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Electrochemical Studies of K_2WCl_6 in Chloride and Oxychloride Melts

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The electrochemical behaviour of W^{IV} in the form of K_2WCl_6 in a LiCl KCl (eutectic melt) has been studied by cyclic voltammetry at 450 °C on glassy carbon electrodes with and without additions of Na_2O. W^{IV} is reduced to tungsten metal via an irreversible four-electron-transfer process. Titration of the system LiCl-KCl-K_2WCl_6 with Na_2O was carried out in order to investigate the influence of oxide ions on the electroreduction of W^{IV}. At a molar ratio of $Na_2O/K_2WCl_6=0.5$, the major complex ion in the melt may be $W_2OCl_{10}^{4-}$ and/or $WOCl_5^{2-}$, while at a molar ratio of $Na_2O/K_2WCl_6=2$ precipitation of WO_2 probably occurs.

Relatively few studies of the electrochemical behaviour of tungsten species formed in molten salt systems have been reported. Several decades ago it was claimed that coherent deposits of tungsten can be obtained from a fluoride melt.[1] Considerable attention has recently been paid to the electrodeposition of other refractory metals, such as Nb and Ta, using different kinds of molten salts. Only sporadic investigations related to the chemistry and electrochemistry of tungsten in fused salts have appeared, and very little is therefore known about how this useful metal behaves in high-temperature liquids. Tungsten is counted among the most complex of the transition metals owing to its many oxidation states, and the behaviour of the metal may be quite different in water than in molten salts. The electrochemical behaviour of tungsten chlorides and oxychlorides has been studied in a sodium chloroaluminate melt saturated with sodium chloride.[2-5] A possible reaction sequence has been proposed, where several reduction steps are observed before the cathodic limit of the solvent. Deposition of tungsten on the cathode via a nucleation and growth mechanism does not seem to occur. A few investigations of the electroreduction of tungsten chlorides in the LiCl–KCl eutectic melt have been published.[6-9] The information available from these studies is contradictory. Zuckerbrod[6] reported that in LiCl–KCl melts W^V can be reversibly reduced to W^{IV}, which can be further reduced irreversibly to W^{II}. The final process is the formation of tungsten metal via a disproportionation reaction of W^{II}. It was also claimed that W^{II} is reduced to W^0, but an electrocrystallization process was not observed.[6] In contrast, Balko[7] found, in the same melt, that W^V and W^{IV} were both reduced to W^{III}, and W^{III} finally to W^0. Recently, Sequeira claimed that W^V and W^{IV} are irreversibly reduced to W^{III} which is not further reduced.[8,9]

There must be a reason for the different reactions paths proposed for electroreduction of tungsten chlorides in the LiCl–KCl melt, and one reason may be the influence of oxide on the above processes. In the cases of Nb and Ta electrodeposition, the existence of a small quantity of oxide ions in the melt has been considered useful for obtaining coherent deposits.[10] There are very few experimental data related to W electrodeposition in melts containing oxychlorides and oxides.[11,12]

In the present paper the electrochemical behaviour of K_2WCl_6 in liquid LiCl–KCl was carried out at 450 °C on glassy carbon electrodes under controlled oxide concentrations. This was done to try to elucidate the controversies found in the literature, and to find out if this melt can be an alternative to fluoride melts for electroplating of tungsten metal.

Experimental

LiCl and KCl were analytical grade chemicals (Merck). Before the preparation of the eutectic mixture (59.5 + 40.5 mol%) they were purified by melt recrystallization. Each alkali chloride was introduced in a glassy carbon crucible (V25 Carbone, Lorraine). The sample was placed in a temperature-controlled furnace and dried for at least 20 h at 400 °C under vacuum. The salts were then heated to 50 °C above the melting point under argon, and slowly cooled, 3–4 °C h^{-1}, to 50 °C below the

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melting point. The solidified salts were transferred at room temperature to a nitrogen-filled drybox (moisture level <1 ppm). The impurities, which were concentrated in the central part of the crucible, were removed. The purified salts were stored in sealed Pyrex tubes. The oxide content of LiCl, KCl and the LiCl–KCl eutectic were determined by carbothermal reduction of the oxide using LECO TC-436. The samples were transferred from the glove box to the oxide analyser in tin capsules to avoid moisture contamination. The Leco method for oxide analysis of hygroscopic salts has been described elsewhere.[13,14] Results are given in Table 1 for the pure alkali chlorides.

The voltammetric characteristics of a purified melt are given in Fig. 1, where the cathodic and anodic limits correspond to the reduction of Li^+ and the oxidation of Cl^-, respectively. The voltammogram of the electrolyte is also characterised by the total absence of any peaks, which could be attributed to impurities, e.g. oxidation of residual oxide ions. This is in accordance with the very low oxide content of the electrolyte determined by the carbothermal reduction method.

K_2WCl_6 was synthesised according to the method proposed by Dickinson *et al.*[15] Firstly, WCl_6, which was obtained from Alfa Chemicals Inc., was sublimed twice under vacuum in a sealed Pyrex tube using a temperature gradient. An equimolar mixture of WCl_6–KCl was then placed in a fused silica tube, sealed under vacuum and heated at 420–430 °C for at least 80 h.[16] During this procedure, Cl_2 evolved. This gas was removed twice. The dark green $KWCl_6$[16] obtained was subsequently placed into another Pyrex tube and heated at ~280 °C under vacuum for several hours. The final dark red product, K_2WCl_6, was then stored in sealed, evacuated Pyrex tubes. Because of the significant air- and moisture-sensitivity of tungsten chlorides all handling and weighing of chemicals were carried out in the glove box. Na_2O was prepared by heating analytical grade Na_2O_2 from Merck in an alumina crucible under vacuum at 600 °C for 12 h.[10,17] Both K_2WCl_6 and Na_2O were pressed into pellets inside the glove box before addition to the melt. All voltammetric experiments were carried out in a furnace tightly connected to a glove box. The cell was placed in an outer silica envelope. A glassy carbon crucible served as container for the melt and it was placed at the bottom of the silica envelope. A glassy carbon cylinder, with the same diameter as the crucible, rested on the crucible. Graphite radiation shields were used to keep a small temperature gradient (±1 °C) over the crucible. A graphite spoon and a graphite blade were used for extraction of melt samples for analysis and stirring of the melt, respectively. In this way the melt and its vapour were in contact with glassy carbon and graphite materials only. The use of alumina ceramics radiation shields resulted in small oxide contamination of the melt, and had to be avoided. Before each experiment the whole set-up was cleaned with boiling dilute HCl solution and thereafter in distilled water. Then, the cell was placed in a quartz tube and heated under vacuum at 900 °C for 12 h. After melting of the LiCl–KCl (eut.)–K_2WCl_6 mixture, Na_2O was added, and the mixture was allowed to equilibrate under stirring before any measurements were carried out. During the voltammetric measurements the crucible served as counter-electrode. The working electrode was a glassy carbon rod (3 mm), while a platinum wire (0.5 mm) was employed as a quasi-reference electrode. Both were isolated from the graphite cell using alumina tubes. An EG & G potentiostat (model 273), controlled by a computer, was used for the voltammetric measurements. The deposit on the working electrodes after controlled potential bulk electrolysis was investigated by SEM.

Table 1. Oxide contents in purified alkali chlorides as determined by carbothermal reduction using LECO TC-436.

Salt	Oxygen (wt%)	Standard deviation
KCl	0.001	±0.002
LiCl	0.002	±0.004
LiCl–KCl (eutectic)	0.004	±0.002

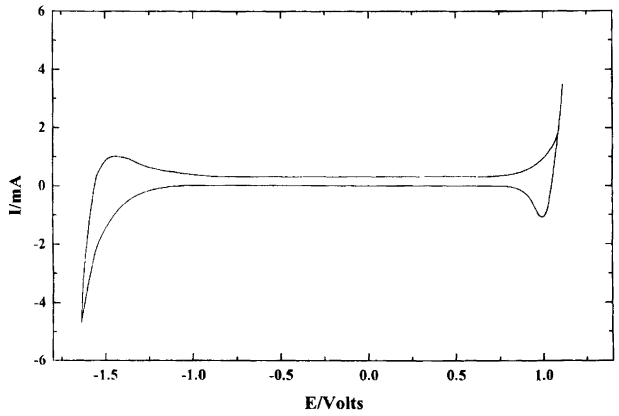


Fig. 1. Cyclic voltammogram of a LiCl–KCl eutectic melt at 450 °C, scan rate 0.1 V s^{-1}, platinum quasi-reference and glassy carbon working electrodes.

Results and discussion

K_2WCl_6 is expected to be a direct source of W^{IV} in the form of the complex ion WCl_6^{2-}.[18] A very small amount of tungsten oxychlorides in the melt cannot be excluded. Since tungsten chlorides exhibit significant moisture sensitivity, the formation of tungsten oxychlorides during the multi-step synthesis of K_2WCl_6 is possible. Consequently, one should determine the oxide content of the hygroscopic melt under investigation. The initial oxide content in the melt was measured by the Leco method. The concentration of oxide ions in the initial LiCl–KCl–K_2WCl_6 melts, was ca. 0.008 wt%. This means that the molar ratio n_O/n_W was 0.18 before any oxide had been added. Figure 2A illustrates a typical cyclic voltammogram of a LiCl–KCl–K_2WCl_6 olive-green melt obtained with a glassy carbon working electrode having

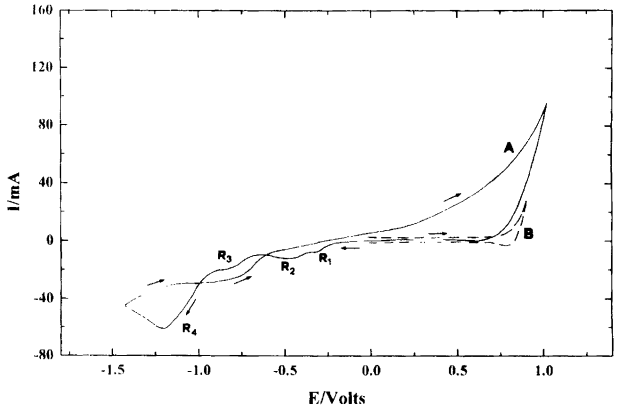


Fig. 2. Cyclic voltammogram of K_2WCl_6 (0.16 mol%) in a LiCl–KCl (eutectic melt) at 450 °C. Scan rate 0.1 V s^{-1}, platinum quasi-reference and glassy carbon working electrodes. (B) shows an initial scan in the positive direction, (A) a normal reproducible scan.

0.008 wt% O. The voltammogram was initially scanned in the positive direction from the rest potential. Given that the melt contains WCl_6^{2-}, one would expect an anodic current to appear. As shown in Fig. 2B, a current due to oxidation of WCl_6^{2-} is not present up to the potential where evolution of Cl_2 occurs. This behaviour implies that the electro-oxidation of WCl_6^{2-} might start at more positive potentials than the Cl^- oxidation.

The cathodic part of the voltammogram was characterised by the appearance of three reduction peaks, R_1, R_2 and R_4, and a shoulder, R_3, before the most negative peak R_4. On the reverse scan anodic currents were recorded at positive potentials, but distinct anodic peaks were not observed. The presence, however, of tungsten oxychlorides in the melt made complications for the interpretation of the cathodic peaks, since they can be attributed either to different steps in the reduction of WCl_6^{2-} or to the reduction of other tungsten chloride and/or oxychloride complexes. The nature of the peaks in the voltammogram, shown in Fig. 2, can be understood through experiments where an oxide is titrated into the melt. We used Na_2O additions, and recorded the changes in the voltammograms.

It is apparent from Fig. 3 that the cathodic peaks R_1 and R_2 correspond to the reduction of tungsten oxychlorides. Additions of small amounts of sodium oxide to the LiCl–KCl–K_2WCl_6 melt resulted in a lowering of the last peak, R_4, and to the growth of the first and second peaks, R_1 and R_2. Three anodic peaks were detected on the reverse scan. These anodic peaks were also recorded when the voltage scan was reversed just after the second peak. This behaviour indicates that the reduction processes occurred irreversibly at R_4 and the shoulder R_3. The height of the peak R_4 reached zero at a molar ratio of O/W = 0.5, suggesting that a reaction of the type

$$2W^{4+} + O^{2-} = W_2O^{6+} \quad (1)$$

took place. The only O^{2-}-bridged complex of W^{IV}, which has been reported in the literature with a ratio W/O = 2,

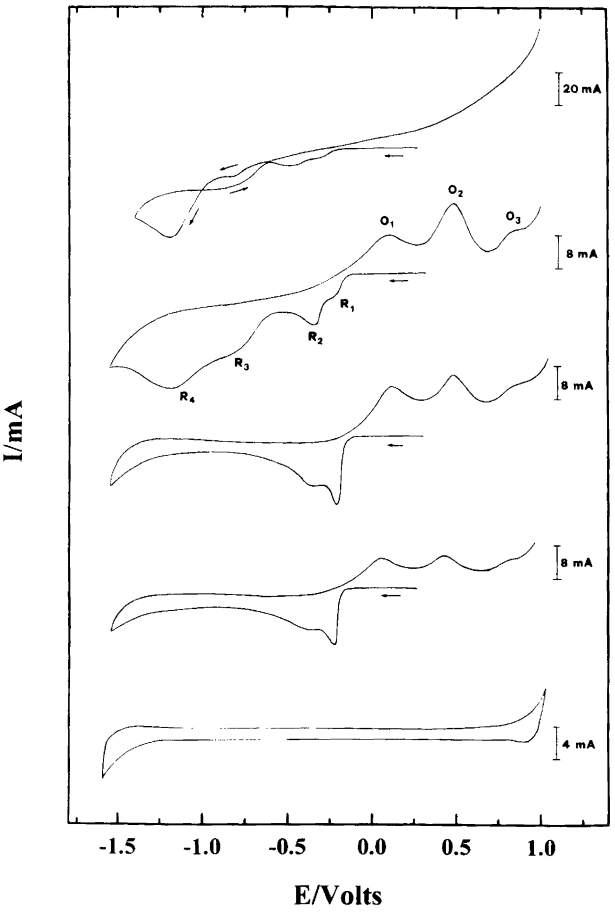


Fig. 3. Cyclic voltammogram of K_2WCl_6 (0.16 mol%) at 450 °C in a LiCl–KCl (eutectic melt). Scan rate 0.1 V s^{-1}, platinum quasi-reference and glassy carbon working electrodes. Counting from the top of the figure the molar ratios Na_2O/K_2WCl_6 are: 0, 0.34, 0.59, 0.91, 2.2, respectively.

is $K_4W_2OCl_{10}$.[19] A ligand displacement reaction can therefore be suggested:

$$2WCl_6^{2-} + O^{2-} = W_2OCl_{10}^{4-} + 2Cl^- \quad (2)$$

However, the complex ion $W_2OCl_{10}^{4-}$ might not be stable. It has been claimed[19] that $WOCl_5^{2-}$ and tungsten species with an oxidation state lower than IV are formed via a disproportionation reaction of $W_2OCl_{10}^{4-}$. The peaks R_1 and R_2 may therefore correspond to a reduction of tungsten oxychlorides different from those indicated. This is further confirmed by the voltammogram shown in Fig. 4. The peak R_1 is coupled to the anodic peaks O_1 and O_3, while the reduction peak R_2 is connected to the oxidation peak O_2. At small oxide additions, R_1 and R_2 are not very pronounced, as can be seen from Fig. 3, but appear distinctly when the oxide content in the melt has been increased to a molar ratio O/W = 0.34. The shape of the R_1 peak also indicates the deposition of an insoluble layer on the cathode. A further investigation concerning the nature and the electrochemical behaviour of different tungsten oxychlorides in chloride melts is in progress at ICE/HT FORTH.

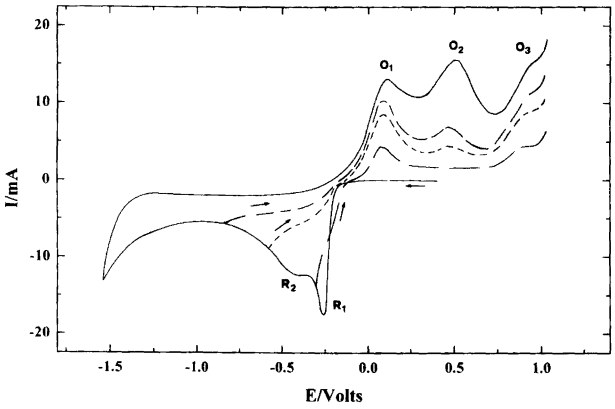


Fig. 4. Cyclic voltammogram of LiCl–KCl–K_2WCl_6–Na_2O melt at 450 °C. Scan rate 0.1 V s^{-1}, platinum quasi-reference and glassy carbon working electrodes, molar ratio $Na_2O/K_2WCl_6 = 0.59$.

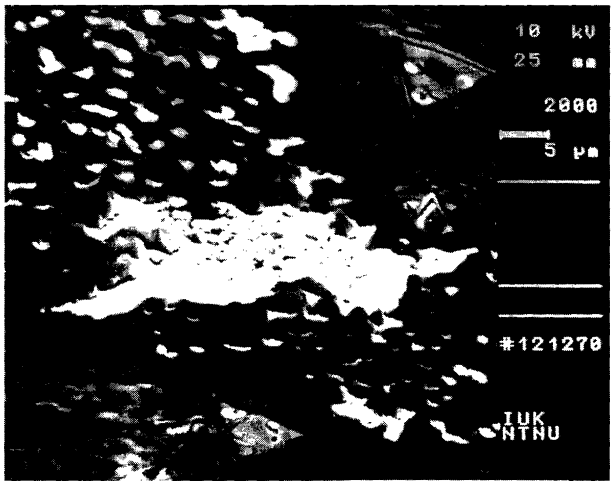
When the sodium oxide additions to the melt exceeded a molar ratio of O/W = 1, all peaks were reduced. The voltammograms corresponding to a molar ratio O/W close to 2 were similar to those observed for the solvent, suggesting an absence of tungsten in the melt. Formation of an insoluble tungsten compound, probably WO_2 according to the reaction

$$\begin{aligned} 2WCl_6^{2-} + O^{2-} &= W_2OCl_{10}^{4-} + 2Cl^- \\ W_2OCl_{10}^{4-} + 3O^{2-} &= 2WO_2(s) + 10Cl^- \\ \hline WCl_6^{2-} + 2O^{2-} &= WO_2(s) + 6Cl^- \end{aligned} \qquad (3)$$

assuming a role of the complex $W_2OCl_{10}^{4-}$, might be possible.

The last peak, R_4, as mentioned above, seems to correspond to the reduction of the ion WCl_6^{2-}. The main features observed at the voltage corresponding to this peak are (i) the sharp change in the current with potential, and (ii) a remarkable hysteresis in the current versus potential curve. This behaviour is typical for phase formation by a nucleation and growth mechanism.

Bulk controlled-potential electrolysis is widely used to prepare sufficient quantities of the reaction products to enable their identification. Potentiostatic electrolysis for a few minutes at potentials corresponding to the peak R_4 was carried out using a glassy carbon cathode. The deposit on the electrode surface was analysed by SEM (Fig. 5). Only tungsten metal and the background electrolyte were identified. This finding implies that W^{IV} is reduced to W via a four-electron-transfer reaction at R_4. Anodic removal of the deposit from the electrode surface was not possible. This behaviour is in accordance with a previous investigation.[20] It was reported that W metal is not anodically oxidized in the LiCl–KCl (eutectic melt). An explanation may be the formation of tungsten polymeric chlorides with low oxidation states on the metallic surface, and these metal–metal bonded clusters inhibit the electro-oxidation of tungsten metal.[20] This behaviour might also explain the nature of the shoulder R_3 just before the reduction of W^{IV} to W. Taking into account



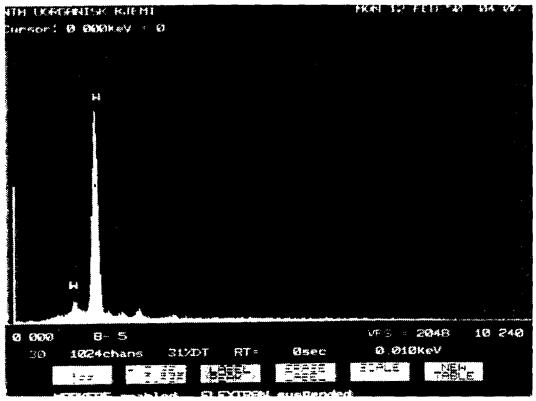


Fig. 5. SEM picture of tungsten on the working glassy carbon electrode obtained by electrolysis at the voltammetric peak R_4 using the melt LiCl–KCl(eutectic)–K_2WCl_6 with 0.16 mol% K_2WCl_6 at 450 °C.

the ratio between current intensities, $i_{R4}/i_{R3} > 4$, the reduction of W^{IV} to W^{III} or W^{II} at potentials where the shoulder R_3 appears, might be excluded. Presumably, lower-valent clusters are formed giving rise to the shoulder on the right side of the peak R_4. A similar behaviour has been observed in the electroreduction of Nb chlorides. In these melts niobium subhalides of non-stoichiometric composition are formed before the deposition of niobium metal.[21] Owing to experimental difficulties, attempts were not made in the present work to identify the products generated at potentials more positive than the potential where tungsten deposition occurred.

The nature of the tungsten electrodeposition process was also studied, in a qualitative way, using the dependence of the voltammetric parameters on the potential sweep rate. The peak potential of the cathodic peak R_3 shifted cathodically with increasing scan rate. This shift implies that an irreversible electron-transfer reaction occurs, as also suggested by the absence of reoxidation waves. The irreversibility of this process was further confirmed by the linear dependence of the peak potential versus the logarithm of the scan rate [Fig. 6 (top)]. The

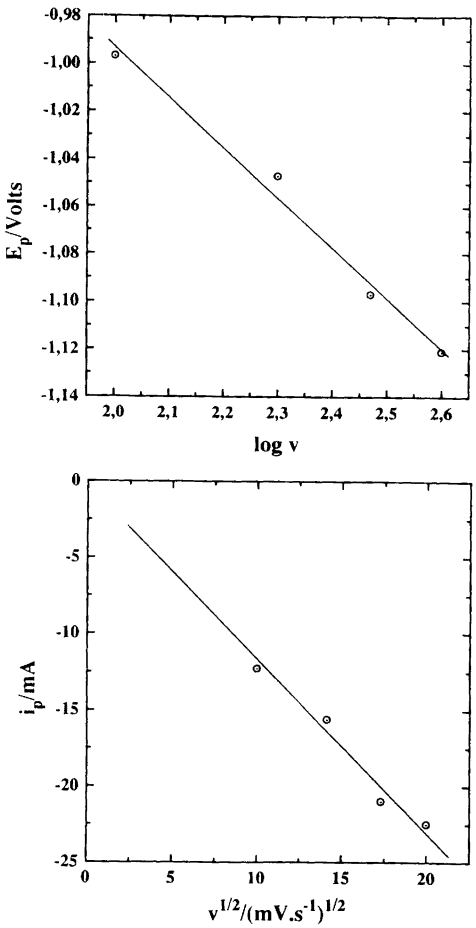


Fig. 6. The effect of the scan rate on: The peak potential (top) and the peak current (bottom) of the electroreduction of WCl_6^{2-} (0.06 mol%) at 450 °C. Platinum quasi-reference and glassy carbon working electrodes.

peak current is diffusion-controlled, as can be seen from the linear dependence of i_p vs. $v^{1/2}$ [Fig. 6 (bottom)].

Conclusions

The electrochemical behaviour of K_2WCl_6 dissolved in the LiCl–KCl eutectic melt has been investigated at 450 °C on glassy carbon cathodes. Cyclic voltammetry shows that W^{IV} is reduced to tungsten metal in a single irreversible four-electron reduction step. This electrodeposition process might be perturbed by the formation of tungsten subhalides on the metal surface. The electrochemistry of tungsten in molten salts appears to be strongly dependent on operating conditions. In particular, the oxide content of the melt is of crucial importance. Titration of WCl_6^{2-} with oxide ions leads to the stepwise formation of $W_2OCl_{10}^{4-}$ and/or $WOCl_5^{2-}$. At the same time a progressive decrease in the height of the peak currents for the W^{IV} reduction with O^{2-} additions is observed. Since electroreduction of tungsten chlorides seem difficult even when extreme precautions are taken to avoid oxide impurities, it is not likely that chloride melts will be used in a technical electrodeposition process for tungsten metal.

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