

Short communication

Comparative study of protonic conducting polymers incorporated in the oxygen electrode of the PEMFC

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Abstract

The kinetics of the reduction of oxygen at the surface of a platinum disc covered with thin layers of polymer has been studied in 0.5 M H_2SO_4 at ambient temperature in order to establish to what extent the polymer affects the reaction mechanism. Experiments were performed particularly to determine the oxygen permeability $D_f C_f$ (product of the diffusion coefficient and the oxygen concentration in the film) for Nafion® and other polymers such as sulfonated polyimide (PIS), sulfonated polyetherketone (PEEKs) and non-sulfonated polybenzimidazole (PBI). The product $D_f C_f$ depends on the nature of the polymer. Furthermore, how well the active layer works depends markedly on the amount of polymer it contains.

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1. Introduction

The use of fuel cells with Nafion® membranes considered for transport applications such as electric vehicles has many advantages for the environment and energy savings. These cells have clear advantages for this application because of their energy densities, which are much higher than those of traditional accumulators. The solid polymer Nafion® electrolyte provides the protons necessary for the reduction of oxygen; it is also a good ionic conductor related to the high mobility of the H^+ ion [1].

Nafion® is widely used as a solid electrolyte because of its high chemical and thermal stability as well as its high ionic conductivity, but it is excessively expensive. Other polymeric materials are currently being studied as replacements for Nafion®. Other incentives for replacement of Nafion® are the possibility to use fuel cells at higher temperatures and the need of membranes less permeable to methanol than Nafion®.

More than 40 polymers for which the thermal and chemical resistances are known have been tested in oxygen and in hydrogen under conditions similar to those of a fuel cell [2].

The aim of this work is to compare the influence of different polymers films on the kinetics of the reduction of oxygen.

The different studied polymers are:

- Nafion® which is a polymer consisting of a fluorinated matrix on which are grafted sulfonate groups SO_3^{2-} , which give to the materials its proton transport ability.
- Commercially available polybenzimidazoles, denoted PBI, characterised by excellent thermal and mechanical stability. It is possible to take advantage of these properties in an electrochemical device operating at temperatures ranging from 100 to 180 °C [3]. Raw PBI is an electronic and ionic insulator, but becomes a very good ionic conductor when it is sulfonated under appropriate conditions [4].
- Polyetherketone (PEEK) is a non-fluorinated polymer consisting of ether and ketone aromatic groups. The stability with respect to oxidation increases when the ketone content increases and the ether content decreases [5]. These polymers are very stable with respect to hydrogen saturated

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with water vapour up to 400 °C and to oxygen-saturated with water vapour up to 300 °C [5].

- Polyimides are good candidates for the preparation of proton-exchange membranes; they have good mechanical characteristics, good chemical resistance to oxidation, low gas permeability and good ionic conductivity. More elaborate materials containing selective groups, such as amines able to react reversibly with CO₂, are studied [6].

Sulfonic groups can be added to a polymeric chain by direct sulfonation of the polymer by sulfuric acid or chlorosulfonic acid [7–9], or by chemically grafting a group containing a sulfonic acid function [10,11], or by copolymerization using high-energy γ radiation followed by sulfonation of an aromatic compound [12], or from monomers containing sulfonic acid groups [13]. The degree of sulfonation is very important, since when it is too high it leads to an unacceptable degree of swelling and to inadequate mechanical properties. The conductivity of the membrane is closely related to the degree of sulfonation. The presence of an inorganic component can compensate for the low degree of sulfonation required to obtain satisfactory mechanical behaviour. Other advantages can be observed when the degree of sulfonation is optimal, as for example:

1. low dependence of the conductivity on the relative humidity;
2. high mechanical resistance;
3. low extent of transport of reactants, such as methanol, across the membrane [5].

2. Experimentation

The main object of this work is to establish to what extent the presence in the catalytic layer of a solid polymer electrolyte affects the mechanism and the kinetics of the reduction of oxygen, by determining the permeability $D_f C_f$ (diffusion coefficient and oxygen concentration in the polymer film) of oxygen in the polymer.

The kinetics of the reduction of oxygen at a platinum electrode in 0.5 M H₂SO₄ solution is studied with the help of a rotating platinum disc electrode (RDE) covered with a film of a polymer such as Nafion[®], non-sulfonated polybenzimidazole (PBI), sulfonated polyetheretherketone (Peek-s) and sulfonated polyimide (PIS). A complete set of experimental results was obtained for membranes of different thicknesses, but to make the discussion simpler it will be based whenever possible on the results for the thicker and thinnest membranes. The interest of the rotating electrode is that it is possible to control the thickness of the liquid diffusion layer.

2.1. Influence of the polymer on the oxygen permeability

This study was performed in a glass cell with five ground-glass sockets, respectively, for the saturated calomel electrode, for the counter electrode (platinum wire), for a gas

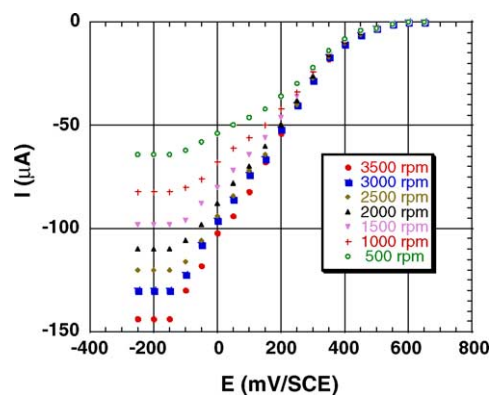


Fig. 1. Polarization curves for the reduction of oxygen on a bare platinum disc in oxygen-saturated 0.5 M H₂SO₄ at different rotation speeds.

circulation system in order to saturate the electrolyte, for a thermocouple and for the working electrode, RDE. This latter consists of a smooth platinum disc (diameter, 2 mm) set in a Teflon body and associated with a regulating system (TACUSSEL CTV 101T) so that the rotation speed can be varied from 0 to 5000 rpm.

After treatment of the surface of the platinum disc the electrode is introduced into the oxygen-saturated 0.5 M H₂SO₄ electrolyte. The polarization curves for the reduction of oxygen are presented in Fig. 1 (the obtained curves are similar to those reported in the literature).

With the help of a micropipette, a known volume of a solution of the polymer is deposited on the RDE; the electrode covered with a Nafion film is allowed to dry at ambient temperature for 1 h. The electrode covered with a film of Peek-s, PIS or non-sulfonated PBI is dried at higher temperature (120 °C) for 1 h. The film thickness is measured by means of a micrometer.

After the film has been dried the electrode is immersed in oxygen-saturated 0.5 M H₂SO₄; the polarization curves for oxygen reduction are presented in Fig. 2.

In all these experiments, the presence of a polymer film on the electrode surface causes, as expected, a decrease in the limiting current density, since the film presents an additional barrier to the transport of dissolved oxygen towards the electrode surface. The limiting currents were expected to depend on the thickness of the film [1] and its nature, this is actually demonstrated in Fig. 2. In the case of non-sulfonated PBI, the limiting current is strongly decreased, as shown in Fig. 2d.

The dependence of the limiting current on the film thickness is due to the fact that the kinetics of oxygen reduction on the electrode covered with a polymer film no longer obeys the LEVICH equation:

$$J_D = 0.62n_e F D^{2/3} \nu^{-1/6} C \omega^{1/2} = B \omega^{1/2}$$

By using the diffusion layer model of Nernst, it is easy to show that the reciprocal of the limiting current for the electrode covered with a polymer film, “ $1/J_{lim}$ ”, is the sum of $1/J_D$, the reciprocal of the limiting current on the surface of bare platinum and of $1/J_f$, the reciprocal of the limiting current for the

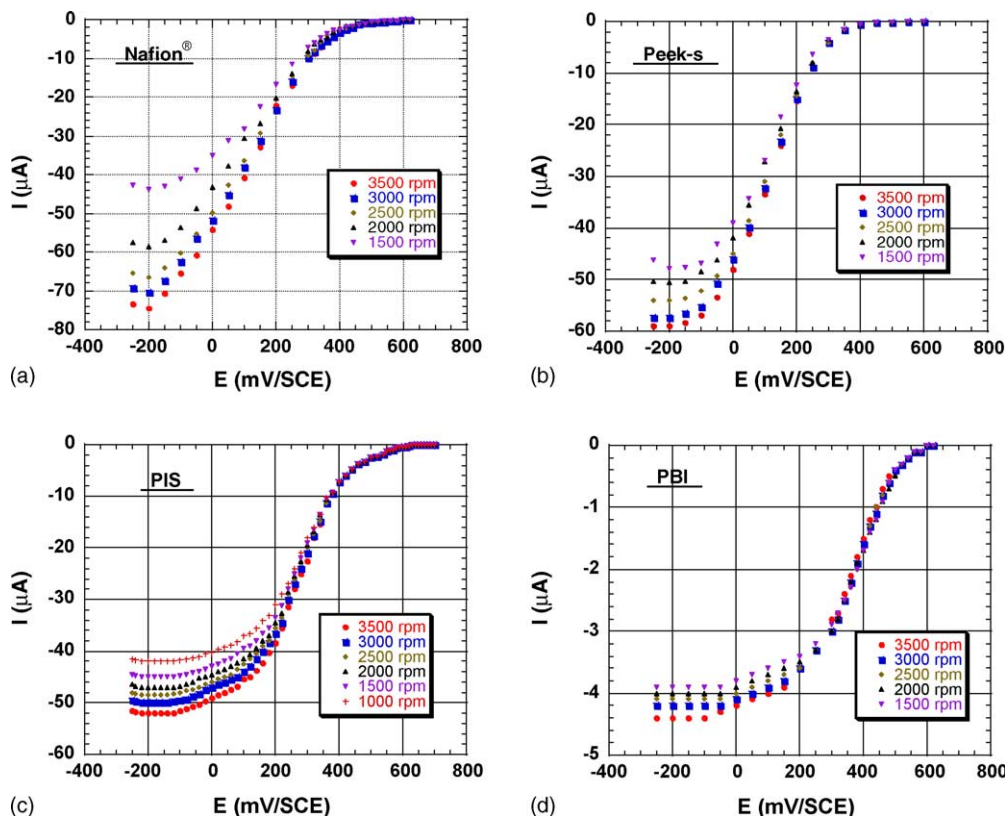


Fig. 2. Polarization curves for the reduction of oxygen on a platinum disc covered with a film of: (a) Nafion[®], (b) Peek-s, (c) PIS and (d) non-sulfonated PBI, in oxygen-saturated 0.5 M H₂SO₄ at different rotation speeds.

diffusion of oxygen in the polymer film (Koutecký–Levich law).

$$\frac{1}{J_{\text{lim}}} = \frac{1}{J_f} + \frac{1}{J_D} \Rightarrow \frac{1}{J_{\text{lim}}} = \frac{\delta_f}{n_e F D_f C_f} + \frac{1}{B} \omega^{-1/2}$$

Applying this law, we obtain parallel straight lines whatever the film thickness, as shown in Fig. 3. The same slope means that there is no modification of the kinetic parameters, such as the number of electrons or the half-wave potential, $E_{1/2}$ [1].

The term $Y = \delta_f / n F D_f C_f$ allows the determination of the value of the product $D_f C_f$, where Y is the extrapolated values of the straight lines obtained for the Koutecký–Levich law on platinum covered by the polymer and δ_f is the thickness of the film of a polymer. The product $D_f C_f$ is an important in the reduction of oxygen.

Fig. 4 shows the variation of the oxygen permeability with the nature of the polymer. The permeability are in the order of 9×10^{-12} mol (cm⁻¹ s) for Nafion[®], 2.5×10^{-12} mol (cm⁻¹ s) for Peek-s, 10^{-12} mol (cm⁻¹ s) for PIS and 0.5×10^{-12} mol (cm⁻¹ s) for non-sulfonated PBI.

This permeability increases by a factor of about two when the temperature increases from 25 to 80 °C.

Fig. 5 shows the variation of the permeability according to the temperature for a film of Nafion[®].

2.2. Effect of the polymer introduced in the active layer

The electrochemical reduction of oxygen on platinum plays an important role in the process of energy conversion, since the cathode over-voltage corresponds to a voltage loss of 200–300 mV at the operational current densities of around 500 mA cm⁻². Much effort has been devoted to improve the performances of the catalysts [14]. In addition to the study of the effect of the polymer film deposited on the platinum on the kinetics of the reduction of oxygen, our work also presents the effect of the polymer introduced into the active layer.

The active layer is prepared by mixing 30% platinumized carbon (the platinum is deposited on vulcan carbon black XC72 (E-TEK)) with the polymer. To prepare the mixture of polymer and platinumized carbon, a solvent in which the polymer is soluble is used. The ink obtained is sonicated for an hour to obtain good homogeneity, and then deposited by means of a micropipette on the glassy carbon disc (diameter 5 mm). In the case of Nafion[®], the alcohol used evaporates rapidly at ambient temperature but for the other polymers such as Peek-s, PIS and non-sulfonated PBI, the deposit is dried at a higher temperature of about 120 °C to evaporate the solvent (DMA), leaving in all cases the active matter glued to the glassy carbon [15,16].

Each of these polymers plays the role of glue and of proton conductor in the active layer. If it is too thick, it introduces

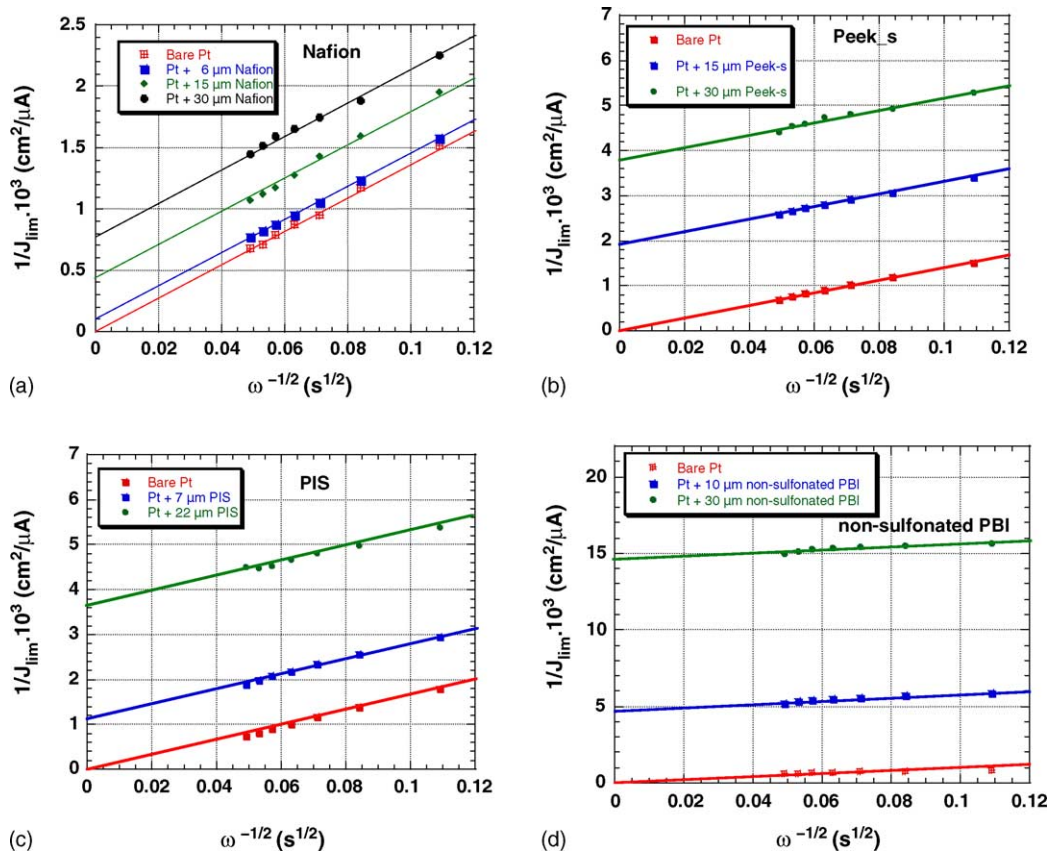


Fig. 3. Koutecky–Levich lines for different polymer film thicknesses: (a) Nafion[®], (b) Peek-s, (c) PIS and (d) non-sulfonated PBI.

an additional resistance to the diffusion of the electroactive species towards the active sites.

Once the active layer has been deposited, the rotating electrode is immersed in an oxygen-saturated 0.5 M H₂SO₄ solution. The polarization curves for the reduction of oxygen are recorded at ambient temperature; during the entire experiment the electrolyte remains in an atmosphere of oxygen. The results obtained with 30% platinumized carbon, E-TEK, follow the Koutecky–Levich law and show that the amount of polymer used as glue to prepare the active layer does not alter the oxygen transport process. The calculated polymer film thickness is less than one micron, as is suggested by the low values of the intercepts in Fig. 6.

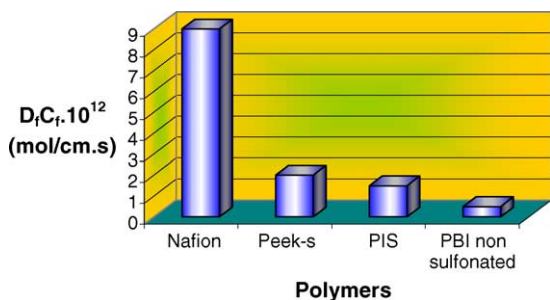


Fig. 4. Oxygen permeability in the different polymers.

The different deposits contain the same amount of platinum and different percentages of the same polymer, the results on the reduction of oxygen show that the ratio of the currents, I/I_{max} , presents a maximum when varying the proportion of polymer (Fig. 7), depending on the polymer used: 25% for Nafion[®] (Fig. 3a), 15% for Peek-s (Fig. 3b) and 15% for PIS (Fig. 3c). In the case of non-sulfonated PBI, the ratio is constant in the range studied.

The presence of an optimum value for the polymer proportion can be explained: increasing the amount of polymer increases the ionic percolation and the number of the active

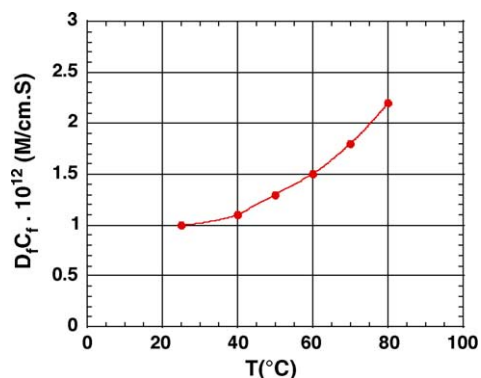


Fig. 5. Variation of the $D_f C_f$ product with the temperature.

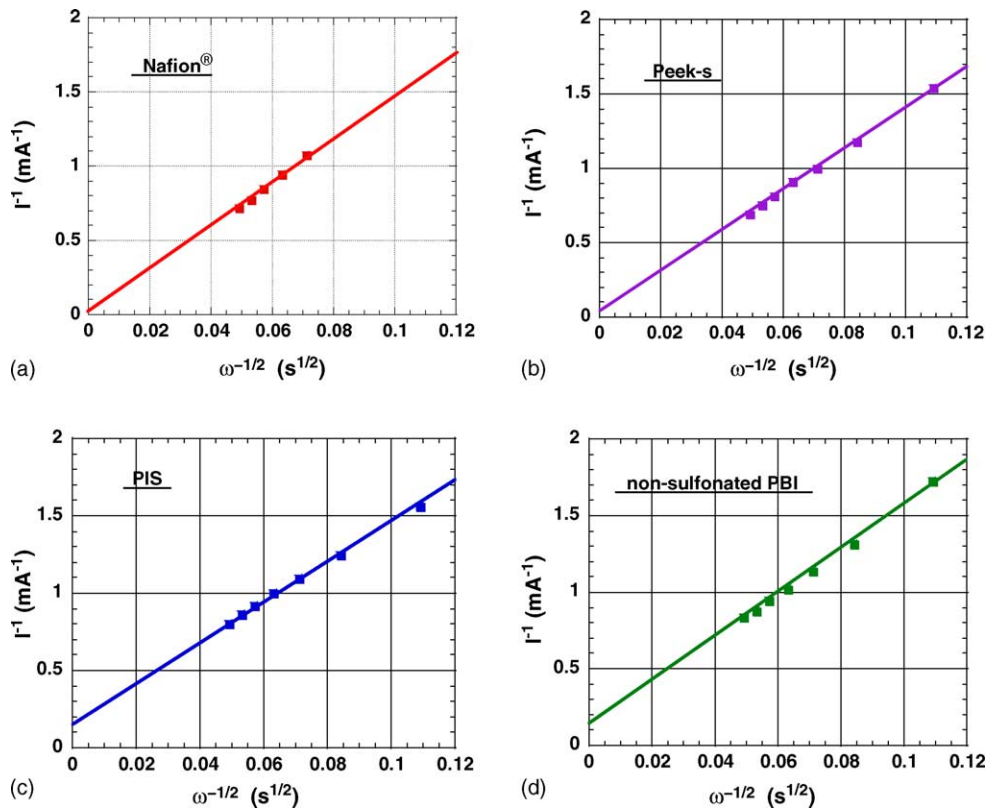


Fig. 6. Evolution of $1/I$ on 30% platinumized carbon with polymer vs. the reciprocal of the square root of the rotation speed: (a) 25% Nafion[®], (b) 15% Peek-s, (c) 15% PIS and (d) 15% non-sulfonated PBI.

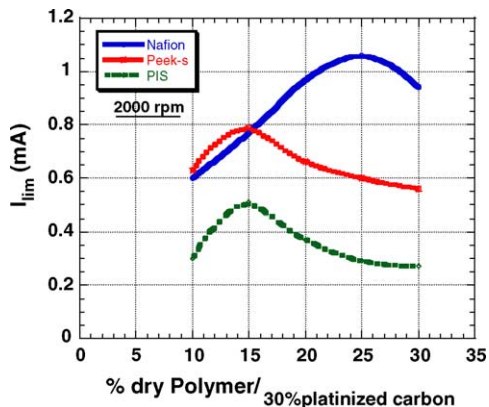


Fig. 7. Evolution of the ratio I/I_{\max} with the percentage of dry polymer in the active layer at ambient temperature: (a) Nafion[®], (b) Peek-s, (c) PIS and (d) non-sulfonated PBI.

sites increases, but increasing the amount of polymer causes an excessive masking of platinum that slows down the diffusion of oxygen [15].

3. Conclusions

The experimental results lead to the following conclusions:

1. The oxygen permeability is greater in Nafion[®] than in the other polymers studied. The low permeability of oxygen across the PBI film may be related to the fact that it is not sulfonated.
2. In addition to the need for a good oxygen permeability in the polymer, the performance of the active layer depends on the amount of polymer introduced. An optimum value is obtained for the proportion of polymer in the active layer.

The following conditions must be satisfied whatever the nature of the polymer:

- Sufficient ionic continuity between the membrane and the active sites.
- Adequate distribution of the polymer between carbon and platinum to obtain a thin ESP film around the platinum particles (low local ohmic drop and high mass transport).
- Good mechanical cohesion of the active layer (glue effect).

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