturated with Nb₂O₅(s) is four, since the model is made having only Nb(IV) in the bulk. UV–VIS–IR absorption measurements gave the same conclusion. Moreover, the standard Gibbs free energy, Δ₀G°, for the reaction

\[ 2\text{NbCl}_3(s) + \text{Nb}_2\text{O}_5(s) + \text{Nb(s)} = 3\text{NbOCl}_2(s) + 2\text{NbO}(s) \]  

(9)

is \(-96.5 \text{ kJ mol}^{-1}\), indicating that NbCl₃(s) will react with Nb₂O₅(s) and Nb(s) to form Nb(IV) oxochlorides and NbO(s). The final reduction steps also changed when niobium metal was added to the melt. No shoulder was present on the deposition peak, and only one corresponding oxidation step was observed, indicating a simpler deposition/stripping mechanism. However, since the shapes of the modelled and experimental deposition peaks are different, the deposition is not completely reversible. With niobium metal present, deposition experiments gave thin, smooth and black non-metallic deposits.

Another interesting feature of the voltammogram in Fig. 6 is that the peak belonging to the deposition of Nb₂O₅(s) has disappeared, suggesting that niobium oxochlorides with O/Nb = 2 are no longer stable in the melt when niobium(V) in the melt is reduced to niobium(IV) by the metal. This agrees with the proposed reduction scheme for NbOCl₃(3−)⁺, which when reduced, deposits as NbO₂(s). NbOCl₃(5−), on the other hand, is reduced to NbOCl₄(5−)⁻, which remains dissolved in the melt.

A summary of the reduction steps is given in Table 2.

**Niobium deposition.** Both bulk valence states and temperatures are important parameters for the quality of the deposited product during electrodeposition of niobium from alkali chloride melts. To obtain dense and coherent metal deposits, equilibrium should be established between niobium metal and the dissolved niobium chlorides. Moreover, our results show that the temperature must be above about 920 K to obtain metallic niobium deposits. This agrees with the work of Lantelme et al. and Kutznetsov et al. They claimed that subvalent niobium compounds that deposits at temperatures below 920 K are unstable at higher temperatures. Formation of metal rather than subvalent niobium compounds is therefore favoured at temperatures above 920 K. In this work, slightly steeper deposition peaks were observed when the temperature was increased, indicating more reversible deposition reactions.

The oxide content of the melt is also important. Christensen et al. obtained good niobium deposits in LiF–NaF–KF eutectic melts with O/Nb < 0.8, while in melts with higher O/Nb ratios partly metallic and non-metallic deposits were obtained. Elizarova et al. also obtained niobium metal deposits from a NaCl–KCl–CsCl melt with an O/Nb ratio equal 0.7. In our deposition experiments from melts with O/Nb ≥ 1, metallic niobium deposits were not obtained. A reasonable explanation for these observations can be given if we consider the volume in the vicinity of the electrode where the reduction takes place. When the niobium oxochlorides are reduced to Nb(s), oxide ions are released and diffuse away from the electrode. This reaction will lead to relatively high concentrations of oxide ions close to the electrode. According to Picard and Bocage, the reduction of NbO(s) to Nb(s) is shifted to more negative potentials with increasing oxide concentration, and at sufficiently high oxide concentrations NbO(s) cannot be reduced to Nb(s) within the potential window of the solvent. The potential for reduction of NbO(s) and NbOCl₄(5−)⁻ decreases rapidly with increasing O²⁻ ion activity. This can be seen from reactions (4) and (5) in Table 3. In melts with O/Nb < 1, niobium chlorides in the vicinity of the electrode will react with the oxide ions, leading to lower oxide activities at the electrode than in melts with O/Nb ≥ 1. Thus, reduction of NbO(s) to Nb(s) can take place. The oxide activity in the melt is therefore an important parameter during electrodeposition of niobium from oxochloride melts.

Electrolysis from melts with niobium-containing ions in equilibrium with niobium metal in fused quartz crucibles gave dense and coherent niobium deposits. Raman spectroscopy has shown that NbCl₄⁻ reacts slowly with fused silica in the CsCl–NaCl eutectic melt, and finally only the oxochloride NbOCl₂⁻ is present. Niobium metal deposits were also expected from melts in equilibrium with niobium metal and Nb₂O₅(s). However, no metal deposits were obtained from such melts. The difference in acid/base properties between a melt saturated with SiO₂(s) and a melt saturated with Nb₂O₅(s) can explain this difference. The standard Gibbs free energy at 900 K for the reaction

\[ 2\text{Nb}_2\text{O}_5(s) + 5\text{SiCl}_4(g) = 5\text{SiO}_2(s) + 4\text{NbCl}_3(g) \]  

(10)

is \(-158.4 \text{ kJ mol}^{-1}\). The oxide donor ability of Nb₂O₅(s) is therefore larger than that of SiO₂(s), and melts saturated with Nb₂O₅(s) will have a larger oxide activity than melts saturated with SiO₂(s). Because the reduction of NbO(s) to Nb metal is shifted to more negative potentials with increasing oxide activity, metal deposits are harder to obtain from melts in contact with Nb₂O₅(s) than with SiO₂(s).

**Calculation of activity coefficients.** The observed peaks in the voltammogram in Fig. 2 together with thermodynamic data allow us to estimate the activity coefficients of niobium-containing species in the melt. When the diffusion coefficients of the oxidised and reduced species are the same, the equation

\[ E_{1/2} - E^\circ = \frac{-RT}{nF} \ln \frac{\gamma_{\text{Red}}}{\gamma_{\text{Ox}}} \]  

(11)

is valid. \( \gamma_{\text{Red}} \) and \( \gamma_{\text{Ox}} \) are the activity coefficients of the reduced and oxidised species, respectively. At the half-

93
Table 4. Activity coefficients of niobium chlorides in the CsCl–NaCl eutectic melt at 823 K and 0.4 mol%.

<table>
<thead>
<tr>
<th>Species</th>
<th>Activity coefficients $^*$ (mole fraction scale)</th>
<th>Standard state</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbCl$_4$</td>
<td>0.036</td>
<td>NbCl$_6$(l)</td>
</tr>
<tr>
<td>NbCl$_5$</td>
<td>1.3</td>
<td>NbCl$_6$(g), 1 atm</td>
</tr>
<tr>
<td>NbCl$_6$</td>
<td>$1.6 \times 10^{-4}$</td>
<td>NbCl$_6$(g), 1 atm</td>
</tr>
<tr>
<td>NbCl$_7$</td>
<td>0.49 $^b$</td>
<td>NbCl$_6$(s)</td>
</tr>
</tbody>
</table>

$^*$ The activity coefficients are calculated from eqn. (13) and $E_{1/2}$ for the reactions Nb(V)$+e^-$ = Nb(IV) and Nb(IV)$+e^-$ = Nb(III). $^b$ Ref. 3.

wave potential, $E_{1/2}$, the current is 85% of the peak current for a reversible and diffusion-controlled reaction, and the concentration of the oxidised and reduced species at the electrode are theoretically the same. In the oxide-free melts, the activity coefficients of NbCl$_4$ and NbCl$_6$ with the standard states listed in Table 3 can be estimated knowing the half-wave potentials for $R_1$ and $R_2$ given in Fig. 2, the standard potentials for reactions (1) and (2) in Table 3 taken at 823 K, and the activity co-efficient of NbCl$_6$. The activity coefficient of NbCl$_4$ can be calculated from thermodynamic data assuming that Henry’s law is valid. At 823 K and 0.2 mol% NbCl$_4$, $\gamma_{\text{NbCl}_4} = 0.49$ using NbCl$_6(s)$ as standard state. The activity coefficients of NbCl$_6$ and NbCl$_8$ in the eutectic containing 0.4 mol% NbCl$_4$ at 823 K obtained from eqn. (11) are given in Table 4. The relation

$$\gamma_{\text{NbCl}_6(l)} = \exp \left( \frac{\Delta_{\text{ref}} G_{823}}{RT} + \ln \gamma_{\text{NbCl}_6(s)} \right)$$

can be used to estimate the activity coefficient of NbCl$_6$ using NbCl$_6(l)$ as standard state [(1) and (g) indicate liquid and gas standard states, respectively]. The Gibbs free energy of vaporisation of NbCl$_6$ at 823 K, $\Delta_{\text{ref}} G_{823}$, is estimated from thermodynamic data to be $-24.6$ kJ mol$^{-1}$. Activity coefficients are given in Table 4. The very low activity coefficient of NbCl$_4$ reflects the high stability of the NbCl$_6^{2-}$ ion in the melt relative to gaseous NbCl$_6$. This means that the standard Gibbs free energy change for the reaction

$$\text{NbCl}_4(g) + 2(\text{Na}, \text{Cs}) = (\text{Na}, \text{Cs})_2\text{NbCl}_6$$  (12)

is large and negative. NbCl$_4$ also shows considerable negative deviation from ideality, although not as negative as NbCl$_6$. The vapour pressure of pure NbCl$_6$ at 823 K is about 40 atm. Above NbCl$_6$–CsCl mixtures the yellow colour of gaseous NbCl$_6$ can be observed, but the vapour pressure is considerably lower than 40 atm. The estimated activity coefficient of NbCl$_6$ therefore seems reasonable. Since the reference pressure for the gaseous species is 1 atm, the partial vapour pressures of NbCl$_4$ and NbCl$_6$ above dilute solutions of NbCl$_6$ and NbCl$_8$ in the CsCl–NaCl eutectic melt can be estimated from the relation $P/\text{atm} = x_7$, indicating very low pressures of NbCl$_4$.

Conclusion

In the oxide-free CsCl–NaCl eutectic melt, reduction of Nb(V) chlorides gives Nb(IV) and Nb(III) chlorides according to the reduction reactions

$$\text{NbCl}_6^- + e^- = \text{NbCl}_6^{2-}$$  (13)
$$\text{NbCl}_6^{2-} + e^- = \text{NbCl}_{4-x}^{(x-3)^-} + (6 - x)\text{Cl}^-,$$

(x = 4, 5 or 6)  (14)

Both reactions are reversible and diffusion-controlled. The reduction products of NbCl$_6^{(x-3)^-}$ are non-metallic solids at temperatures below about 920 K and metallic niobium above this temperature.

The stable niobium oxochlorides in melts saturated with Nb$_2$O$_5(s)$ are NbOCl$_3^{2-}$, NbO$_2$Cl$_4^{(x-1)^-}$ and NbOCl$_4^{(x-2)^-}$. The reaction

$$\text{NbOCl}_3^{2-} + e^- = \text{NbOCl}_2^{(2-x)^-} + (5 - x)\text{Cl}^-,$$

(x = 3, 4 or 5)  (15)

is reversible and diffusion-controlled. The reduction products of NbOCl$_4^{(x-1)^-}$ and NbOCl$_4^{(x-2)^-}$ are probably NbO$_2(s)$ and NbO$_2(s)$, respectively.

To obtain dense and coherent niobium metal deposits from the CsCl–NaCl melt, the molar ratio O/Nb must be lower than one, niobium-containing ions must be in equilibrium with niobium metal, and temperatures must be higher than about 920 K.

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