STUDY OF SOME RENIUM ELECTROCHEMICAL PROPERTIES IN THE FUSED LiF-NaF-KF EUTECTIC.

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ABSTRACT

The electrochemical properties of K₂ReCl₆ and KReO₄ dissolved in molten flinak at 700°C were studied. K₂ReCl₆ decomposed to a Re(II) species which could be reduced to Re in one reversible step, or it could be oxidized to a soluble Re(III) species. KReO₄ was reduced to Re via a two step mechanism.

INTRODUCTION

Few studies (1-5) have been published on the chemical or electrochemical properties of rhenium in fused salts. Some electrochemical properties of K₂ReCl₆ dissolved in the molten LiCl-KCl eutectic have been studied by Nobile and Bailey (3). These authors observed that Re(IV) was quite stable once in solution, although some decomposition reaction yielding the metal occurred during the dissolution process of K₂ReCl₆. From potentiometric experiments they gave some evidence for the reversibility of the Re(IV)/Re exchange and measured the corresponding standard potential. Using solid electrode polarography, they showed that the half-wave potential was very close to the standard potential, but they could not unambiguously demonstrate that the number of electrons exchanged was four. Rhenium metal was deposited by potentiostatic electrolysis in the vicinity of the reversible Re(IV)/Re equilibrium potential. Galvanostatic electrolysis ultimately yielded Li predeposition because of the formation of a Re-Li solid solution. The same authors obtained rather similar results in the case of KReO₄ solutions.

Russian authors (5) have obtained W-Re solid solutions from a NaCl-KCl melt containing 15 to 20 mol% WF₆, 1 to 3 mol% ReCl₃, and 20 mol% NaF.

To our knowledge, the electrochemistry of rhenium compounds has not been investigated in molten fluoride solvents, and this paper deals with the study of K₂ReCl₆ and KReO₄ solutions in the LiF-NaF-KF molten eutectic.
EXPERIMENTAL TECHNIQUES

The experimental setup has been described previously (6). The electrolyte was contained in a graphite crucible situated inside an air-tight stainless steel cell. In order to dehydrate the melt, 1.5 mol% KHF₂ were added to the salts. The mixture was heated to 200°C under vacuum then melted under argon flow. K₂ReCl₆ or KReF₄ were then added through a lock-chamber and proved to be quite soluble in the melt. Voltammetric and chronopotentiometric studies were performed using platinum, silver, tungsten or rhenium electrodes. Owing to the difficulties in obtaining good reference electrodes in molten fluorides, we used a platinum wire or the graphite crucible as a comparison electrode.

RESULTS AND DISCUSSION

A- PURE SOLVENT

Reference potential.—Our results were referred to the K⁺/K limit of the solvent, which could be reached with the whole set of electrodes used, whereas oxidation of the electrode was the anodic limit. In order to compare our results to literature data, we have determined the standard equilibrium potential \( E^{\circ}_{Ni^{II}/Ni} \) versus our K⁺/K reference, after having proved the reversibility of the Ni(II)/Ni exchange by making a convolutional analysis of nickel oxidation voltammograms. The result was:

\[
E^{\circ}_{Ni^{II}/Ni} = + 2.20 \text{ V vs } K^+/K \]

Electrochemical window at a rhenium electrode.—On the voltammogram of Figure 1, rhenium oxidation occurs at +2.8 V vs K⁺/K (value taken for \( i = 10 \text{ mA/cm}^2 \)). The shape of the curves corresponding to various sweep rates (Figure 2) suggests that the oxidation product is soluble in the melt and shows the irreversible character of the reduction wave (peak A). Further anodic polarization resulted in gas evolution.
B- K$_2$ReCl$_6$ SOLUTIONS

Figure 3 shows a typical voltammogram on a silver electrode, with two well-characterized couples: in the 1.2 to 1.6 V potential range, the B/B' couple corresponds to reduction of the rhenium species yielding an insoluble product, followed by a stripping reoxidation peak of this product; in the 2.0 to 2.5 V potential range, the C/C' couple is related to the oxidation of the rhenium species yielding a soluble product, followed by reduction of this product.

Study of the B/B' couple. Figure 4 presents several voltammograms obtained on a silver electrode in a 0.014 M K$_2$ReCl$_6$ solution. Due to the ohmic drop, the voltammograms were subsequently analysed by convolution procedures (8,9). The reversibility test was the comparison of the semi-integral curves obtained for different sweep rates (Figure 5). These curves were similar and for any given curve the direct and the reverse scans were identical within a large potential domain. These results indicate that the B'/B exchange may be considered as reversible in the sweep rate domain studied.

Figure 6 presents cathodic chronopotentiograms obtained on a silver electrode in a 0.014 molar ReCl$_6$ solution. A single transition is observed, and the shape of the curves reveal a soluble-insoluble exchange. The transport of the rhenium species is governed by linear diffusion since Sand's law is obeyed (Figure 7). The potential measured at the quarter of the transition time is independent of the current density (Figure 6), which confirms the reversibility of the exchange. Figure 8 shows the logarithmic analysis of the chronopotentiograms in the case of an insoluble product (curve a) and of a soluble product (curve b). The best fit is obtained in the case of the insoluble product. The insoluble character of the reaction product is confirmed by the equality of the reduction and reoxidation transition times on current reversal chronopotentiograms (Figure 9). We therefore postulated that the product was rhenium metal. From the slope of the straight part of curve a (Figure 8), we calculated the number of electrons exchanged as $n = 2$. From the value of the potential at the quarter of the transition time, we calculated the value of the apparent standard potential:

$$E_0^{b/b'} = 1.97 \text{ V vs } K^+/K$$

Study of the C/C' couple. A few voltammograms restricted to the C/C' exchange are presented in Figure 10. In spite of a large residual current in this potential range, we could analyse the curves and concluded that the
exchange was reversible. Firstly, the anodic and cathodic peaks potentials are independent of the sweep rate. Secondly, the \( \frac{i_{pa}}{i_{pc}} \) ratio remains close to one for all of the sweep rates studied. Moreover, the value of \( E_{pa} - E_{pc} \) is about 200 mV and not too far from the theoretical value corresponding to a one-electron exchange, which is 183 mV at 650°C. The semi-integral curves (Figure 11) do not yield a decisive reversibility criterion in this case, possibly because of the high residual current already mentioned. We can, however, observe that for a given sweep rate the direct and forward curves are identical.

Finally, assuming that the exchange is reversible, we can calculate the \( \frac{C}{C'} \) apparent standard potential from the half-peak potential by using the relation:

\[
E_{p/2} = E_{1/2} + 1.09 \frac{RT}{F} \quad [3]
\]

Assuming that the diffusion coefficients of both species are equal, we obtained \( E^{\circ}_{C/C'} = 2.14 \) V vs K+/K²

Interpretation of the results.- The K₂ReCl₄ solutions appear to be cathodically reduced to rhenium(0) by a two-electron reversible exchange step and anodically oxidized to a soluble species by a one-electron reversible exchange process. This suggests that some divalent rhenium species could be present in the solution. Looking into the literature, we found that ReI₁ can be obtained by heating K₂ReI₄ to 350°C (10). In fact, two divalent rhenium halogenides seem to be known : ReF₂ and ReI₁. At the present state of our study, we assume that, in molten flinak at 650°C, K₂ReCl₄ is, like the corresponding iodide, decomposed to a stable Re(II) species. The B/B' and C/C' exchange reactions may then be formulated as:

\[
\text{Re(II) + 2 e} \rightarrow \text{Re (B/B')} \quad [4]
\]

\[
\text{Re(II)} \rightarrow \text{Re(III) + e (C/C')} \quad [5]
\]

KReO₄ SOLUTIONS

Figure 12 presents a typical voltammogram obtained on a platinum electrode. The characteristic features of the voltammograms did not depend on the nature of the electrode (Pt, W or Re). The cathodic part of the voltammogram shows two steps : waves D and E. The heights of these waves increase with the KReO₄ concentration. When, during the direct scan, the potential reaches the domain of wave E, a shoulder F appears on the reverse scan in the vicinity of the generalized electrode oxidation domain. The potential domain of this shoulder is close to the potential at which rhenium was oxidized in the pure solvent.
Potentiostatic and galvanostatic electrolysis in the region of wave E yielded metallic rhenium, characterized by X-ray analysis (Figure 13). We can therefore conclude that the ReO₄⁻ solutions undergo a two-step reduction process according to the following reactions:

\[
\text{ReO}_4^- + (7-x)\, e^- \rightarrow \text{Re}(x) + 4\, \text{O}_2^- \quad \text{(wave D)} \quad [6]
\]

\[
\text{Re}(x) + x\, e^- \rightarrow \text{Re}(0) \quad \text{(wave E)} \quad [7]
\]

The anodic oxidation of Re can be written as:

\[
\text{Re} + 6\, F^- \rightarrow \text{ReF}_6 + 6\, e^- \quad \text{(shoulder F, wave A/A')} \quad [8]
\]

CONCLUSION

From electrochemical studies of K₂ReCl₆ solutions in the fused LiF-NaF-KF eutectic, it appears that the solute is first decomposed to give stable Re(II) solutions. This situation is different from the case of molten LiCl-KCl at lower temperatures, where Re(IV) is quite stable.

The Re(II) species is cathodically reduced to rhenium metal through a reversible two-electron step. This species can be anodically oxidized to a soluble Re(III) species in a reversible reaction.

The apparent standard potentials, referred to the standard Ni(II)/Ni couple are:

\[ E^{\circ}_{\text{Re}^{(II)}/\text{Re}^{(I)}} = -0.06 \, \text{V} \quad \text{and} \quad E^{\circ}_{\text{Re}^{(III)}/\text{Re}^{(II)}} = -0.23 \, \text{V} \]

The reduction of KReO₄ solutions to metallic rhenium proceeds through two electrochemical steps:

\[
\text{ReO}_4^- + (7-x)\, e^- \rightarrow \text{Re}(x)
\]

\[
\text{Re}(x) + x\, e^- \rightarrow \text{Re}(0)
\]

By comparison of the voltammograms resulting from ReO₄⁻ solutions and those resulting from Re in pure solvent, we can postulate that in both cases the metal is passivated and can only be oxidized to ReF₆ at very anodic potentials.

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Figure 1: Voltammetric study in the pure LiF-NaF-KF solvent at a rhenium electrode. Temperature: 700°C; a) 0.2 V/s.

Figure 2: Voltammetric study in the pure LiF-NaF-KF solvent at a rhenium electrode. Temperature: 700°C; a) 0.05 V/s, b) 0.1 V/s, c) 0.2 V/s, d) 0.5 V/s, e) 1 V/s.

Figure 3: K2ReCl6 voltammetry. Temperature: 650°C; Working electrode: silver; a) 0.2 V/s.

Figure 4: Voltammetric transients related to K2ReCl6 reduction. Temperature: 650°C; Working electrode: silver; C0 = 0.014 mol/l: a) 0.1 V/s, b) 0.2 V/s, c) 0.5 V/s, d) 1 V/s, e) 2 V/s.
Figure 5: Semi-integral curves related to the voltammograms of figure 4.

Figure 6: K2ReC16 chronopotentiometry. Temperature: 550°C; Working electrode: silver; CO = 0.014 mol/l; i (mA/cm²): a) 60, b) 38, c) 25, d) 15.

Figure 7: K2ReC16 chronopotentiometry. Verification of the SAND's relation.
Figure 8: K2ReCl6 chronopotentiometry. Logarithmic analysis of chronopotentiograms.

Figure 9: Current reversal chronopotentiograms obtained for K2ReCl6 at a silver electrode.

Figure 10: Voltammetric transients related to K2ReCl6 oxidation. Temperature: 650°C.
Working electrode: silver.
CC=0.014 mol/l; (a) 0.2 V/s, (b) 0.5 V/s, (c) 1 V/s, (d) 2 V/s, (e) 5 V/s.
Figure 11: Semi-integral curves related to the voltammograms of the figure 10.

Figure 12: XReO$_4$ voltammetry. Temperature 700°C. Working electrode: platinum; $v=0.2V/s; C_0=0.587\text{mol/L}$.

Figure 13: Rhenium deposit X-ray analysis.