

Short communication

Oxygen reduction on platinum electrode coated with Nafion®

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Abstract

The kinetics of the reduction of oxygen on platinum covered by a Nafion® film in sulfuric acid (0.5 M) has been studied in order to determine to what extent the solid polymer electrolyte modifies this reaction. As electrode we used a rotating electrode which is particularly well adapted to the measurement of the permeability $D_f C_f$ (product of the diffusion coefficient and of the oxygen concentration in the film) of oxygen in the Nafion® film. This product is of the order of $6 \times 10^{-12} \text{ M cm}^{-1} \text{ s}^{-1}$ whatever the state of division of the platinum, and is of the same order of magnitude as the permeability $D_s C_s$ of oxygen in the adjacent sulfuric acid solution. It is shown, moreover, that the oxygen concentration in the film is very high, about five times that in the solution.

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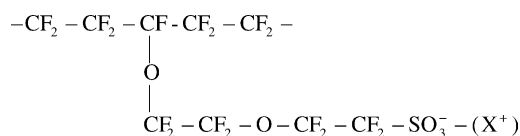
Keywords: PEMFC; Oxygen reduction; Rotating disk electrode; Nafion®

1. Introduction

A fuel cell (PEMFC) consists of two electrodes separated by a solid electrolyte: the negative electrode (anode) is supplied with a fuel (hydrogen, methanol, etc.); and the positive one (cathode) with a comburant (oxygen, air, etc.).

The electrolyte is a membrane consisting of a proton-conducting organic polymer. The most used membranes consist of a skeleton of polytetrafluorocarbon chains bearing acid groups statistically distributed along the chain.

The electrolyte used in this work is Nafion® whose chemical configuration is represented as follows [1]:



Nafion® membran structure

Nafion® is a cation-exchange membrane used in different electrochemical systems because of its selectivity, chemical and thermal stability, and high proton conductivity [2].

The main aim of this work is to improve the performances of fuel cells and of the cathode in particular, by optimizing the interface between the solid electrolyte and the platinum.

In this work we shall determine the concentration and the diffusion coefficient of oxygen in a Nafion® film deposited on platinum for different states of division of the latter.

2. Study of the reduction of dissolved oxygen on platinum either bare or covered with Nafion® film

2.1. Measurement of the permeability of oxygen through a Nafion® film

The best electrochemical method adapted to this study is based on the use of a rotating electrode which readily gives information about the activity of the platinum catalyst, either bare or covered with a Nafion® film, upon the kinetics of oxygen reduction, without the need to construct an element of a fuel cell [3].

To perform this study we use a glass cell with five ground-glass sockets for the reference electrode (saturated calomel), the counter-electrode (platinum wire), a gas circulation system to saturate the electrolyte, a thermocouple and the working electrode (EDT); this latter consists of a smooth platinum disc 2 mm in diameter. The regulating system (Tacussel CTV 101T) allows the rotation speed of the disc to be varied from 0 to 5000 rpm.

The electrolyte solution (0.5 M H₂SO₄), is a commercial product (Merck Eurolab). The Nafion® deposit is obtained from a 5% (w/w) solution of Nafion® (Aldrich).

In order to obtain a planar surface the platinum electrode is lightly polished with emery cloth, cleaned with acetone,

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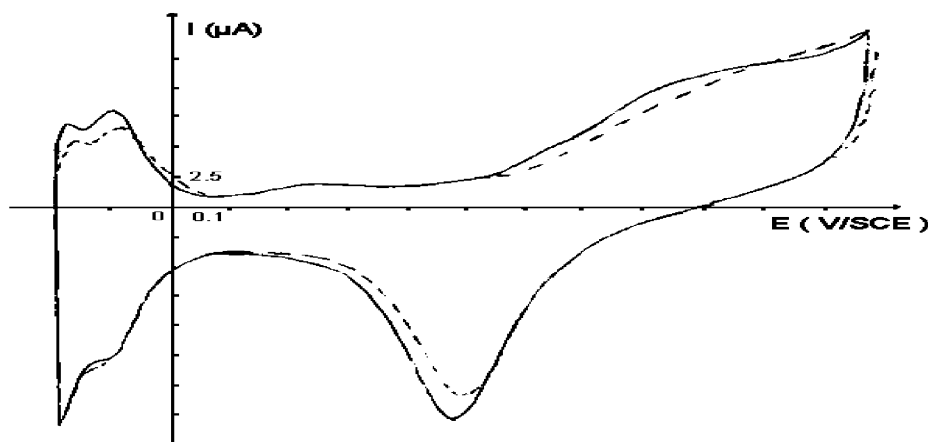


Fig. 1. Voltammogram for bare platinum (—) and for platinum covered with a Nafion[®] film (---) at room temperature in argon-saturated 0.5 M H₂SO₄ with a sweep rate of 100 mV s⁻¹.

then rinsed in distilled water and finally electrolytically polished by repeated cycling between -0.2 and 1.2 V/SCE to minimize the effects of impurities during the measurements.

The Nafion[®] film is applied by depositing a known volume of the 5% solution by means of a microsyringe. The electrode thus covered with Nafion[®] film is then dried at room temperature for 1 h.

The thickness of the film is calculated by taking into account the volume of the drop, the density of the Nafion[®] solution and the area of the electrode.

Fig. 1 shows the voltammograms obtained in argon-saturated 0.5 M H₂SO₄ on bare platinum and on platinum covered with a Nafion[®] film.

The voltammogram obtained (Fig. 1) under these conditions with a sweep rate of 100 mV s⁻¹ is identical to that given in the literature [4–7]; the area of platinum really active is calculated from the areas of the hydrogen adsorption/desorption peaks. This area is defined as the amount of electricity $Q = \int I dt$ associated with the adsorption or the desorption of hydrogen compared to the theoretical amount of electricity ($Q^\circ = 210 \mu\text{C cm}^{-2}$) corresponding to an electrode of unit area (roughness factor = 1) assuming an adsorption of one hydrogen atom per platinum atom [8]. The roughness factor (f), defined as the ratio of the true active surface area to the apparent geometric area ($f = S_{\text{real}}/S_{\text{apparent}}$), is of the order of 3.

The voltammogram obtained for platinum covered with a Nafion[®] film is similar to that for bare platinum, the essential difference being that the hydrogen adsorption/desorption peaks are weaker, which indicates that some active sites have been filled in by the Nafion[®]. In the literature the proportion of active sites blocked by Nafion[®] ranges from 15 to 20% [3]. The fact that peaks remain in the presence of polymer indicates that the mechanisms of H⁺ ion adsorption/desorption have not been substantially modified.

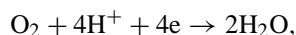
To study the kinetics of the reduction of oxygen on platinum we have used a rotating electrode immersed in

oxygen-saturated 0.5 M H₂SO₄, saturation being achieved by bubbling oxygen for 40 min. A potential varying from 1 to -0.2 V/SCE is applied to the electrode at a sweep rate of 50 mV s⁻¹ [3]. Throughout the experiment the electrolyte remains in an atmosphere of oxygen. The voltammogram (Fig. 2a) shows a plateau corresponding to the limiting diffusion current, which increases with the rotation speed of the electrode.

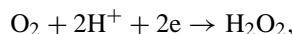
The Nafion[®]-covered electrode gives the voltammogram shown in Fig. 2b. The two voltammograms are similar but the height of the diffusion plateau is lower in the presence of Nafion[®].

Despite the fact that the limiting currents are different, the two voltammograms suggest that the reduction of oxygen follows the same mechanism in both cases [3].

Oxygen can be reduced in acid in the presence of platinum by the following two overall reactions:



$$E^\circ = 1.23 \text{ V/ENH (1)}/0.98 \text{ V/SCE}$$



$$E^\circ = 0.67 \text{ V/ENH (2)}/0.42 \text{ V/SCE}$$

The role of the catalyst is to favor the formation of water (reaction 1) relative to that of hydrogen peroxide (reaction 2). The thickness of the diffusion layer for a rotating disc electrode is inversely proportional to the square root of the rotation speed. The expression for the limiting diffusion current density obey the Levich's Law:

$$J_D = 0.62 n_e F D^{2/3} v^{-1/6} C \omega^{1/2} \quad (3)$$

$$J_D = B \omega^{1/2} \quad (4)$$

where n_e is the number of electron; F , the Faradic coefficient; D , the diffusion coefficient of oxygen in the solution; v , the kinematic viscosity; C , the oxygen concentration in the bulk and $B = 0.62 n_e F D^{2/3} v^{-1/6} C$.

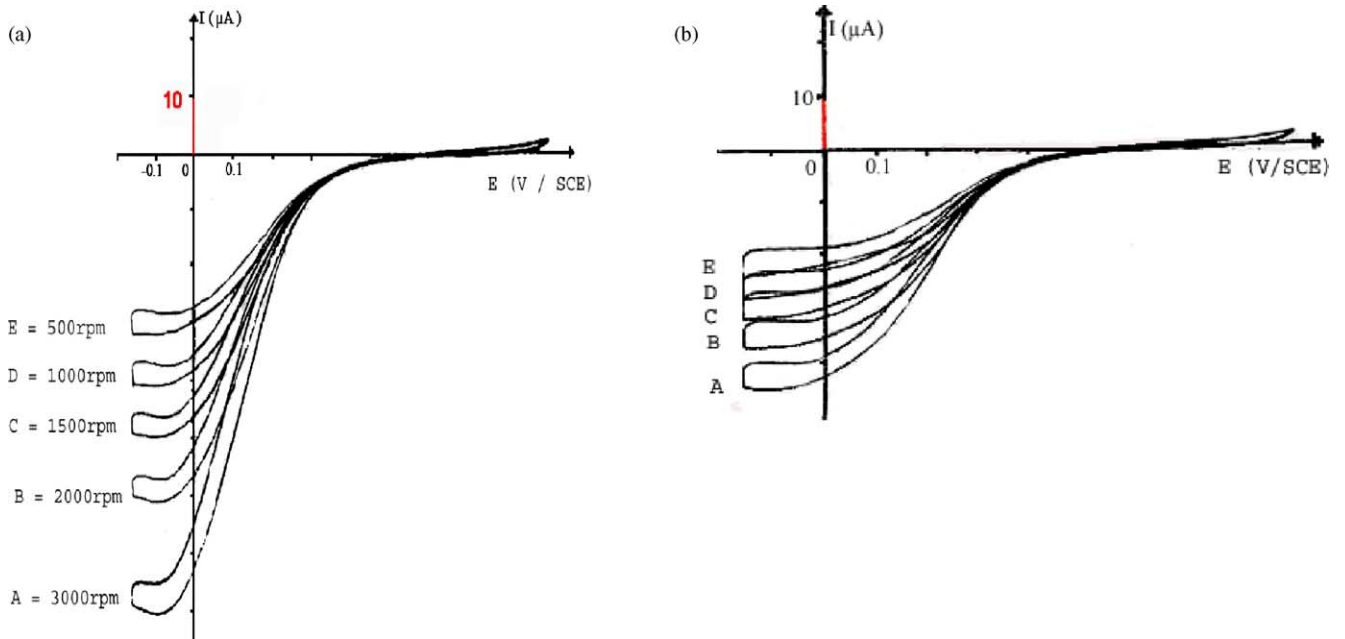


Fig. 2. (a) Voltammogram for O₂ reduction on bare platinum; (b) voltammogram for O₂ reduction on Nafion[®]-covered platinum.

In the presence of a polymer film on the electrode surface the equation for the current density becomes [3–6] (Koutecky–Levich Law)

$$\frac{1}{J} = \frac{1}{J_f} + \frac{1}{J_D} \tag{5}$$

with $J_f = n_e F D_f C_f / \delta_f$ which gives:

$$\frac{1}{J_f} = \frac{\delta_f}{n_e F D_f C_f} + \frac{1}{B} \omega^{-1/2} \tag{6}$$

where D_f is the diffusion coefficient of oxygen in the solution; C_f , the oxygen concentration in the bulk; and δ_f , the thickness of the Nafion[®].

By applying the Koutecky–Levich Law (Eq. (6)), one obtains parallel straight lines, as shown in Fig. 3.

Extrapolation of these lines to the origin allows us to determine the value of the product $D_f C_f$ (oxygen permeabil-

ity in Nafion[®]) which is close to $6 \times 10^{-12} \text{ M cm}^{-1} \text{ s}^{-1}$ at ambient temperature whatever the film thickness.

The effect of the state of division of the platinum (platinized platinum) on the oxygen reduction kinetics was also studied. Platinum was electrodeposited on glassy carbon EDT using a 1% solution of hexachloroplatinic acid (platinum tetrachloride) $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The electrode is then rinsed with distilled water, and the electrolysis is completed with a 5% solution of sulfuric acid for 5 min to eliminate impurities, before a final rinse with distilled water. The whole operation is carried out at ambient temperature with a current density of 25 mA cm^{-2} . To determine the permeability $D_f C_f$ of oxygen in the Nafion[®] film the same operating conditions are used as for smooth platinum.

With an argon-saturated 0.5 M H_2SO_4 solution the voltammogram in Fig. 4 is obtained. The roughness factor, measured from the area under the hydrogen adsorption/

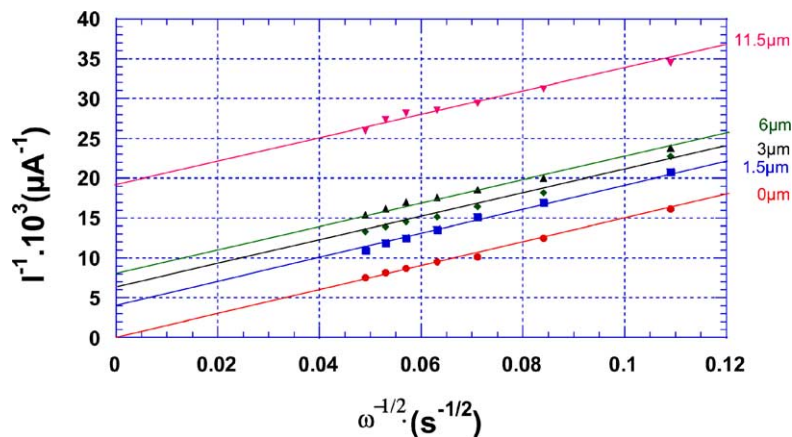


Fig. 3. Dependence of Koutecky–Levich plots on the thickness of Nafion[®] film.

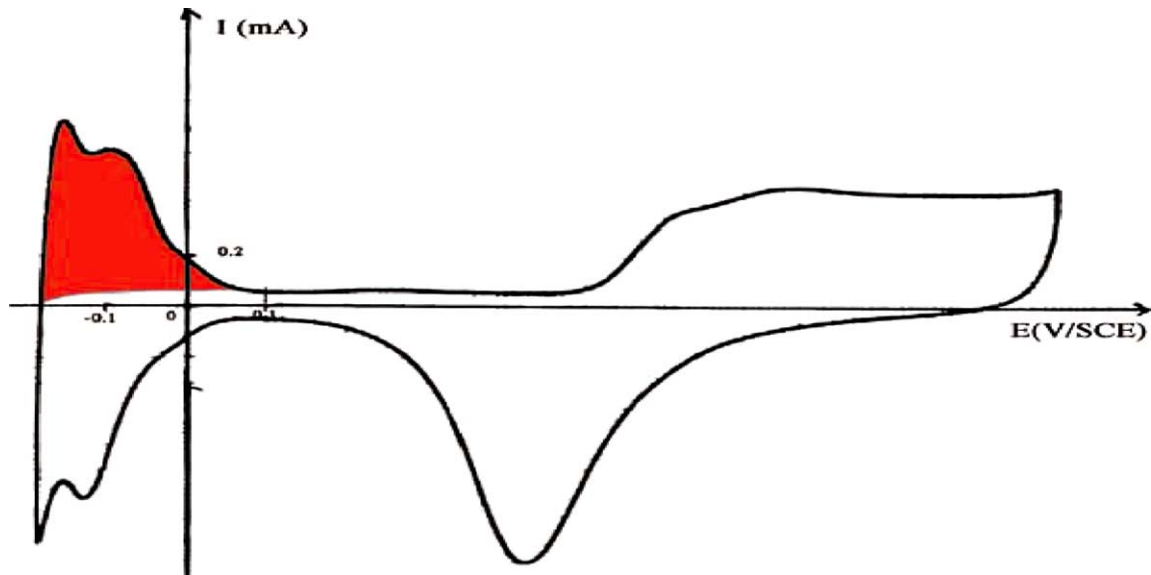


Fig. 4. Voltammogram for platinized platinum in 0.5 M H₂SO₄ at room temperature.

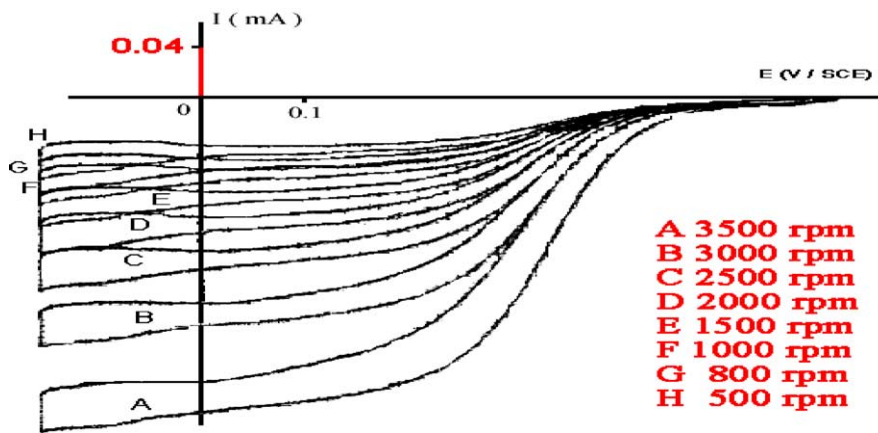


Fig. 5. Voltammogram for platinized platinum corresponding to the reduction of dissolved oxygen.

desorption peaks, is 160. As for smooth platinum, the reduction of oxygen leads to the voltammogram in Fig. 5; it is seen that the limiting currents also follow the Koutecky–Levich Law (Fig. 6).

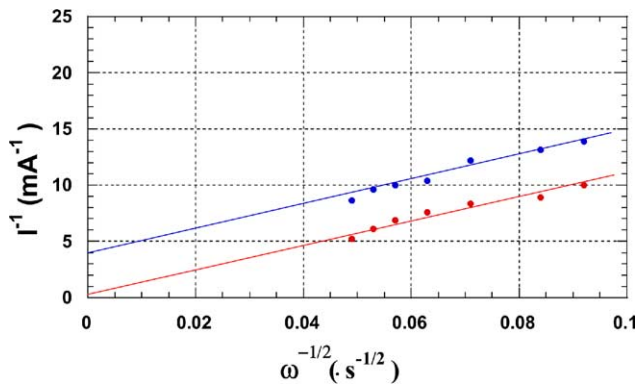


Fig. 6. Koutecky–Levich plots for platinized platinum.

It is observed that whatever is the mass of electrodeposited platinum the currents have similar value, which means that the kinetic of oxygen reduction is independent of the amount of platinum. As can be seen in Fig. 7, the areas involved in the reduction of oxygen (S_{O_2}) and in the oxidation of hydrogen (S_{H_2}) differ depending on the amount of platinum electrodeposited.

The following scheme offers an explanation how to show that S_{H_2} is greater than S_{O_2} and that S_{O_2} is practically independent of the amount of platinum deposited.

The reduction of dissolved oxygen only occurs on the external surface of the platinum exposed to the solution, whereas the oxidation of dissolved hydrogen takes place in depth over the entire platinum surface, since it has been generated by electrolysis.

By means of a dissolved oxygen meter MO 128 (Mettler) the concentration of oxygen dissolved in the solution (C_s) is measured and, from the literature value of the diffusion coefficient of oxygen in the solution (D_s), it is found that

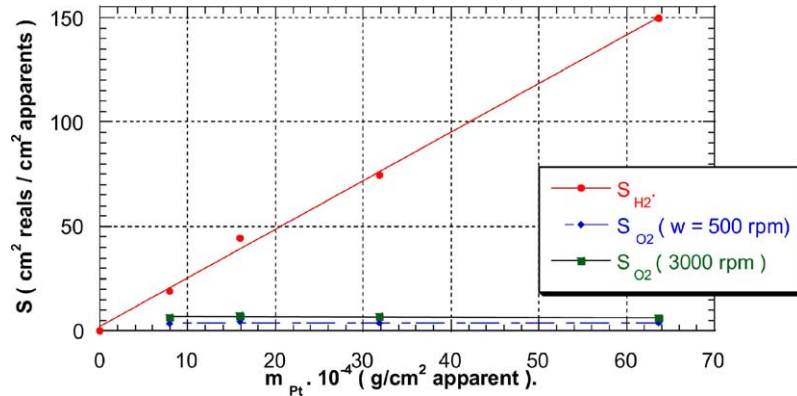


Fig. 7. Surface area of platinum involved in the reduction of dissolved oxygen vs. specific amount of platinum electrodeposited.

the product $D_s C_s$ is of the same order of magnitude as the product $D_f C_f$. Since the viscosity is greater in the film than in the solution, this shows that the oxygen concentration in the film is greater than that in the solution (ratio of 5) [3–6].

Fig. 8 shows the variation of the product $D_f C_f$ with the temperature; this increases by a factor of 2 between 25 and 80 °C.

The values of $D_f C_f$ obtained in the presence of air are 1/3 and not 1/5 of the values obtained with pure oxygen [2], which shows that, assuming D_f constant, the oxygen concentration in the hydrated Nafion® is not proportional to the partial pressure of oxygen in the solution.

2.2. Effect of a Nafion® film on the kinetic parameters of oxygen reduction on platinum

The Koutecky–Levich Law (Eq. (4)) allows to study the effect of a Nafion® film on the kinetic parameters of the reduction of oxygen on platinum, such as the number of electrons and the half-wave potential. When this law is applied one obtains parallel straight lines (Fig. 3), which indicates that the kinetic parameters of the reduction are not modified (same number of electrons and same half-wave potential) [3]. To determine another kinetic parameters for the reduction of oxygen on platinum, like the exchange current i_0 , Tafel plots were used. These were obtained from the

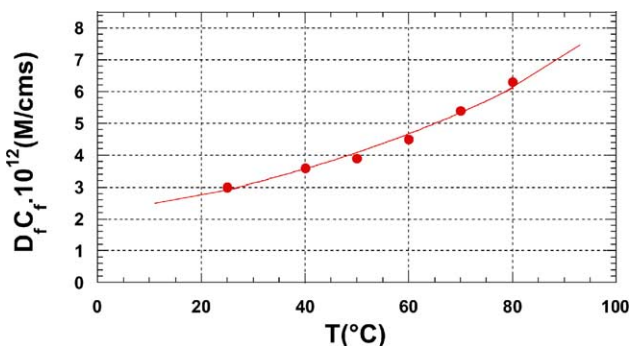


Fig. 8. Temperature dependence of the product $D_f C_f$.

Butler–Volmer equation:

$$i = i_0 s [\exp(-\alpha_c f \eta) - \exp(\alpha_a f \eta)], \quad \text{with } f = \frac{RT}{F} \quad (7)$$

where α_a and α_c represent the transfer coefficients of the complex oxido-reduction of oxygen on platinum, the over-voltage η being negative in reduction and positive in oxidation. For a high reduction over-voltage the reverse reaction is suppressed and there remains:

$$\eta = \left(\frac{RT}{\alpha_c F} \right) \ln(i_0 s) - \left(\frac{RT}{\alpha_c F} \right) \ln(i) \quad (8)$$

This equation is that of Tafel, also known in the following simplified form:

$$\eta = a + \log(i) \quad (9)$$

with $a = 2.303(RT/\alpha_c F) \log(i_0 s)$ and $b = -2.3(RT/\alpha_c F)$

By plotting the potential (E) against the logarithm of the ratio $((I_L \times I/I_L) - I)$ one obtains the curves in Fig. 9. These show a linear section, extrapolation of which $E = E_{eq}(\text{theoric}) = 980 \text{ mV/ECS}$, allowing the determination of the exchange current i_0 .

The exchange currents are low: $i_0 = 10^{-13} \text{ A cm}^{-2}$ of the real surface area and are of the same order of magnitude with bare platinum or covered with Nafion®. The Tafel slope is close to or equal to 60 mV per decade for low polarization. In this region of activation where there is no diffusion phenomenon, the reduction of oxygen to H_2O_2 occurs mainly on the oxidized platinum. In contrast, when the polarization is high and one is in the region of the limiting current, calculation was performed for n using the slope of the plot $7 \times 10^{-6} \text{ A s}^{-1/2}$, and the values: $F = 96,485 \text{ C mol}^{-1}$; $S = 0.0314 \text{ cm}^2$; $D = 19.10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [9]; $C = 0.53 \times 10^{-6} \text{ mol cm}^{-3}$; $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ [9] to obtain the value of 4.2, which corresponds to a reduction of oxygen on the non-oxidized platinum (cf. voltammograms of platinum (Pt) (Fig. 2) where it can be seen that PtO_x is reduced) [10].

To reduce a large amount of oxygen it must be in contact with the maximum of catalyst surface. For this reason, in fuel cells one uses porous electrodes based on platinumized

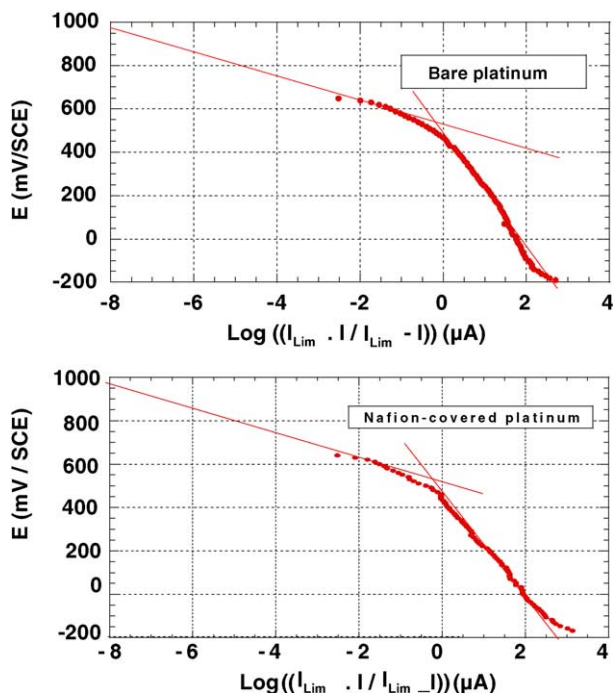


Fig. 9. Tafel plots for smooth bare platinum and Nafion[®]-covered platinum.

carbon. The theoretical analysis of the properties of these electrodes is very difficult because of the complexity of their structure. Mass transport and the variation of the potential with the current can only be described by very complex multidimensional equations.

3. Conclusion

This study has enabled us to deduce the permeability of oxygen in a Nafion[®] film, that is, the product $D_f C_f$ (product of the diffusion coefficient and the oxygen concentration in the film). This product is the same whatever the state of division of the platinum, smooth or platinized; it is also of

the same order of magnitude, $6 \times 10^{-12} \text{ mol cm}^{-1} \text{ s}^{-1}$, as the product $D_s C_s$ in the H_2SO_4 solution. Our experimental results agree with those of the literature.

Our work shows that the rotating electrode is a very efficient tool for studying the effect of certain factors on the components of a fuel cell.

The product $D_f C_f$ increases with the temperature. Allowing for the fact that the diffusion coefficient in Nafion[®] is less than that in the solution, it is shown that the oxygen concentration in the Nafion[®] is very high and that it is five times that in the solution.

These experiments show that the presence of Nafion[®] does not modify the kinetic parameters of oxygen reduction.

Acknowledgements

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