

Influence of Nafion loading in the catalyst layer of gas-diffusion electrodes for PEFC

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Abstract

The effect of Nafion loading in the catalyst layer of cathodes for polymer electrolyte fuel cells (PEFCs) was investigated. Steady-state galvanostatic polarisation (GP), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were carried out at 25°C in 1.0 M H₂SO₄ on electrodes with different Nafion loadings. EIS supplied information on the polarization resistance and CV on the electrochemical active area for the oxygen reduction reaction (ORR). These parameters, together with those derived from GP, allowed a better identification of the features governing the ORR. An optimum Nafion loading was identified. This loading was found to correspond to a minimum in the polarization resistance and in the oxygen reduction overpotential and a maximum in the electrochemical active area. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polymer electrolyte fuel cells; Cathode; Nafion; Oxygen reduction

1. Introduction

The kinetic of oxygen reduction reaction (ORR) on platinum at solid polymer electrolyte interfaces has been extensively investigated in recent years [1–3] to improve the efficiency of fuel cell operating at low temperatures [4,5]. Hydrated poly-perfluorosulphonic acid polymers, such as Nafion, are used as electrolytes in low temperature fuel cell systems (polymer electrolyte fuel cells, PEFCs). The achievement of high efficiencies for ORR with electrodes containing low platinum loadings has been made possible by incorporating the Nafion ionomer within the catalyst (platinum on carbon, Pt/C). Nafion enables the porous catalyzed carbon to be integrate into the electrolyte by extending the three-dimensional reaction zone [4,11].

Many works deal on the optimisation of the amount of Nafion incorporated into the electrode structure. Ticianelli et al. [6] studied the effect of Nafion loading of Prototech electrodes (0.35 mg Pt cm⁻², 20 wt.% Pt/C) on the cell performance. Nafion was incorporated within the catalyst by brushing a 5 wt.% Nafion solution onto the electrodes.

They found that an increase in Nafion loading increases the cell performance in the low current density region. For the high current density region, the increase of Nafion content has positive effects only up to 3.3 wt.% of Nafion (referred to the total electrode weight), after which the performance starts to decrease rapidly. Poltarzewski et al. [7] reported the influence of Nafion loading in dual-layer electrodes, made with a catalyst layer, constituted by Pt/C and PTFE, superimposed to a wetproofed carbon paper (0.5 mg Pt cm⁻², 20 wt.% Pt/C), on their electrochemical activity. The impregnation of the electrolyte in the catalyst layer was made by floating the electrodes on a 5 wt.% Nafion solution. Their results indicated that the Nafion loading mostly influences the ionic resistance of the catalyst layer. From 0.8 to 1.0 mg Nafion cm⁻² a maximum in electrochemical activity was found. In this range the ionic conductivity of the electrodes reaches its lowest value. This phenomenon has been explained according to a physical model based on the fact that, for a low amount, the electrolyte is located within the pores of the electrodes, and the resistance decreases when the pores fill with Nafion. Above 0.9 mg cm⁻², due to the hydrophobic–hydrophilic properties of the Nafion structure, a further supply of electrolyte does not fill the pores but forms films on

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the external surface of the electrodes, giving an additional contribution to the overall resistance. Uchida et al. [8] also studied the effect of perfluorosulphonate ionomer (PFSI) content in dual-layer electrodes ($0.5 \text{ mg Pt cm}^{-2}$, 25 wt.% Pt/C) on cell performance. In this case the electrolyte was introduced into the electrodes by spreading over the carbon paper a catalyst paste constituted by the catalyst (Pt/C) and PFSI. The optimum content of PFSI was 1.0 mg cm^{-2} . Paganin et al. [9] performed electrochemical studies on the effect of Nafion loading in three-layer electrodes ($0.4 \text{ mg Pt cm}^{-2}$, 10 wt.% Pt/C) by measuring the cell voltage as a function of current density. They deposited a catalyst ink formed by Pt/C catalyst and Nafion solution, with isopropanol as solvent, into the diffusion layer of the electrode by a brushing procedure. The Nafion loading ranged from 0.87 to 2.60 mg cm^{-2} . The best results were obtained by Nafion loading in the range $1.75 \div 2.2 \text{ mg cm}^{-2}$.

Aim of this work was to gain more information on the effect of Nafion loading on the oxygen reduction at PEFC electrodes by steady state galvanostatic polarization (GP), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements. The kinetic parameters, derived from GP experiments are complemented by polarization resistance data obtained from EIS and by the hydrogen absorption charge from CV. Three-layer gas-diffusion electrodes ($0.2 \text{ mg Pt cm}^{-2}$, 20 wt.% Pt/C) were chosen for the present investigation. This study covered a wide Nafion loading range from 0 to 1.5 mg cm^{-2} .

2. Experimental

2.1. Electrode preparation

The three-layer electrodes were prepared by a combined spraying/brushing procedure [11] using platinum-on-carbon (20 wt.% Pt/C) catalyst (Electrochem), carbon powder (Vulcan XC-72, Cabot), carbon paper substrate (Toray TGPH-090), glycerol, poly-tetrafluoroethylene (PTFE) suspension (Teflon T-30, DuPont) and Nafion solution (Aldrich, 5 wt.% in 10% water/low aliphatic alcohols).

A homogeneous suspension composed of PTFE and carbon powder was sprayed onto the carbon paper to form the diffusion layer (thickness about $100 \mu\text{m}$) of the electrode [10,13]. The composite structure was then dried in air at 120°C for 1 h, followed by thermal treatment at 280°C for 30 min to remove the dispersion agent contained in PTFE, and finally sintered in air at 350°C for 30 min. The amount of PTFE in the diffusion layer was 20 wt.%.

To prepare the catalyst layer, a homogeneous suspension was formed from the Pt/C catalyst, glycerol and the Nafion solution with ethanol/isopropanol mixture as solvent. The resulting ink was deposited onto the composite diffusion layer of the electrode by a brushing procedure to

produce the catalyst layer (thickness about $40 \mu\text{m}$). Platinum loading was 0.2 mg cm^{-2} . Finally, the samples were dried at 70°C for 30 min.

2.2. Electrochemical measurements

The reduction of oxygen was investigated at the porous gas-diffusion electrode (geometric exposed area 1 cm^2) in $1 \text{ M H}_2\text{SO}_4$. The electrochemical measurements (GP, CV and EIS) were carried out at 25°C in a conventional three-electrode cell, with O_2 flowing at 100 ml min^{-1} . The gas-diffusion electrodes were mounted into a Teflon holder containing a platinum ring as current collector and having provision for oxygen feeding from the electrode back. A large area platinum flat electrode was used as counter electrode. A Hg/HgSO₄ reference electrode was placed externally to the cell and connected to the main compartment through a Luggin capillary whose tip was placed close to the working electrode surface. The potential values are reported with reference to the normal hydrogen electrode (NHE). The electrochemical cell was connected to a Solartron 1286 potentiostat/galvanostat, for galvanostatic polarization and cyclic voltammetry, and also to a Solartron 1260 frequency response analyzer, for electrochemical impedance spectroscopy.

3. Results and discussion

The galvanostatic steady-state polarisation curves for oxygen reduction at 25°C on PEFC electrodes containing various Nafion loadings are shown in Fig. 1. A single Tafel region is observed which extends over two decades of current density.

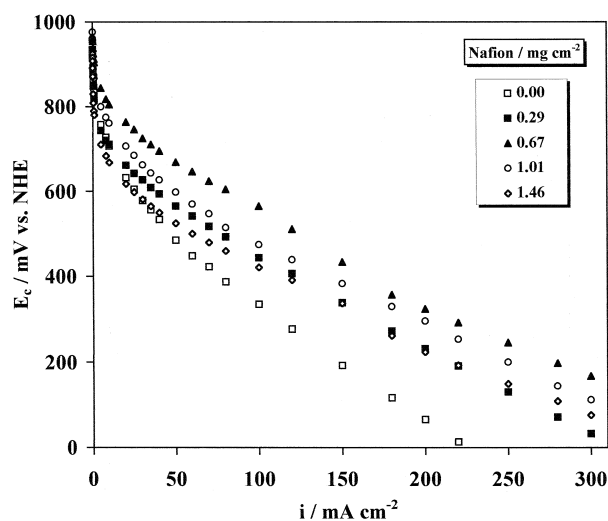


Fig. 1. Galvanostatic steady state polarizations for oxygen reduction at porous gas-diffusion electrodes (20 wt.% PTFE/C in diffusion layer, $0.2 \text{ mg Pt cm}^{-2}$ in catalyst layer) with different Nafion loading in the catalyst layer, in $1 \text{ M H}_2\text{SO}_4$ at 25°C , under O_2 flux.

Table 1

Electrochemical parameters for ORR derived by NLLS fitting of galvanostatic steady state polarizations

Nafion loading (mg cm ⁻²)	E° (mV vs. NHE)	$-b$ (mV dec ⁻¹)	R_u (Ω cm ²)	$i^\circ \cdot 10^5$ (A cm ⁻²)
0.0	532 ± 18	91 ± 6	2.74 ± 0.05	3.0 ± 0.5
0.29	571 ± 5	72 ± 2	2.09 ± 0.02	0.6 ± 0.1
0.67	697 ± 11	62 ± 4	1.97 ± 0.05	9.5 ± 1.2
1.01	609 ± 13	75 ± 4	1.71 ± 0.06	3.3 ± 0.6
1.46	492 ± 5	92 ± 2	1.60 ± 0.02	1.2 ± 0.1

An increase in Nafion loading (up to 0.67 mg cm⁻²) improves the electrode performance. This can be explained by an increase of the electrochemically active area in the electrodes. Also, at low Nafion loading, the electrodes have poor electrolytic conductivity, which accounts for the poor electrode performance; the conductivity increases with increasing the Nafion content. But a thicker layer of polymer inside the pores of the electrode introduces mass transport problems either by retarding the access of gas to the active sites and by flooding the electrode.

The electrode containing 0.67 mg cm⁻² of Nafion shows the best performances (i.e., lowest overpotentials), by minimizing ohmic, charge transfer and mass transport limitations.

Analysis of the experimental polarization data was made using the semi-empirical equation proposed by Rho et al. [12]:

$$E = E^\circ - b \log i - R_u i$$

$$= E_r + b \log i^\circ - b \log i - R_u i \quad (1)$$

where E_r is the reversible potential for the electrode, b the Tafel slope, i° the exchange current density for the ORR in the Pt/C catalyst, and R_u represents the total contributions of the polarization components, which include the charge transfer resistance (R_{ct}), the electrolyte resistance (R_e) and the mass transfer resistance (R_d) due to the gas crossing through the diffusion and catalytic layer. The

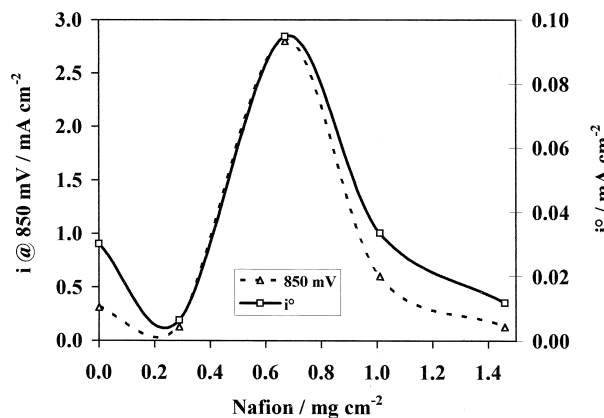


Fig. 2. Effect of Nafion loading on the exchange current density (i°) and the current density at 850 mV vs. NHE for oxygen reduction at porous gas-diffusion electrodes (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm⁻² in catalyst layer) in 1 M H₂SO₄ at 25°C, under O₂ flux.

fitting of the above equation to the experimental data was made by a non-linear least squares (NLLS) method, and the derived kinetic parameters are reported in Table 1.

The Tafel slope values are between -62 and -92 mV dec⁻¹. These changes can be attributed to a variation of the interphase conditions, and imply the influence of different rate determining steps for ORR as a function of Nafion loading. A Tafel slope of -60 mV dec⁻¹ has been explained [3] by a mechanism of oxygen reduction where the reaction involves an initial fast charge transfer step followed by a chemical step, which is the rate determining under Langmuir conditions. The Tafel slope assumes a higher value for low O₂ concentration, due to a mixed activation/mass transport control [12]; by increasing the O₂ concentration, the mass transport limitations are overcome.

The strong influence of the Nafion loading on the ORR kinetic is evident from Fig. 2: the exchange current density has a maximum value at 0.67 mg Nafion cm⁻². In this plot, the current density at 850 mV vs. NHE (i.e., at a potential near to the equilibrium one) is also showed.

The changes of current density at different cathode potential are reported in Fig. 3 as a function of Nafion loading. The highest activity is verified, both at high and low overvoltage, with a Nafion loading of 0.67 mg cm⁻².

The reduction of R_u with the increase of Nafion content in the catalyst ink (Table 1) can be explained in terms

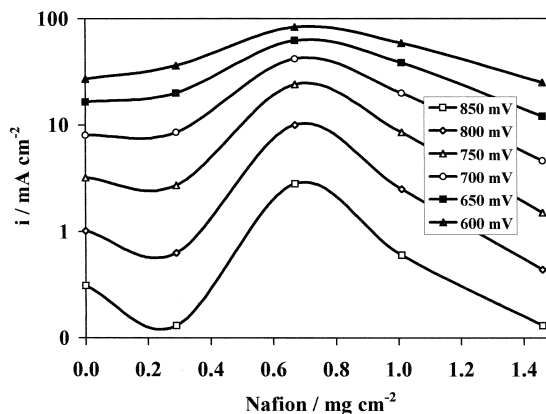


Fig. 3. Effect of Nafion loading on the current density at different electrode potential for oxygen reduction at porous gas-diffusion electrodes (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm⁻² in catalyst layer) in 1 M H₂SO₄ at 25°C, under O₂ flux.

of increase of ionic conductivity and extension of the gas/electrolyte/electrode interface. An increase in R_u is indicative of a reduction of the active area and/or an increase in the electrolyte resistance. Both phenomena are related to an inadequate amount of Nafion into the electrode, which is insufficient to provide a sufficient electrolytic conductivity inside the catalyst layer, leading to a low platinum utilization and a high ohmic drop.

To gain more information on the electrode behaviour, impedance spectra were recorded at two different potential. Figs. 4 and 5 show the impedance data in the Nyquist (after ohmic resistance subtraction) representation obtained at 800 mV (low overvoltage) and 542 mV (high overvoltage). In the insert of Fig. 4 the equivalent circuit used for the representation of the electrode/electrolyte interface is showed; the circuit elements are: R_{ct} charge transfer resistance, Z_d diffusive impedance, C_{pc} pseudo-capacitance. The last term is related to electrochemical double layer, morphological properties of the electrode and adsorption phenomena. The dependence of polarization resistance R_p (sum of R_{ct} and Z_d) from Nafion loading at 542 and 800 mV vs. NHE shows a minimum at 0.67 mg cm^{-2} , according to the galvanostatic polarization data.

To calculate the electrochemically active surface (EAS), the hydrogen adsorption charge (Q_{ads}) was determined from CV measurements. The EAS ($\text{m}^2 \text{ g}^{-1}$) was calculated using the following equation:

$$\text{EAS} = 0.1 \frac{Q_{ads}}{Q_{ref} L_{Pt}} \quad (2)$$

where Q_{ads} is the hydrogen adsorption charge on the electrode, Q_{ref} the hydrogen adsorption charge on a smooth

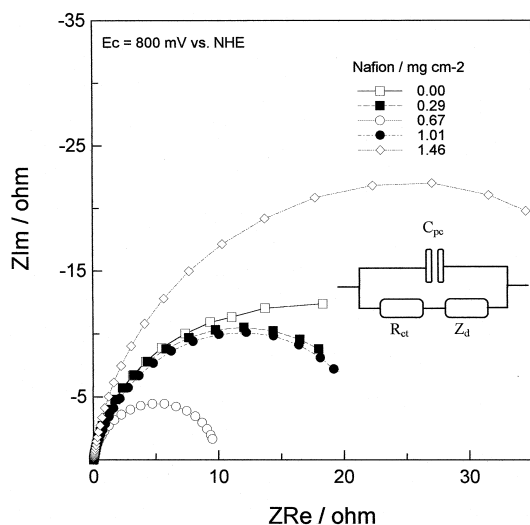


Fig. 4. Impedance response in the Nyquist form (20 kHz \div 50 mHz) of the porous gas-diffusion electrodes (20 wt.% Pt/C in diffusion layer, $0.2 \text{ mg Pt cm}^{-2}$ in catalyst layer) at 800 vs. NHE, in $1 \text{ M H}_2\text{SO}_4$ at 25°C , under O_2 flux. (20 wt.% PTFE/C in diffusion layer, $0.2 \text{ mg Pt cm}^{-2}$ in catalyst layer) and equivalent circuit (R_{ct} : charge transfer resistance, Z_d : mass transfer impedance, C_{pc} : double layer capacitance).

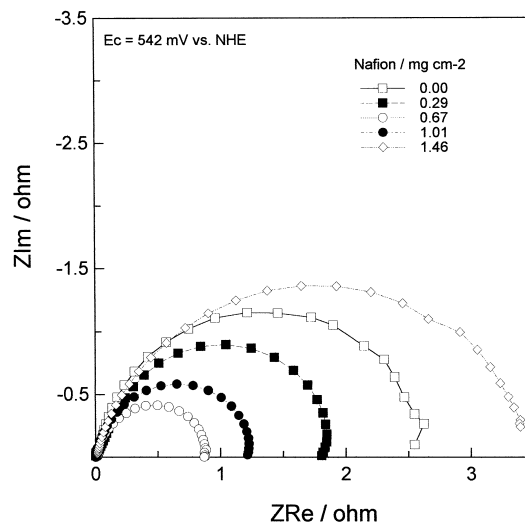


Fig. 5. Impedance response in the Nyquist form (20 kHz \div 50 mHz) of the porous gas-diffusion electrodes (20 wt.% PTFE/C in diffusion layer, $0.2 \text{ mg Pt cm}^{-2}$ in catalyst layer) at 542 vs. NHE, in $1 \text{ M H}_2\text{SO}_4$ at 25°C , under O_2 flux.

platinum electrode (0.21 mC cm^{-2}) and L_{Pt} the Pt loading (mg cm^{-2}).

The EAS, as determined by cyclic voltammetry, reflects the electrochemically active surface area of the electrode for adsorption/desorption processes of hydrogen and oxygen on platinum at its interface with Nafion. Some of the platinum sites, covered with thick layer of polymer, can introduce mass transport problems for ORR. Thus, the effective area for the ORR can be smaller than the suggested by cyclic voltammograms. Nevertheless, cyclic voltammetry is a powerful tool to lend insight on the effect of Nafion loading on the extension of three-dimensional region.

The electrochemically active surface as a function of Nafion content in the electrode goes through a maximum at 0.67 mg cm^{-2} (Fig. 6). The decrease of R_u , as the

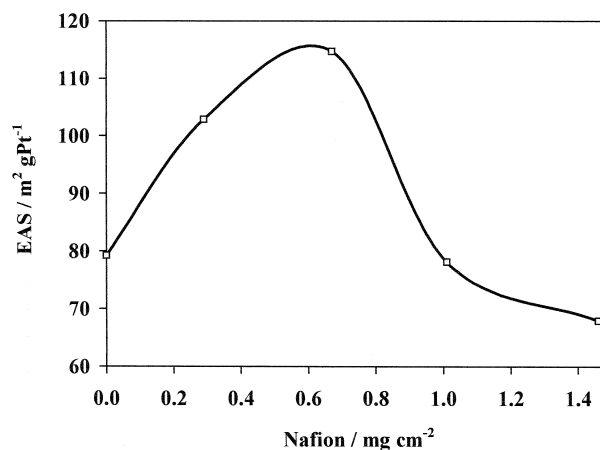


Fig. 6. Electrochemically active surface (EAS) from cyclic voltammetry as a function of Nafion content in the catalytic layer (20 wt.% PTFE/C in diffusion layer, $0.2 \text{ mg Pt cm}^{-2}$ in catalyst layer).

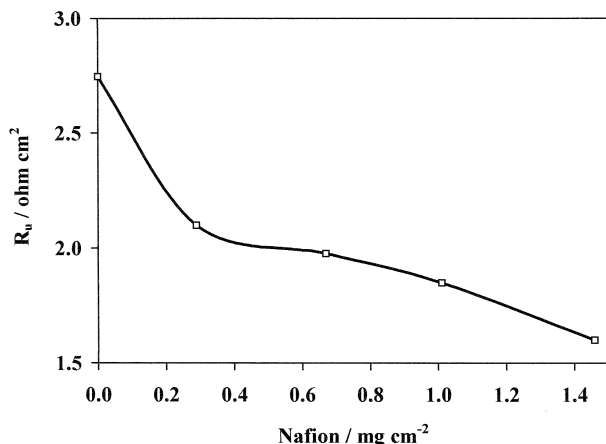


Fig. 7. Effect of Nafion loading on the uncompensated resistance during oxygen reduction at porous gas-diffusion electrodes (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm^{-2} in catalyst layer) in 1 M H_2SO_4 at 25°C, under O_2 flux.

Nafion content in the catalytic ink increases, (Fig. 7) can be explained in terms of ionic conductivity improvement and extension of gas/electrolyte/electrode interface.

By taking into account the EAS, no changes in the dependence of i° (Fig. 8) and R_p (Figs. 9 and 10) on Nafion loading was seen. Therefore, we are not in the presence of surface area effects, but only of Nafion concentration effects.

The oxygen reduction overpotentials (from galvanostatic measurements), polarization resistance (from EIS) and EAS (from CV), show an optimum value for Nafion loading of 0.67 mg cm^{-2} . This behaviour is related to opposite contributions of Nafion which involve an increase of the active area of platinum covered with Nafion and an easier migrations of the protons through the electrolyte retained inside the pores of the catalyst layer (positive

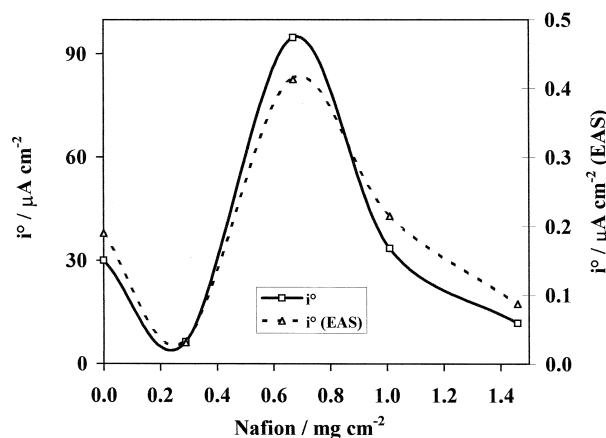


Fig. 8. Effect of Nafion loading on the exchange current density for oxygen reduction at porous gas-diffusion electrodes in 1 M H_2SO_4 at 25°C, under O_2 flux (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm^{-2} in catalyst layer): comparison between geometric and electrochemically active surface.

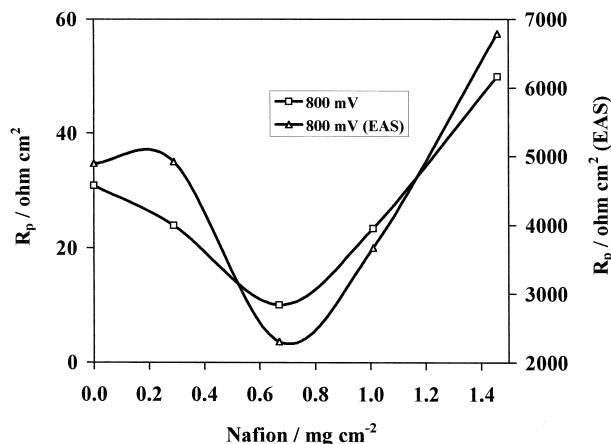


Fig. 9. Effect of Nafion loading on the polarization resistance (from EIS data) for oxygen reduction at 800 mV vs. NHE in porous gas-diffusion electrodes in 1 M H_2SO_4 at 25°C, under O_2 flux (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm^{-2} in catalyst layer): comparison between geometric and electrochemically active surface.

contribution) and an increased hindrance of gas-diffusion by the polymer in the pores of the catalyst (negative contribution).

Table 2 shows the optimum Nafion loading values from various authors compared with the data of the present work. The Nafion loadings are expressed in terms of the weight percentage of Nafion with respect to the total weight of the Nafion + Pt dry mixture [6]. As shown in Table 2 the values of optimum Nafion loading are in good agreement when the Nafion is introduced into the electrode by mixing it with the catalyst powder. The average value of the Nafion/(Nafion + Pt + C) ratio is 0.36. The incorporation of Nafion in the catalyst ink allows the polymer to obtain a good interaction with all catalyst particles. When Nafion is incorporated into the electrode by impreg-

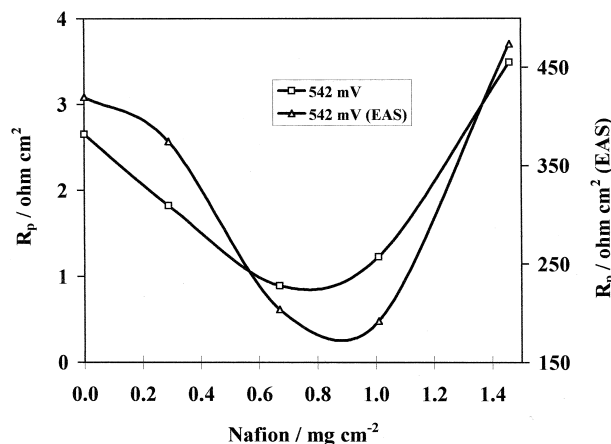


Fig. 10. Effect of Nafion loading on the polarization resistance (from EIS data) for oxygen reduction at 542 mV vs. NHE in porous gas-diffusion electrodes in 1 M H_2SO_4 at 25°C, under O_2 flux (20 wt.% PTFE/C in diffusion layer, 0.2 mg Pt cm^{-2} in catalyst layer): comparison between geometric and electrochemically active surface.

Table 2
Comparison of optimum Nafion loading from different works

Electrode	Pt in the catalyst layer (mg cm ⁻²)	Pt/C (wt.%)	PTFE in the catalyst layer	Nafion incorporation in the catalyst layer	Optimum Nafion/(Nafion + Pt + C) (w/w)	Ref.
dual-layer	0.5	20	yes	by impregnation	0.27	[7]
dual-layer	0.5	25	no	in the catalyst ink	0.33	[8]
three-layer	0.4	10	no	in the catalyst ink	0.36	[6]
three-layer	0.2	20	no	in the catalyst ink	0.40	this work

nation the optimum value is lower than those by mixing. This behaviour is explained by the difficult for the Nafion, introduced by impregnation, to reach all catalyst particles, especially the inner Pt/C particles in the catalyst layer. Above the 0.27 Nafion/(Nafion + Pt + C) ratio, by impregnation the polymer forms a film on the external surface of the electrodes, while by mixing with the catalyst the polymer occupies the space between the catalyst particles up to 0.36 of Nafion/(Nafion + Pt + C). Another way to explain the low optimal value of Nafion introduced by impregnation is the following: PTFE and Nafion in the catalyst layer are in competition for that regarding the interactions with the catalyst particles. Considering the sum of PTFE and Nafion contents of the catalyst layer, the value of (PTFE + Nafion)/(PTFE + Nafion + Pt) is in agreement with the values reported in Table 2.

To verify which of these two hypothesis is correct, a dual electrode obtained by mixing Nafion with PTFE and catalyst powder should be prepared. This is not possible as the thermal treatment at 350°C to sinter the electrode should destroy the Nafion polymer.

The internal structure of the catalytic layer is composed by Pt/C agglomerates; Uchida et al. [8] reported that the catalytic layer has two distinct pore size distributions: the smaller pores (primary pores) have been identified with the space in and between the primary pores in the agglomerate; the larger pores (secondary pores) are located between the agglomerates. In the Uchida's hypothesis, the Nafion is localized only in the secondary pores and it coats the Pt/C agglomerates. By considering such a model, we can suppose the oxygen reduction reaction should be under the control of the following transport phenomena: (i) oxygen diffusion in the secondary and primary pores, and its dissolution in the Nafion; (ii) oxygen diffusion in the Nafion; (iii) protons transport in the Nafion. These phenomena are influenced by Nafion that coats the agglomerates. A Nafion-less pore means a lack of protons on the catalytic sites and, as a consequence, a low oxygen concentration. An increase of Nafion concentration allows an increase of oxygen concentration and ionic portion. By increasing the Nafion concentration, the ionic conductivity is enhanced, but a too much thick polymer layer inside the pores introduces mass transport limitations by retarding the gas access to active sites. The optimal Nafion loading

(0.67 mg cm⁻²) minimizes charge transfer resistance, ionic and gas transport limitations.

4. Conclusions

From the work carried out it results that:

- impregnation of electrodes with a proton conductor (Nafion) extends the three-dimensional reaction zone;
- an optimum Nafion content in the electrode is necessary to minimize ohmic and mass transport overpotentials within the electrode;
- the extension of the three-dimensional region with Nafion loading was confirmed by analysis of cathode potential vs. current density behaviour and by cyclic voltammetry.

For a practical use, it is possible to calculate, as a function of the electrode type, the optimal Nafion loading by using some empirical equations obtained from the data of the present work and literature. In the case of catalytic layer containing Pt/C and Nafion, the optimal load (mg cm⁻²) is given by:

$$\text{Nafion} \cong 56 \frac{L_{\text{Pt}}}{P_{\text{Pt}}} \quad (3)$$

where L_{Pt} is the platinum loading (mg cm⁻²) and P_{Pt} the weight percentage of metal supported on carbon (Pt/C). In the case of dual layer electrodes, it is necessary to take into account for the presence of PTFE in the catalytic layer, and the following relationship must be used:

$$\text{Nafion} \cong 56 \frac{L_{\text{Pt}}}{P_{\text{Pt}}} (1 - X_{\text{PTFE}}) \quad (4)$$

in which X_{PTFE} is the Teflon weight fraction in the catalyst layer.

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