SHORT COMMUNICATION

Electrochemical behaviour of perrhenate ions in molten alkali fluorides

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1. Introduction

Rhenium electrowinning from $KReO_4$ has been the subject of several studies [1–7]. In aqueous solutions [1–6], electrochemical $KReO_4$ reduction occurs in several steps yielding a mixture of rhenium metal and rhenium oxides. At 25 °C, potassium perrhenate dissolved in aqueous KCl solution is reduced to the metal [7] during the first polarographic wave. The second wave corresponds to hydrogen evolution.

In fused LiCl–KCl eutectic, at 450 °C, it was assumed [8] that the reduction of $KReO_4$ is a two-step process: first, the predeposition of lithium then the reduction of perrhenate ions by the predeposited lithium. In Na_2WO_4–WO_3–$KReO_4$ mixtures, in the temperature range 800–850 °C, it was suggested [9, 10] that the $KReO_4$ reduction involved a unique seven-electron-exchange process.

The present paper describes an investigation of perrhenate ion reduction in molten LiF–NaF–KF eutectic at 600 °C, by transient electrochemical techniques. The electrochemical reduction of ReF_6 solutions in the same solvent was also studied [17], but the solutions were difficult to prepare due to the high corrosivity of ReF_6. The potassium perrhenate product was easier to use. In a previous paper [11], $KReO_4$ reduction to Re(0) had been assumed to occur via a two-step mechanism. In this work, electrochemical $KReO_4$ reduction is reexamined and a different mechanism proposed.

2. Experimental details

The LiF–NaF–KF eutectic mixture (46.5–11.5–42 mol %) was contained in a graphite crucible placed in an air-tight stainless steel cell, as described previously [12]. KHF_2 amounts (0.26 mol %) were added to the solvent before melting to improve the dehydration of the melt. The salts were heated to 300 °C under vacuum for 6 h, then heated at a rate of 100 °C per hour up to 600 °C under an argon flow. The $KReO_4$ was then added through a lock-in chamber.

A three-electrode arrangement was used for the electrochemical studies. Most of the time the working electrode was a silver wire, the graphite crucible acted as counter electrode. A platinum wire was used as reference electrode, however all the potentials were referred to the equilibrium potential of the K^+/K couple, the cathodic limit of the solvent.

Potentiostatic and galvanostatic transients were achieved by means of a PAR 273 EEG Instruments potentiostat. The curves were stored using a Nicolet 2093 memory digital oscilloscope and processed with a HP Vectra microcomputer.

3. Results

3.1. *Linear sweep voltammetry (LSV)*

3.1.1. Phenomenological analysis. A typical voltammogram obtained with a silver electrode dipped in the pure solvent is shown in Fig. 1. The potential range is limited anodically by silver oxidation, and cathodically by potassium ion reduction. After the addition of $KReO_4$, three new redox couples, A/A′, B/B′ and C/C′, were observed (Fig. 2). The current increased regularly along each of cathodic waves A and B, and so a new phase-formation process was not involved.

New information was obtained by selecting appropriate parameters for the voltage scans. When the scan was started in the cathodic direction (Fig. 2(b)), two well-characterized A/A′ and B/B′ redox couples could be seen at low potentials, and a third couple C/C′ appeared in the high potential range, just prior to silver oxidation.

When the scan started anodically, the C/C′ couple did not exist. Therefore, it can be concluded that the species which corresponded to the C/C′ couple was not initially present in the solution, but was produced during cathodic polarisation. Moreover, if the potential scan was reversed in the potential domain of wave A, the C/C′ couple was again not visible (Fig. 2(a)). This couple appeared if the potential had been previously maintained in the domain of wave A for over 10 s. This indicated that the C/C′ couple could be related to the A/A′ couple, and possibly to the B/B′ couple.

Rhenium metal deposits were obtained by potentiostatic electrolysis either in the potential range of wave A or in the potential range of wave B.

Figure 3 shows the current-potential curves obtained with a tungsten electrode in $KReO_4$ solutions (Fig. 3(a)) and with a rhenium electrode (Fig. 3(b)) in the pure solvent. Comparison of these curves shows that the C/C′ couple occurs at the

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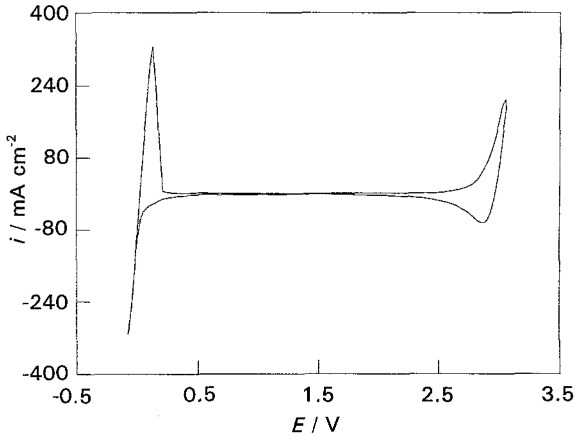

Fig. 1. Voltammogram obtained on a silver electrode in LiF–NaF–KF. $T = 600\,°C$; $v = 0.5 V s^{-1}$.

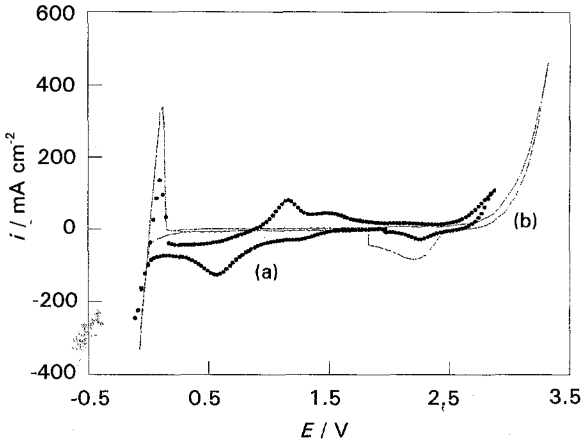

Fig. 3. Voltammograms obtained: (a) on a rhenium electrode in LiF–NaF–KF; (b) on a silver electrode in LiF–NaF–KF–KReO$_4$. $T = 600\,°C$; $v = 0.5\,V\,s^{-1}$.

same potential as the rhenium oxidation/deposition process.

Although no insoluble species were indicated by LSV, the production of metallic rhenium, which occurred along waves A and B, could be accounted for if the soluble products of wave A and B yielded Re by disproportionation. But metallic rhenium powder has not been detected in the bulk of the solution, and perhaps a catalytic effect of the surface could be involved.

3.1.2. Study of the A/A′ and B/B′ couples. The cathodic peak current densities, $i_{pc}(A)$ and $I_{pc}(B)$, were proportional to the square root of the potential sweep rate. This indicates diffusion control and, consequently, that the disproportionation reaction of one of the intermediate soluble species must be very slow so that the concentration profile is not significantly affected.

Some information about the reversibility of the A/A′ and B/B′ couples was gained from classical and convolutional analysis of the voltammograms. First, the quantities $[E_{pc/2}(A) - E_{pc}(A)] = 160 \pm 10\,mV$, and $[E_{pa}(A) - E_{pc}(A)] = 195 \pm 10\,mV$ were estimated from the voltammograms shown in Fig. 2. These values are very similar to the theoretical values, 166 and 173 mV, (13) calculated for a soluble/soluble reversible exchange of one electron at 600 °C.

Second, Fig. 4 shows the semiintegral curves related to the voltammograms presented on Fig. 2. The direct and reverse convoluted curves (Fig. 4(a)) corresponding to the A/A′ couple are superimposed in the whole potential domain, which proves the reversibility of the A/A′ exchange. But a significant hysteresis can be observed between the direct and the reverse semiintegral curves corresponding to the two reduction waves (Fig. 4(b)) of the perrhenate ions. This observation suggests that the B/B′ exchange is irreversible. Moreover, it can be seen that the reverse semi-integral transients do not cross the abscissa, proving that the species formed along the waves A′ and B′ are soluble.

3.2. *Chronopotentiometry*

A series of current reversal chronopotentiograms corresponding to perrhenate ion reduction/reoxidation is shown in Fig. 5. The two successive cathodic waves (transition times τ_1 and τ_2) corresponding to steps A and B and also the reoxidation steps (transition times τ_1' and τ_2') on the reverse transients can be seen. A third anodic wave (C′) situated just before

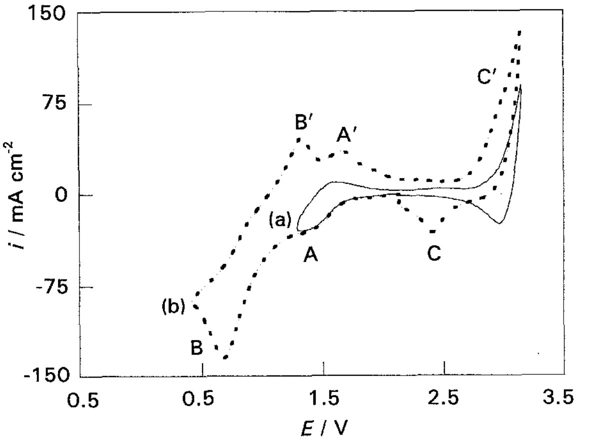

Fig. 2. Voltammograms obtained on a silver electrode in LiF–NaF–KF–KReO$_4$. Conc. $6.75 \times 10^{-5}\,mol\,cm^{-3}$; $T = 600\,°C$; $v = 0.5\,V\,s^{-1}$.

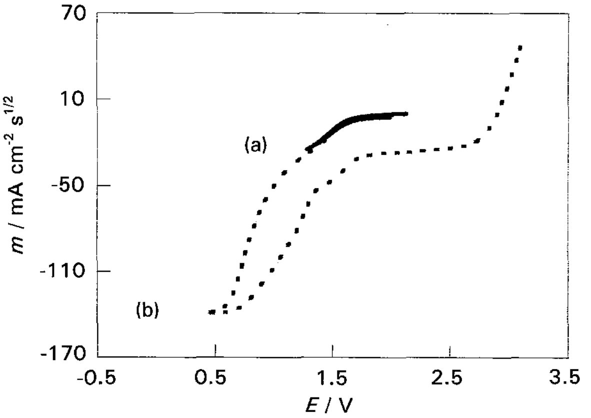

Fig. 4. Semiintegral curves of the voltammograms of the Fig. 2.

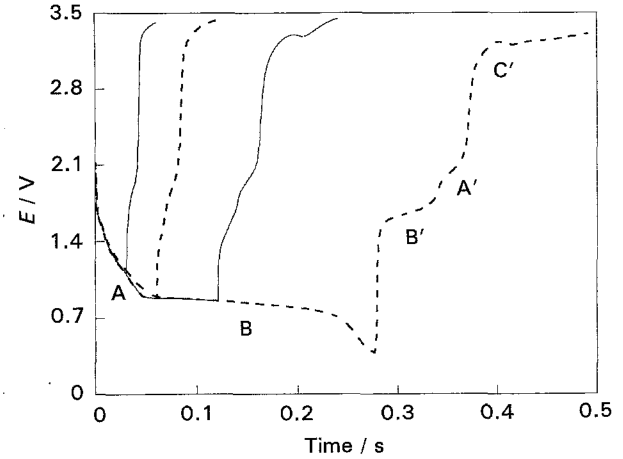

Fig. 5. Current reversal chronopotentiograms. $|i| = 460\,\mathrm{mA\,cm^{-2}}$, conc. $5.3 \times 10^{-5}\,\mathrm{mol\,cm^{-3}}$.

the silver electrode oxidation also exists. This anodic wave only appears when the current has been reversed after the first cathodic transition. These observations are in agreement with the voltammetric studies. The ratio $(\tau_1 + \tau_2)/(\tau_1' + \tau_2')$ is approximately equal to 1/3 as can be expected for two successive soluble/soluble exchanges [14].

It may be concluded that rhenium metal is not directly formed by the electrochemical reduction of the perrhenate ions, but through the disproportionation of one of species A or B.

For the successive transfer of n_1 and n_2 electrons involving soluble species with diffusion control, the ratio of the two transition times are linked by the theoretical relation [15]:

$$\frac{\tau_2}{\tau_1} = 2\frac{n_2}{n_1} + \left(\frac{n_2}{n_1}\right)^2$$

From the chronopotentiometric experiments, it was found that $8 < \tau_2/\tau_1 < 9$, the chronopotentiogram on Fig. 5 yielding, for example, the value $\tau_2/\tau_1 = 8.7$. Taking $\tau_2/\tau_1 = 8$, the equation yields $n_2/n_1 = 2$. This result is in agreement with one-electron exchange for wave A and a two-electron exchange for wave B.

3.3. *Electrodeposition of rhenium layers*

Rhenium metal layers were obtained either by potentiostatic or by galvanostatic electrolysis when the electrode potential was kept inferior to the potential of wave A. Compact rhenium layers, up to 50 μm thick, with good adhesion to the substrate were obtained. The deposits were characterized by chemical, SEM and X-ray analysis. A typical rhenium layer is shown in Fig. 6.

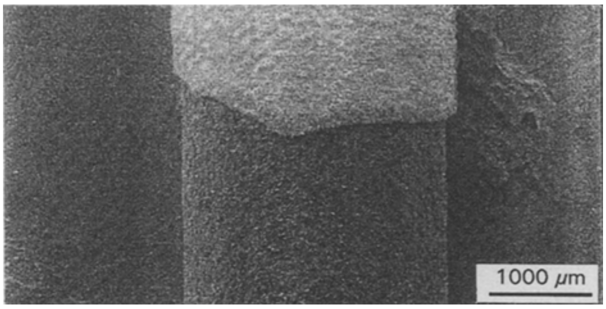

Fig. 6. A scanning electron micrograph (20×) of a rhenium deposit on a graphite substrate. Conc. $4.5 \times 10^{-5}\,\mathrm{mol\,cm^{-3}}$; $|i| = 50\,\mathrm{mA\,cm^{-2}}$; $T = 600\,°\mathrm{C}$.

4. Discussion and conclusion

$KReO_4$ solutions in molten LiF–NaF–KF eutectic mixtures appeared to be stable. Their electrochemical study using LSV and chronopotentiometric techniques showed two reduction steps, corresponding respectively to the exchange of one and two electrons and both yielding soluble species. The first step was assumed to be reversible, and the second irreversible.

The feasibility of rhenium formation by applying a potential value within the potential range of the first or the second steps suggested the disproportionation of each of these two soluble species. Such reactions have also been proposed for the intermediate rhenium oxides, ReO_3 and ReO_2, formed during the perrhenate reduction in aqueous solutions [16]. If this mechanism can be transposed to molten salts, the intermediate soluble products obtained on wave A and B would be ReO_4^{2-} and ReO_3^{2-}, corresponding, respectively, to the ReO_3 and ReO_2, oxides obtained in aqueous solution.

These rhenium oxoanions species can be assumed to be unstable and to disproportionate yielding metallic rhenium through the following reaction scheme:

$$(\mathrm{A/A'}) \quad \begin{cases} \mathrm{ReO_4^-} + 1\mathrm{e^-} \Longleftrightarrow \mathrm{ReO_4^{2-}} \\ 3\mathrm{ReO_4^{2-}} \Rightarrow 2\mathrm{ReO_4^-} + \mathrm{ReO_3^{2-}} + \mathrm{O^{2-}} \\ 7\mathrm{ReO_3^{2-}} \Rightarrow 4\mathrm{ReO_4^-} + 3\mathrm{Re} + 5\mathrm{O^{2-}} \end{cases}$$

$$(\mathrm{B/B'}) \quad \begin{cases} \mathrm{ReO_4^{2-}} + 2\mathrm{e^-} \Rightarrow 2\mathrm{ReO_3^{2-}} + \mathrm{O^{2-}} \\ 7\mathrm{ReO_3^{2-}} \Rightarrow 4\mathrm{ReO_4^-} + 3\mathrm{Re} + 5\mathrm{O^{2-}} \end{cases}$$

$$(\mathrm{C/C'}) \quad \mathrm{Re} + 8\mathrm{F^-} \Rightarrow \mathrm{ReF_8^{2-}} + 6\mathrm{e^-}$$

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