CONVOLUTIONAL VOLTAMMETRY STUDY OF THE ELECTROCHEMICAL OXIDATION OF SILVER AND RHENIUM IN MOLTEN FLUORIDES.

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The electrodeposition of refractory metals is often carried using the molten LiF-NaF-KF eutectic mixture as a solvent, due to its wide electrochemical window. This potential stability range is limited cathodically by the reduction of potassium ions and anodically by the oxidation of the metalllic materials used as working electrodes[1]. In fused LiF-NaF-KF eutectic, the anodic behaviour of copper, iron and nickel electrodes has been studied by several authors [2-4] using cyclic and convolutionnal voltammetry. In molten NaCl-KCl, Berghoute *et al.* [5] investigated the anodic oxidation of platinum by cyclic voltammetry. Later, Adhoum *et al.* [6] studied the electrochemical behaviour of sodium, nickel, molybdenum and iron in molten sodium fluoride using convolutionnal voltammetry and galvanostatic pulses.

In this work we studied the behaviour of silver and rhenium electrodes in molten LiF-NaF-KF eutectic at 600 °C, focussing on the study of the reversibility of the processes and on the determination of standard potentials using voltammetry and semi-integration techniques.

Figure 1 shows a typical voltammogram (curve a) of the silver anodic dissolution and the corresponding semi-integral (m) analysis (curve b). The direct and reverse semi-integral curves , well superpimposed, show the reversible character of the Ag(I)/Ag exchange. This property has already been demonstrated in other molten salts media [7]. The following equation:

$E = E^0 + (RT/nF)\ln(m/nF\sqrt{D_{ox}})$,

which corresponds to a reversible electron exchange [8], where D_{ox} represents the diffusion coefficient of oxidised species, was used to determine the number of electrons exchanged and the standard potential E^0.

We obtained : $n= 0.83$ and $E^0 = 3.73$ (V/ K^+/K).

This couple of values (n, E^0) was used to simulate a theoretical voltammogram shown in Figure 1, curve c.

In the case of the anodic oxidation of rhenium (Figure2), The semi-integral analysis shows a large hysteresis between the direct and reverse scans. This indicates that the electron exchange process is not reversible and the above relationship cannot be used to estimate the standard potential. To overcome this difficulty, we have derived the following equation [9]:

$E_{i=0}=E^0 + (RT/((\alpha+\beta)nF)) \ln(m_{i=0}/(nF\sqrt{Dox}))$,

which is valid at the zero current point following current reversal after anodic oxidation.

αn and βn were determined by Tafel plots.

We found : $E^0 = 2.81 \pm 0.03$ (V/K^+/K).

The rather large value of the error ΔE^0=0.03 V is due to the fact that the n values used in the calculations are in the range 1 to 7.

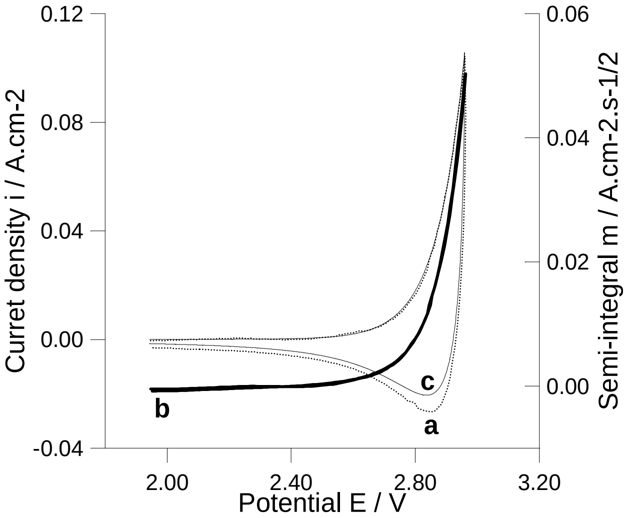

Figure 1 Voltammetric study of the anodic oxidation and reverse reduction of silver in the molten LiF-NaK-KF eutectic. T = 600 °C, v = 0.5 Vs^{-1},
(a) : experimental voltammogram, (b) : semi-integral of curve a, (c) : calculated voltammogram.

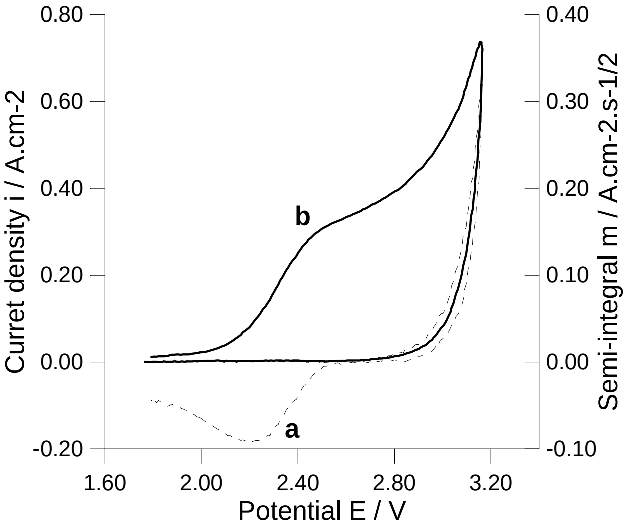

Figure 2 Voltammetric study of the anodic oxidation and reverse reduction of rhenium in the molten LiF-NaK-KF eutectic. T = 600 °C , v = 1 Vs^{-1}
(a) : voltammogram , (b) : semi-integral of curve a.

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