ELECTROCHEMICAL BEHAVIOR OF NICKEL IN THE 2HF-KF MIXTURE AT 80°C

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ABSTRACT

The electrochemical process of fluorine electrowinning may be improved in replacing the usual carbon anode which generally limits the cell life-time with a nickel anode. Therefore, we have investigated the electrochemical behavior of nickel in the 2HF-KF mixture at 80°C, using cyclic voltammetry and a.c. impedance measurements. A four step reaction pathway involving two adsorbed species has been proposed to account the experimental data, and its consistency was checked by a computerized simulation procedure taking into account the electrical properties of the corrosion layer formed.

INTRODUCTION

Industrial-scale fluorine electrowinning is nowadays performed from 2HF-KF mixture at 80°C. The current trends are to improve the electrochemical process in replacing the carbon anode which is responsible for an important anodic overpotential, and also, due to its fragility, to a severe limitation of the cell life-time. Knowing that before each electrolysis run with carbon anode, the electrolyte is electrochemically dehydrated using a nickel anode, it would be attractive to use also metallic nickel anode for the electrowinning of fluorine. In fact, nickel and platinum seem to be the only metals that can be used for this purpose[1-3].

Therefore, we have investigated the electrochemical behavior of nickel in a strictly fundamental point of view. A preliminary thermodynamic study[3] has shown that nickel oxide NiO can only be formed for very high and unrealistic water concentrations. So we have further only considered
the nickel fluoride formation, because the water content of our mixture is about 50 ppm.

TECHNICAL

The lab-scale electrolysis cell and the experimental procedure have already been described in detail elsewhere[4]. The working and the counter electrodes were respectively a pure nickel wire supplied by Johnson Matthey (Ø=1mm) and a carbon rod (Ø=3mm) from Carbone Lorraine (carbon for spectrography 205). The reference electrode was constituted by a copper rod (Weber, Ø=3mm) electrochemically coated by CuF2.

Voltammetric experiments were performed with a EG&G PAR Model 176 potentiostat-galvanostat connected to an Apple II microcomputer via a Model 273 interface. Chronoamperograms and impedance spectra were obtained using a Tacussel Z Computer System coupled to a Hewlett-Packard 9826A microcomputer. For a.c. impedance measurements, frequency ranged from $10^5$ Hz to $10^{-2}$ Hz and the sinewave amplitude was 10 mV. The acquired experimental data were analysed (simulation curves) using a HP 9000 'series 300' microcomputer.

VOLTAMMETRIC STUDY:

REACTION STEPS OF THE OXIDATION OF NICKEL

Experimental results.

Steady-state voltammetry at a nickel electrode.

Fig.1b shows a typical sampled-current voltammogram obtained from chronoamperograms (Fig.1a) with a sample time of 20 mn. We observe that anodic current density increases from - 0.150 V to 0.057 V to reach a maximum value close to 0.26 mA.cm$^{-2}$, and then deeply decreases for reaching a constant value of 0.039 mA.cm$^{-2}$ from 0.4 V. The shape of this steady state voltammogram can be explained by considering that two main electrochemical reaction steps occur[3] as it was further confirmed by the Linear Sweep Voltammetry (L.S.V.) study. The limiting current density observed for potential values higher than 0.4 V is due to either a desorption or solubilization process of an adsorbed high oxidation state species of nickel. This is consistent whatever the nature (adsorbed or soluble) of the
intermediate nickel species formed. In order to clarify the reaction mechanism, a L.S.V. study was undertaken.

**Linear Sweep Voltammetry study at low sweep rates.**

The shape of the cyclic voltammograms depends on the sweep rate (Fig. 2 and 3). For values lower than 0.1 V.s\(^{-1}\), we can observe during the forward scans two oxidation current density peaks respectively at about 0 V and 0.2 V. They are followed by a fairly constant low current density value. During the reverse scan, one oxidation peak of lower current density is only observed.

**Forward scans.** The two oxidation peaks observed in the forward scans can be attributed to two electrochemical subsequent reaction steps. This confirms the steady state voltammetry results. The sharp decrease of the current density after the first oxidation peak for 0.005 V.s\(^{-1}\) (Fig. 2a) clearly evidences the blockage of the nickel electroactive sites, which suggests the formation of an adsorbed species of nickel in the first electrochemical step. Moreover, this intermediate species has to be electrical conductive because a second oxidation peak is observed. Similarly, this latter corresponds to the formation of an adsorbed species of nickel of higher oxidation state, the desorption of which is responsible for the low limiting current observed at potential values higher than 0.4 V.

**Reverse scans.** The value of the oxidation current density relative to the oxidation peak observed in the reverse scans, decreases with an increase of the sweep rate (Fig. 2). This peak is observed in the potential range for which there is no oxidation of the intermediate species. In fact, this peak corresponds to the oxidation of metallic nickel, which requires regenerating of electroactive sites by desorption of the intermediate and the ultimate species. So, this peak can only be exist for low sweep rates in order to allow the electroactive sites to be regenerated. This peak does not appear for sweep rates higher than 0.1 V.s\(^{-1}\) (Fig. 3). In fact for high sweep rate values, the reverse oxidation peak cannot be observed because the desorption of this species is impossible during the scan-time. Moreover, the desorption rate of the intermediate species of nickel must be higher than the one of the ultimate oxidized species of nickel. In fact, otherwise a decreasing current density would be expected for potential values for which the second electrochemical oxidation reaction does not occur\(^{[3]}\).
Linear Sweep Voltammetry study at high sweep rates.

For very high values of the sweep rate, the shape of the voltammograms is quite different (Fig. 3). Only one oxidation peak is observed and there is no current flow during the reverse scan. This type of voltammogram was first studied by Calandra et al[5] which explained the shape observed by the formation of an insulating layer. They proposed a pure resistive model to analyze this type of curve. This model was further extensively used and improved especially by Devilliers et al[6] for accounting their experimental results relative to the oxidation of carbon in HF-KF melts, and by Lamirault[7] in her study on the electrochemical properties of copper in the 2HF-KF mixture. The obtention of this type of voltammogram proves the insulating character of the ultimate species of nickel electrochemically formed.

Discussion.

Proposal of a reaction pathway.

This electrochemical behavior of nickel can be explained by considering the following reaction mechanism:

- oxidation of metallic Ni into an adsorbed nickel species:
  \[ \text{Ni} - n_1 \text{e}^- = \text{Ni(N}1\text{)}\text{ads} \]
- desorption (or solubilizing) of Ni(N1)ads:
  \[ \text{Ni(N}1\text{)}\text{ads} = \text{Ni(N}1\text{)} \]
- oxidation of adsorbed Ni(N1) into adsorbed Ni(N2):
  \[ \text{Ni(N}1\text{)}\text{ads} - (n_2 - n_1) \text{e}^- = \text{Ni(N}2\text{)}\text{ads} \]
- desorption (or solubilizing) of Ni(N2)ads:
  \[ \text{Ni(N}2\text{)}\text{ads} = \text{Ni(N}2\text{)} \]

Ni(N1)ads being an electrical conductive species and Ni(N2)ads an insulated species.

In anhydrous HF and HF-NaF mixtures[2,8-11] oxidation of metallic nickel seems to lead to the formation of NiF2, analysed by Hackerman et al[8]. This compound is an electrical conductor[12,13]. On contrast, in potassium fluoride containing media, the analysis of the compound formed during electrochemical oxidation of nickel is K2NiF6[14] which is an insulating compound. Based on these literature data, we can assume that \( n_1 = n_2 = 2 \), i.e. the formation of Ni(II) (probably NiF2) and Ni(IV) (probably K2NiF6).
Kinetic constants (regression analysis of the steady state j-E curve).

The simplest mechanism corresponds to the oxidation of Ni into Ni(II) and subsequently into Ni(IV) coupled with the desorptions of this two species. The four kinetic steps may then be written as follows:

\[
\begin{align*}
\text{Ni, s} & \quad \leftrightarrow \quad \text{Ni(II), s} + 2e^- \\
\Gamma (1 - \theta_1 - \theta_2) & \quad k_{b1} \quad k_{f1} \quad \Gamma \theta_1 \\
\text{Ni(II), s} & \quad \leftrightarrow \quad \text{Ni(IV), s} + 2e^- \\
\Gamma \theta_1 & \quad k_{b2} \quad k_{f2} \quad \Gamma \theta_2 \\
\text{Ni(II), s} & \quad \rightarrow \quad \text{Ni(II)} + \text{s} \\
\Gamma \theta_1 & \quad K_1 \quad C_1 \quad \Gamma (1 - \theta_1 - \theta_2) \\
\text{Ni(IV), s} & \quad \rightarrow \quad \text{Ni(IV)} + \text{s} \\
\Gamma \theta_2 & \quad K_2 \quad C_2 \quad \Gamma (1 - \theta_1 - \theta_2)
\end{align*}
\]

where \( C_1 \) and \( C_2 \) are respectively the electrode concentrations of Ni(II) and Ni(IV), \( k_{b1}, k_{b2}, k_{f1} \) and \( k_{f2} \) are the forward and reverse rate constants for the two electrochemical steps; they are connected to the intrinsic rate constants \( k^o_1 \) and \( k^o_2 \) by:

\[
\begin{align*}
k_{b1} &= k^o_1 \exp \left( \frac{(1 - \alpha_1) n F}{R T} (E - E^o_1) \right) \quad (1) \\
k_{f1} &= k^o_1 \exp \left( -\frac{\alpha_1 n F}{R T} (E - E^o_1) \right) \quad (2)
\end{align*}
\]
where $\alpha_1$ and $\alpha_2$ are the charge transfer coefficients, $E^{\circ}_1$ and $E^{\circ}_2$ the standard potentials, respectively for the two electrochemical reactions, and $E$ the applied potential.

$\Gamma$ is the electroactive site number and $\theta_1$, $\theta_2$ are the fractional coverage of the electrode surface by Ni(II)ads and Ni(IV)ads respectively.

Because of the very large number of parameters involved (nine) to be determined, we have preferred instead of a direct simulation, to use a simplest and more systematic procedure for obtaining estimates of constants under consideration.

It was demonstrated elsewhere[3] that the steady state $j$-$E$ curve may be approximated by the following expressions:

\[
\begin{align*}
  j &= n \frac{F S \Gamma}{k_{b1}} \\
  j &= n \frac{F S \Gamma K_1 K_2 / k_{b2}}{k_{b2}} \\
  j &= 2 n \frac{F S K_2}{k_{b2}}
\end{align*}
\]

applying respectively to the increasing-current part, the decreasing-current part and to the constant-current part of the curve, when neglecting the reverse electrochemical reactions.
Defining \( k^*1 \) and \( k^*2 \) as:

\[
k^*1 = k^o1 \exp \left( \frac{(1 - \alpha_1) n F}{RT} \right) (-E^o_1) \quad (8)
\]

\[
k^*2 = k^o2 \exp \left( \frac{(1 - \alpha_2) n F}{RT} \right) (-E^o_2) \quad (9)
\]

and from (1) we can write:

\[
j = n F S \Gamma k^*1 \exp \left( \frac{(1 - \alpha_1) n F}{RT} \right) E
\]

or

\[
j = A \exp (BE)
\]

By fitting the first part of the experimental curve, we have found for \( A \) and \( B \) the values 2.12.10^{-4} and 15.44 which led for \( \Gamma k^*1 \) and \( \alpha_1 \) to the following values:

\[
\Gamma k^*1 = (1.10 \pm 0.05) \times 10^{-9} \text{ s}^{-1} \text{mol.cm}^{-2}.
\]

and

\[
\alpha_1 = 0.765 \pm 0.001
\]

In a similar manner, fitting the last part of the curve by applying (7) gives:

\[
\Gamma K_2 = (10.0 \pm 0.2) \times 10^{-11} \text{ s}^{-1} \text{mol.cm}^{-2}.
\]

and, the second part of the curve by applying (6) allows us to obtain the ratio \( K_1/k^*2 = (77 \pm 2) \) and \( \alpha_2 = 0.720 \pm 0.01 \)

Using these kinetic parameters, the steady state j-E curve was simulated (Fig. 4). We can observe a good fitting of the experimental data with the calculated curve, confirming the consistency of both the mechanism and the method used for obtaining the various parameters.
A.C. IMPEDANCE SPECTROSCOPY

Experimental data.

Impedance spectra were then performed in the three potential areas previously defined. For potential values ranging from -0.150 to 0.057 V the j-E curve exponentially increases and the impedance spectra show one or several capacitive loops (Fig.5a). When potentials ranged from 0.057 to 0.2 V (decreasing part of the j-E curve) the impedance spectra show a negative polarisation resistance (Fig.5b), and for potentials higher than 0.2 V (constant current density part) the spectra are characterized by a capacitive loop followed by a vertical line which corresponds to an infinite value of the polarisation resistance (Fig.5c).

In order to make easier the interpretation of the impedance spectra, we have considered the equivalent electrical circuit given in Fig.6 which takes into account the electrical properties of the Ni-layer (capacitance $C_C$ and resistance $R_C$) as usually considered\textsuperscript{15-17}, the faradaic impedance $Z_f$ and the double layer capacitance $C_d$ as well as the electrolyte resistance $R_e$.

Electrical properties of the Ni-layer formed.

Analysis of impedance spectra at high frequencies:
Ni-layer capacitance $C_C$.

The overall impedance $Z$ corresponding to the considered equivalent electrical circuit is given by:

$$Z = R_e + Z_1 + Z_2$$

$$Z = R_e + \frac{R_c}{1 + j\omega C_C R_C} + \frac{Z_f}{1 + j\omega C_d Z_f}$$

When the angular velocity $\omega \to \infty$, it is easy to demonstrate that the opposite of the imaginary part $Z_i$ of the impedance is practically equal to $1/\omega C_c$ when $C_d$ is higher than $C_C$ which has been verified a posteriori. In that case, the high frequency response has to be attributed only to the Ni-layer capacitance. A plot of $-Z_i$ vs. $1/\omega$ for the experimental data obtained at high frequencies leads to a straight line the slope of which (equal to $1/C_C$) giving the Ni-layer capacitance. Such plots obtained as a function of
potential are given in Fig.7. The values so derived for the Ni-layer capacitance were the reported in Fig.8a vs. the applied potential. We can notice a sharp decrease of the capacitance value when potential becomes higher than 0.1 V. From the potential dependence of the fractional coverages \( \theta_1 \) and \( \theta_2 \) giving by the following expressions\[^3\]:

\[
\theta_1 = \frac{k_{b1}K_2}{K_2(K_1 + k_{b2} + k_{b1}) + k_{b1}k_{b2}}
\]

\[
\theta_2 = \frac{k_{b1}k_{b2}}{K_2(K_1 + k_{b2} + k_{b1}) + k_{b1}k_{b2}}
\]

\[
(1 - \theta_1 - \theta_2) = \frac{K_2(K_1 + k_{b2})}{K_2(K_1 + k_{b2} + k_{b1}) + k_{b1}k_{b2}}
\]

we can notice (Fig.9b) that the nickel electrode is covered both by NiF\(_2\) (\( \theta_1 \)) and K\(_2\)NiF\(_6\) (\( \theta_2 \)) for potential values ranging from -0.30 V to 0.15 V. On the contrary, when the applied potential is higher than 0.15 V, the fractional coverage \( \theta_2 \) of K\(_2\)NiF\(_6\) tends to unity and the average value observed (5.3.10\^-6 F.cm\(^{-2}\)) may be attributed to the K\(_2\)NiF\(_6\) layer. The average capacitance value obtained for potentials lower than 0.15 V is higher (2.4.10\^-5 F.cm\(^{-2}\)) and by comparing with the Fig.8b, we can deduce that the capacitance of the NiF\(_2\) compound is likely higher than that of K\(_2\)NiF\(_6\).

Simulation of the experimental overall impedance :
Ni-layer resistance \( R_c \) and double layer capacitance.

The electrolyte resistance was determined by regression analysis of experimental data acquired at high frequencies. The value obtained is 3.85 \( \Omega \).cm\(^2\). The calculated faradaic impedance is given by \[^3\]:
The expression of $Z_f$ is then function of $\Gamma$, $k_1^*$, $k_2^*$, $K_1$, $K_2$, $\alpha_1$, $\alpha_2$, and $E$. We have noticed that the faradaic impedance value depends on all the preceding parameters itselfs excepted for $K_1$ and $k_2^*$ which intervene only by their ratio $K_1/k_2^*$. Besides, as the quantities $\Gamma k_1^*$, $\Gamma K_2$, $K_1/k_2^*$, $\alpha_1$
and $\alpha_2$ are known (see above), only $\Gamma$ remains to be varied for fitting the faradaic impedance.

For simulating the overall impedance we need also to know the values of the double layer capacitance $C_d$ and the Ni-layer resistance $R_c$ (the Ni-layer capacitance $C_c$ and the electrolyte resistance $R_e$ are known). Therefore, we have considered the three unknown parameters $\Gamma$, $C_d$ and $R_c$ as variables and determined their values leading to the best fitting of the experimental impedance spectra as a function of the applied potential $E$. This was obtained for the values reported in Table 1.

The resulting simulated spectra are represented Fig.9 to 11 and compared with the experimental data. Thus, we see that the simple mechanism we envisaged accounts pretty well for all our experiments performed at various potentials proving the consistency of the proposed model.

CONCLUSION

The electrochemical behaviour of nickel in the 2HF-KF mixture at 80°C may be described by a simple four step mechanism involving two adsorbed species and two desorption steps. Values of kinetic constants and electrical parameters have been determined by analysing both the steady state voltammogram and impedance spectra. Works are in progress to use these values for simulating the experimental cyclic voltammograms.

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Table 1: Values of $C_d$ and $R_c$ derived from the simulation of experimental impedance spectra.

| E (V) | $C_d$ (F/cm²) | $R_c$ (Ω.cm²) |
|-------|---------------|---------------|
| -0.25 | $2.9 \times 10^{-4}$ | 1350          |
| -0.15 | $2.6 \times 10^{-4}$ | 1800          |
| -0.1  | $1.3 \times 10^{-4}$ | 720           |
| 0.1   | $3 \times 10^{-4}$ | 160           |
| 0.12  | $1.25 \times 10^{-4}$ | 250          |
| 0.14  | $7 \times 10^{-5}$ | 700           |
| 0.5   | $4 \times 10^{-3}$ | 3100          |
| 0.8   | $3.7 \times 10^{-3}$ | 3600         |
Fig. 1: a) Typical chronoamperograms obtained on a nickel electrode in the 2HF-KF mixture at 80°C. (curve A : $E = -0.250 \text{ V}$; curve B : $E = -0.100 \text{ V}$; curve C : $E = 0.020 \text{ V}$)
b) Sampled-current voltammogram derived from chronoamperograms represented Fig. 1a, with a sample time of 20 mn.
Fig. 2: Linear sweep voltammograms obtained on a nickel electrode in the 2HF-KF mixture at 80°C with various voltage sweep rates:
a = 0.005 V.s⁻¹, b = 0.02 V.s⁻¹, c = 0.05 V.s⁻¹.
Fig. 3: Linear sweep voltammograms obtained on a nickel electrode in the 2HF-KF mixture at 80°C with various voltage sweep rates: 
1 = 0.4 \text{ V.s}^{-1}, \ 2 = 0.8 \text{ V.s}^{-1}, \ 3 = 1 \text{ V.s}^{-1}, \ 4 = 4 \text{ V.s}^{-1}, \ 5 = 6.5 \text{ V.s}^{-1}.
Fig. 4: Steady state j-E curve of Ni electrochemical oxidation in the 2HF-KF mixture at 80°C:
- : experimental data.
-- : simulated curve (see text).
Fig. 5: A.C. Impedance spectroscopy in the 2HF-KF mixture at 80°C: Nyquist plots obtained with a working Ni electrode at various applied potentials. 1st frequency: $10^5$ Hz, □: 10 Hz, ◇: 1 Hz, △: 0.1 Hz; last frequency: 0.01 Hz.
Fig. 6: Equivalent electrical circuit.

Fig. 7: Determination of the Ni-layer capacitance. Plots of $-Z_i$ vs. $1/\omega$ for high frequency data obtained at various applied potentials ($S = 1 \text{ cm}^2$).
Fig. 8:  
(a) Plot of the Ni-layer capacitance vs. applied potential. 
(b) Potential dependence of the fractional coverages $\theta_1$ and $\theta_2$. 

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Fig. 9: Impedance spectrum obtained on a nickel electrode in the 2HF-KF mixture at 80°C (applied potential: -0.1 V)

- : experimental data.
— : simulated curve.
Fig. 10: Impedance spectrum obtained on a nickel electrode in the 2HF-KF mixture at 80°C (applied potential: 0.1 V)
- : experimental data.
— : simulated curve.
Fig. 11: Impedance spectrum obtained on a nickel electrode in the 2HF-KF mixture at 80°C (applied potential: 0.5 V)
- : experimental data.
— : simulated curve.