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# Determination of the diffusion coefficient of an inserted species by impedance spectroscopy: application to the $H/H_xNb_2O_5$ system

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Impedance spectroscopy, unlike large signal methods, allows the diffusion coefficient of an inserted species to be determined as a function of the electrode potential. The expression for the restricted linear diffusion impedance may be modified to empirically account for the difference of the electrochemical system behaviour from the ideal. It is then possible to estimate the diffusion coefficient of the inserted species from characteristic frequencies on the Nyquist diagrams and/or from the frequencies corresponding to the intersection of the asymptotes of the $\log(-\mathrm{Im}\,Z)$, $\log f$ graphs. These estimations are independent of assumptions concerning the active area of the electrode. The method has been applied to the study of hydrogen insertion in $H_xNb_2O_5$.

## 1. Introduction

The expression for the impedance of restricted linear diffusion of a species in a thin film has been established by various authors investigating insertion reactions [1–5] or reactions on polymer film coated electrodes [6–9]

$$Z = R\coth(\mathrm{j}\nu)^{1/2}/(\mathrm{j}\nu)^{1/2} \qquad (1)$$

where:

$$R = \frac{1}{FA(D/l)\,|\,\mathrm{d}C_{\mathrm{eq}}/\mathrm{d}E|} \qquad (2)$$

where $\mathrm{j} = (-1)^{1/2}$, $\nu$ designates the reduced frequency $\nu = 2\pi f l^2/D$ and $A$ is the active area of the electrode, $l$ the thickness of the film and $D$ the species chemical diffusion coefficient. $\mathrm{d}C_{\mathrm{eq}}/\mathrm{d}E$ corresponds to the equilibrium concentration variation of the species versus the electrode voltage at the polarization point where the impedance measurements are made.

The $Z/R$ impedance graph in the Nyquist plane is shown in Fig. 1a. It has been shown [2,5,7,9] that the diffusion impedance can be approximated by the Warburg impedance in the high frequency (HF) range:

$$Z_{\mathrm{HF}} = R/(\mathrm{j}\nu)^{1/2} = R(1-\mathrm{j})/(2\nu)^{1/2} \qquad (3)$$

and, in the low frequency (LF) range, by the impedance

$$Z_{\mathrm{LF}} = R[(1/3) - (\mathrm{j}/\nu)] \qquad (4)$$

equivalent to that of an electrical circuit consisting of a resistance with a value $R/3$ in series with a capacitance with a value $l^2/(DR)$.

## 2. Measuring the diffusion coefficient of an inserted species for an "ideal" electrochemical system

Equations 1–4 allow the chemical diffusion coefficient of an inserted species to be determined using experimental impedance measurements when the system studied behaves as shown in Fig. 1a.

Ho *et al.* [2] used the frequency distribution along the Warburg straight line to calculate the diffusion coefficient of lithium in $WO_3$ on the basis of the slopes of straight lines $\mathrm{Re}\,Z_{\mathrm{HF}}, f^{1/2}$ and $-\mathrm{Im}\,Z_{\mathrm{HF}}, f^{1/2}$. Armstrong *et al.* [8] used the same method to measure the apparent coefficient of diffusion in a poly(4-vinylpyridine) film containing the species $IrCl_6^{2-}$ and $IrCl_6^{3-}$. In both cases, an estimation of the active area of the electrode is necessary to obtain the diffusion coefficient value.

A second method consists in determining a characteristic frequency on the impedance graph. Armstrong [7] chose the reduced frequency $\nu_1 = 2\pi f_1 l^2/D = 5.12$ corresponding to the point at which the slope of the impedance graph in the Nyquist plane is 2, which allows the diffusion coefficient to be determined from the measurement of the corresponding frequency $f_1$,

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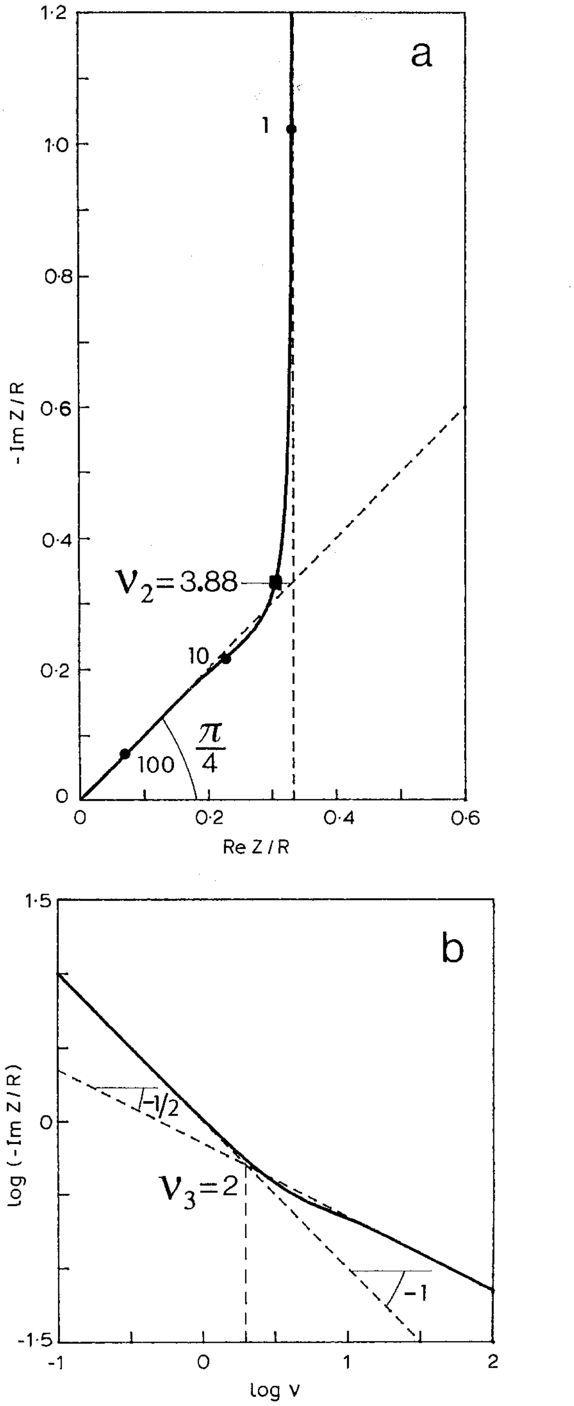

Fig. 1. Graphs of the restricted linear diffusion impedance $Z/R$. (a) Nyquist plane, $(2\pi f l^2/D$ values indicated on the graph); (b) $\log(-\mathrm{Im}\,Z/R)$, $\log(2\pi f l^2/D)$ graph.

using the equation

$$D = \pi f_1 l^2/2.56 \qquad (5)$$

We proposed [5,10] the reduced frequency choice of $\nu_2 = 3.88$ for which $\mathrm{Im}\,Z = -R/3$ (Fig. 1a), the value of $D$ then being deduced from the measurement of the corresponding frequency $f_2$ as follows:

$$D = \pi f_2 l^2/1.94 \qquad (6)$$

A graphical method, which has apparently not been published, consists in plotting the logarithm of the imaginary part of the impedance, with the sign changed, against the logarithm of frequency. The graph exhibits two asymptotes with slopes $-1$ and $-1/2$ at low and high frequency respectively (Fig. 1b). The intersection of the two asymptotes defines the reduced frequency $\nu_3 = 2$, which allows $D$ to be determined from the measurement of the corresponding frequency $f_3$, as follows:

$$D = \pi f_3 l^2 \qquad (7)$$

The calculation of the diffusion coefficient using Equations 5–7 requires no assumptions as to the value of the active area of the electrode and the nature of the insertion isotherm, but implies knowledge of the thickness, $l$, of the thin film.

Another method consists finally in identifying the experimental impedance results with theoretical expression 1 throughout the total frequency range. This method was used by Randin and Viennet [11] to measure the diffusion coefficient of hydrogen in $WO_3$.

## 3. Measuring the diffusion coefficient of an inserted species for a real electrochemical system: $H/H_xNb_2O_5$

Experimental impedance measurements show that the behaviour of electrochemical systems exhibiting an insertion reaction sometimes differ from the theoretical behaviour expressed by Equation 1. The impedance graph in the Nyquist plane thus does not always exhibit a Warburg straight line in the high frequency range, nor a vertical line in the low frequency range.

Figure 2a shows, for example, a characteristic diagram of hydrogen insertion in a thin film of $Nb_2O_5$ prepared at the Centre de Recherches sur les Très Basses Températures de Grenoble. The oxide was prepared as follows. A $NbN_x$ thin film was sputtered on antimony-doped $SnO_2$ which was first deposited on glass substrate. Oxidation in air for 2 h at 300° C entirely transforms the film to amorphous $Nb_2O_5$. Sample preparation details and physical properties of the oxide film have been described elsewhere [10,12].

The reaction $Nb_2O_5 + xH^+ + xe^- \Leftrightarrow H_xNb_2O_5$ modifies the optical properties of this oxide in the visible range and thus endows it with attractive electrochromic properties [10,13].

Other examples of experimental impedance diagrams which differ from the theoretical diagram shown in Fig. 1a have been published in the literature concerning insertion of hydrogen in $WO_3$ [11], insertion of lithium in $V_2O_5$ [14] or the reactions on polymer film coated electrodes [8,9].

In Fig. 2b, the logarithms of $\mathrm{Re}\,Z - R_0$ and $-\mathrm{Im}\,Z$ are plotted against the logarithm of frequency. The graphs obtained at low frequency are straight lines with a slope $-0.88$. This leads to the following expressions:

$$\mathrm{Re}\,Z_{\mathrm{LF}} = R_0 + K\cos(\alpha\pi/2)/f^{\alpha} \qquad (8)$$

$$\mathrm{Im}\,Z_{\mathrm{LF}} = -K\sin(\alpha\pi/2)/f^{\alpha} \qquad (9)$$

where $K$ is a constant and $\alpha = 0.88$.

In the low frequency range, the electrode impedance is not equivalent to that of the resistance, capacitance circuit given by Equation 4, but to that of a constant phase element (CPE) [15] in series with the resistance

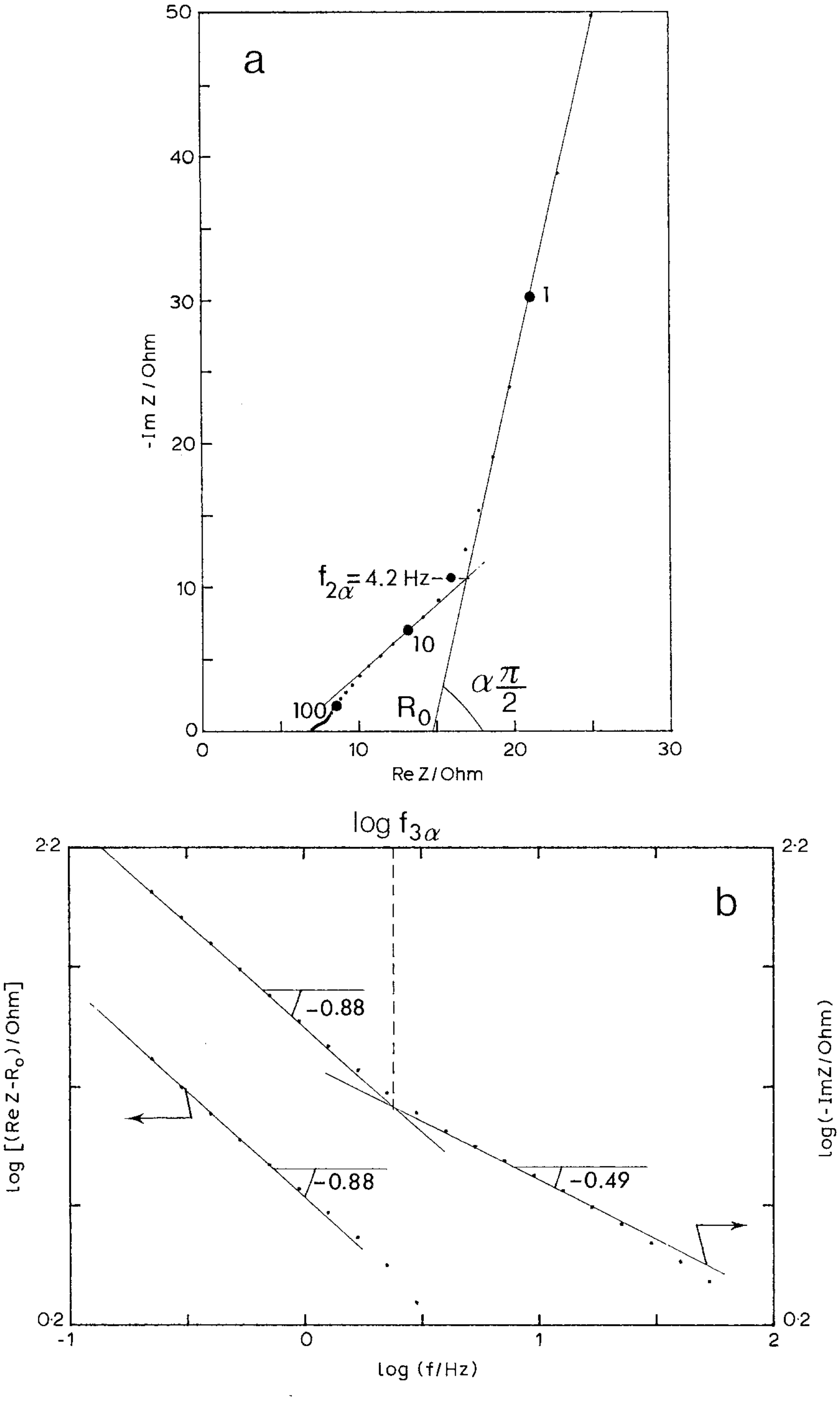

Fig. 2. Graphs of the impedance of a 1.5 $\mu$m film of $H_xNb_2O_5$ ($x = 7 \times 10^{-4}$) in a de-aerated solution of $H_2SO_4$M at 20° C at a voltage of $-325$ mV/SCE. (a) Nyquist plane; (frequency values in hertz indicated on the graph); (b) $\log(-\mathrm{Im}\,Z)$ and $\log(\mathrm{Re}\,Z - R_0)$, $\log f$ graphs.

$R_0$. Thus,

$$Z_{\mathrm{LF}} = R_0 + K/(\mathrm{j}f)^{\alpha} \qquad (10)$$

The presence of a CPE in the equivalent electrical circuit of an electrode has often been found experimentally and attributed to distributions [15], porosity effects [16] or fractal geometry effects [17,18]. However, to our knowledge, no model exists allowing the impedance diagrams of Fig. 2a,b to be interpreted throughout the total frequency range.

The $\log(-\mathrm{Im}\,Z)$, $\log f$ graph of Fig. 2b exhibits two asymptotes with slopes $-0.88$ and $-0.49$ at low frequency and high frequency, respectively. The ratio of the slopes remains near to two, a value which corresponds to the theoretical case of Fig. 1b. The diffusion impedance can thus be approximated by the empirical expression

$$Z_{\alpha} = R \coth(\mathrm{j}\nu)^{\alpha/2}/(\mathrm{j}\nu)^{\alpha/2} \qquad (11)$$

the ideal behaviour of the electrochemical system corresponding to $\alpha = 1$ and its real behaviour to $\alpha < 1$.

The graph of $Z_{\alpha}/R$ in the Nyquist plane (Fig. 3a) exhibits a linear asymptote at high frequency or pseudo Warburg straight line of slope $\mathrm{tg}(\alpha\pi/4)$ and another linear asymptote of slope $\mathrm{tg}(\alpha\pi/2)$ at low frequency such that:

$$Z_{\alpha\mathrm{HF}} = R[\cos(\alpha\pi/4) - \mathrm{j}\sin(\alpha\pi/4)]/\nu^{\alpha/2} \qquad (12)$$

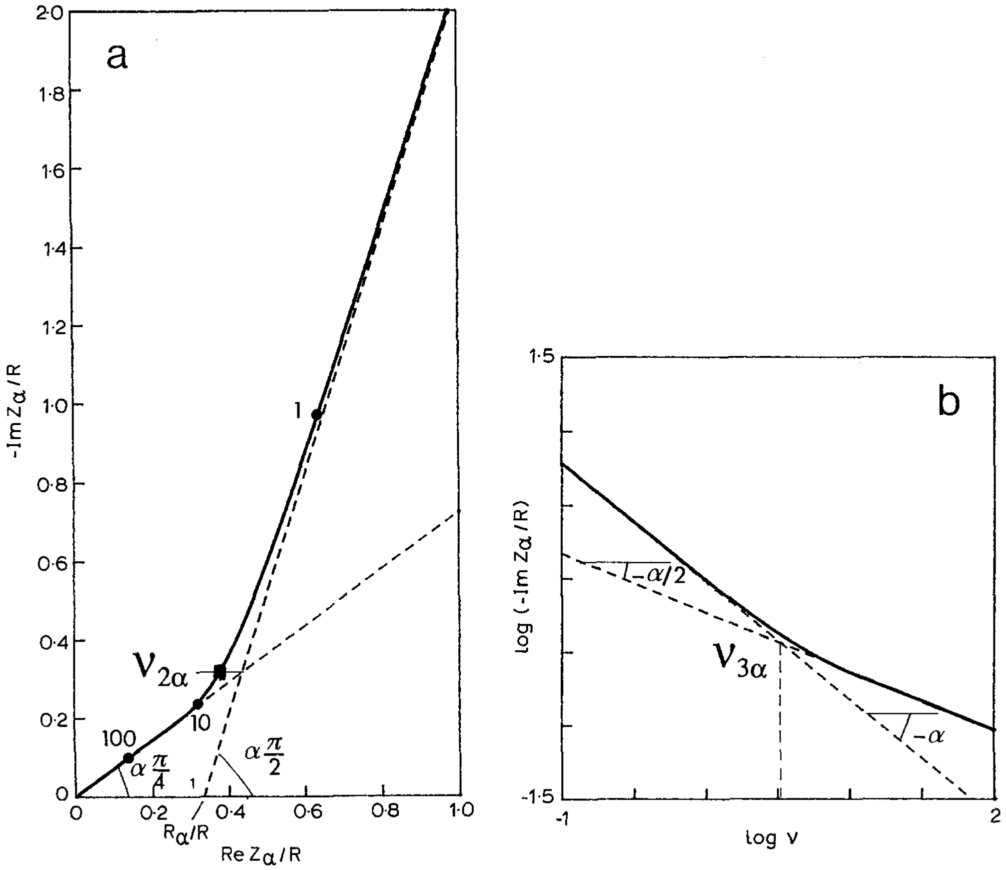

Fig. 3. Graphs of the modified restricted linear diffusion impedance $Z_\alpha/R$ plotted for $\alpha = 0.8$. (a) Nyquist plane, $(2\pi f l^2/D$ values indicated on the graph); (b) $\log(-\operatorname{Im} Z_\alpha/R)$, $\log(2\pi f l^2/D)$ graph.

$$\begin{aligned}\operatorname{Re} Z_{\alpha\mathrm{LF}} &= R_\alpha + R\cos(\alpha\pi/2)/\nu^\alpha;\\ \operatorname{Im} Z_{\alpha\mathrm{LF}} &= -R\sin(\alpha\pi/2)/\nu^\alpha \qquad (13)\\ R_\alpha &= (2R/3)[\cos(\alpha\pi/4)^4 + \sin(\alpha\pi/4)^4]\\ &\quad - (R/3)\cos(\alpha\pi/2)^2 \qquad (14)\end{aligned}$$

It is possible to determine on the impedance graphs the characteristic reduced frequency $\nu_{2\alpha}$ defined in the Nyquist plane (Fig. 3a) and the frequency $\nu_{3\alpha}$ corresponding to the intersection of the LF and HF asymptotes of the $\log(-\operatorname{Im} Z_\alpha)$, $\log \nu$ graph of Fig. 3b.

The reduced frequency $\nu_{2\alpha}$ (Fig. 3a) has no analytical expression and its values calculated numerically are plotted in Fig. 4 against $\alpha$. A first estimation of the diffusion coefficient of the inserted species can thus be drawn from the measurement of the frequency $f_{2\alpha}$ in Fig. 2a, as

$$D = 2\pi f_{2\alpha} l^2/\nu_{2\alpha} \qquad (15)$$

The reduced frequency $\nu_{3\alpha}$ (Fig. 3b) can be expressed analytically as

$$\nu_{3\alpha} = [2\cos(\alpha\pi/4)]^{2/\alpha} \qquad (16)$$

from which a second estimation of the diffusion coefficient value can be deduced from the measurement of the characteristic frequency $f_{3\alpha}$ of Fig. 2b. Thus,

$$D = 2\pi f_{3\alpha} l^2/[2\cos(\alpha\pi/4)]^{2/\alpha} \qquad (17)$$

The estimations of $D$ expressed by Equations 6 and 7 can of course be confirmed by setting $\alpha = 1$ in Equations 15 and 17.

The values of the chemical diffusion coefficient of H in $H_xNb_2O_5$ calculated using Equations 15 and 17 on the basis of the graphs of Fig. 2a,b and similar graphs plotted at various electrode voltages are given in Table 1. The thickness of the oxide film was determined by an optical method, using the variation of the optical transmission coefficient of the film with wavelength [12,19]. The value for $\alpha$ was taken as the average of the values $\alpha_{\mathrm{HF}}$ and $\alpha_{\mathrm{BF}}$ given by the slopes of the HF and BF asymptotes of the $\log(-\operatorname{Im} Z)$, $\log f$ graphs. The values of the diffusion coefficient derived from

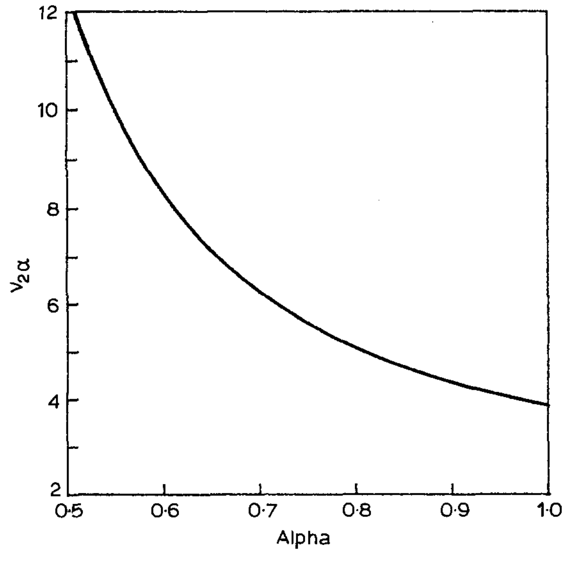

Fig. 4. Variation of the characteristic reduced frequency $\nu_{2\alpha}$ with the parameter $\alpha$.

*Table 1. Values of the chemical diffusion coefficient of H in $H_xNb_2O_5$ calculated by approximating the real behaviour of the electrochemical system*

| $E$ (mV/SCE) | $f_{2\alpha}$ (Hz) | $f_{3\alpha}$ (Hz) | $\alpha$ | $D$(cm$^2$ s$^{-1}$) | |
|---|---|---|---|---|---|
| | | | | Eq. 15 | Eq. 17 |
| −325 | 4.20 | 2.40 | 0.93 | $1.4 \times 10^{-7}$ | $1.4 \times 10^{-7}$ |
| −350 | 3.30 | 2.10 | 0.89 | $1.1 \times 10^{-7}$ | $1.2 \times 10^{-7}$ |
| −400 | 2.24 | 1.30 | 0.86 | $6.9 \times 10^{-8}$ | $6.5 \times 10^{-8}$ |
| −450 | 1.26 | 0.80 | 0.83 | $3.7 \times 10^{-8}$ | $3.7 \times 10^{-8}$ |
| −500 | 0.80 | 0.60 | 0.79 | $2.2 \times 10^{-8}$ | $2.5 \times 10^{-8}$ |
| −550 | 0.53 | 0.43 | 0.75 | $1.4 \times 10^{-8}$ | $1.6 \times 10^{-8}$ |

Equations 15 and 17 show good agreement (relative difference less than 15%).

The logarithms of these values are plotted in Fig. 5 against the equilibrium concentration $C_{eq}$ of hydrogen in the oxide and versus the insertion fraction $x$. $C_{eq}$ is calculated by integrating the function $dC_{eq}/dE$ deduced, using Equations 2 and 13, from the measurements of the imaginary parts of the electrode impedance at low frequency. Assuming that one H by one Nb atom can be inserted at the most and taking $\rho_{Nb2O5} = 4.5\,g\,cm^{-3}$, the maximum equilibrium concentration of H in $Nb_2O_5$ is $C_{max} = 3.3 \times 10^{-2}\,mol\,cm^{-3}$ and the insertion fraction $x$ is defined as $x = C_{eq}/C_{max}$.

The diffusion coefficient of hydrogen decreases sharply when its equilibrium concentration increases in the oxide. This variation of $D$ agrees with that observed by Gomes *et al.*, using a chronopotentiometric method, for hydrogen insertion in a $Nb_2O_5$ film obtained by thermal oxidation of niobium [20].

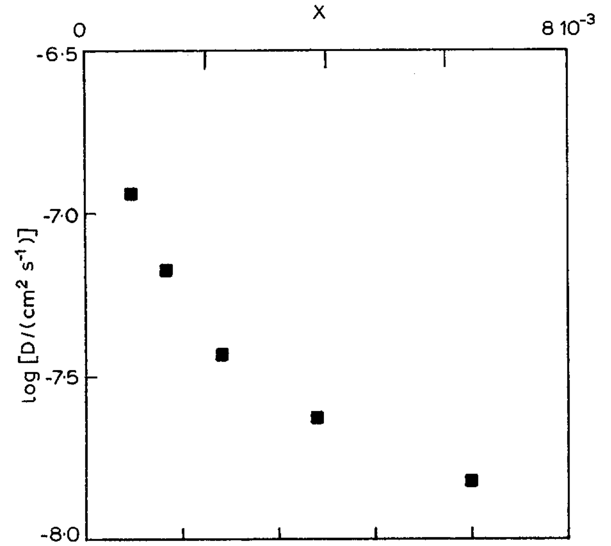

Fig. 5. Variation of the logarithm of the chemical diffusion coefficient of hydrogen in $H_xNb_2O_5$ against its equilibrium concentration and the insertion fraction $x$.

The same phenomenon has been observed for the diffusion of lithium in $V_2O_5$ [14].

## 4. Conclusion

The impedance measurements made on a thin film insertion electrode have enabled us to determine the chemical diffusion coefficient of the inserted species using the values of the characteristic frequency of impedance diagrams plotted in the Nyquist plane and the values of the intersection frequency of the low and high frequency asymptotes of the $\log(-\mathrm{Im}\,Z)$, $\log f$ graphs.

These measurements are independent of any assumptions as to the active area of the electrode and the nature of the electroinsertion isotherm; they only require knowledge of the thickness of the thin film.

The two methods for determining the diffusion coefficient can be applied directly when the behaviour of the electrochemical system is ideal. When the real behaviour of the system studied differs from the ideal behaviour, it is possible to put forward an empirical expression for the restricted linear diffusion impedance thereby generalizing previous methods.

These methods have been applied to studying the diffusion of H in a thin layer of $H_xNb_2O_5$, the thickness of which was measured optically. It has been shown that, in the low concentration range ($x < 10^{-2}$), the diffusion coefficient of hydrogen decreases sharply when its concentration in the oxide increases.

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