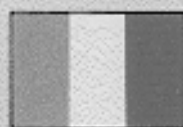


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INFLUENCE OF THE TEFLON IN THE DIFFUSION LAYER AND NAFION IN THE CATALYTIC LAYER ON THE PERFORMANCE OF LOW-Pt CATHODES FOR PEFC

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ABSTRACT

The influence of the structure and composition of the diffusion and catalytic layers on polymer electrolyte fuel cell (PEFC) cathode performance was investigated. Low-Pt loading electrodes were prepared in two ways: by varying poly-tetrafluoroethylene (PTFE) content in the diffusion layer, maintaining a constant composition for the catalytic layer and by varying Nafion content in the catalytic layer, maintaining a constant composition for the diffusion layer.

Electrodes were characterised by Hg-intrusion porosimetry, scanning electron microscopy and electrochemical techniques (cyclic voltammetry, galvanostatic polarisation and ac-impedance spectroscopy).

INTRODUCTION

Electrode structures in polymer electrolyte fuel cell (PEFC) evolved from two layer structure to three layer structure [1]. Dual-layer electrodes are constituted by a hydrophobic support layer and a porous electrocatalyst layer formed by Pt on carbon (Pt/C) as a catalyst agent, polytetrafluoroethylene (PTFE) and polyperfluorosulphonic acid (Nafion). Three layer electrodes are made by a porous support layer, a diffusion layer consisting of carbon particles and PTFE, a catalyst layer formed by Pt/C and Nafion. The performances of the electrodes depend on many parameters [2-5]: type of support (carbon paper or carbon cloth) and its characteristics (porosity and thickness), type of catalyst (Pt alone, Pt with other metals, macrocycles, Pt amount, Pt particles size, type of carbon as the support), PTFE amount, Nafion amount, thermal treatment, thickness of diffusion and catalytic layers, fabrication process.

The incorporation of PTFE into the diffusion or catalyst layer serves two functions: binding the high surface carbon particles into a cohesive layer, and imparting some hydrophobic character to the layer. Recently, Paganin et al. [6] investigated the influence of PTFE loading in the diffusion layer for a three layer structure, in the case of 20 wt % Pt/C and 0.4 mg Pt/cm²; they found a small increase in the performance when the PTFE content is diminished from 40 to 15 wt

%.

Also the Nafion loading and its distribution in the catalyst layer play an important role in determining the electrochemical activity. In fact, optimising of these parameters results not only in a high utilisation of the noble metal due to a larger active area in the electrode, but also in an easier migration of the protons through the electrolyte retained in the pores of the catalyst layer. The influence of Nafion loading on cell performance has been reported by Ticianelli et al. [8] and Giordano et al. [5]. In their works they used different electrodes and different impregnation methods of the catalytic layer with Nafion. Ticianelli used a three layers electrode, the catalytic layer was prepared by brushing a homogeneous suspension of Pt/C catalyst and Nafion solution on the electrode diffusion layer. Giordano used dual layer electrodes made with a catalytic layer superimposed to a wetproofed carbon paper. Impregnation of the Nafion in the catalyst layer was made by floating the final electrodes on to a Nafion solution. In their experiments they found both a maximum in cell performance, which can be correlated to an optimum in the Nafion loading. Nevertheless the obtained values are different showing that the optimum Nafion amount is depending by the electrode preparative method.

The aim of this paper was to investigate the influence of the diffusion layer porosity due to PTFE loading and loading distribution of Nafion on the effective catalyst activity for the cathodic oxygen reduction.

EXPERIMENTAL

Three layers electrodes were prepared by a spray technique using platinum-on-carbon (20% Pt/C) catalyst (Electrochem. Inc.), carbon powder (Vulcan XC-72, Cabot), a carbon paper substrate (Toray TGPH-090), a polytetrafluoroethylene (PTFE) dispersion (35 wt% PTFE aqueous dispersion, Hostaflon 5033 Hoechst), a Nafion solution (5 wt% Nafion 1100 EW solution, Solution Technology Inc.) and glycerol. The carbon loading in the diffusion layer was 2 mg/cm^2 ; the platinum loading in the catalyst layer was 0.1 mg cm^{-2} or 0.2 mg cm^{-2} .

For the preparation of the diffusion layer, a homogeneous suspension was prepared by mixing and stirring in an ultrasonic bath at room temperature for 25 min the carbon powder (grinded Vulcan XC-72 powder, Cabot Inc.) with an appropriate amount of PTFE dispersion. The suspension was spray deposited onto a porous support. The layer was dried in air atmosphere at 120°C for 1 h, followed by a thermal treatment at 280°C for 30 min to remove the dispersion agent contained in PTFE, and finally sintered at 350°C for 30 min.

To prepare the catalyst layer, a homogeneous suspension, formed by the desired amounts of the Pt/C catalyst (20 % Pt/C. Electrochem Inc.), the glycerol and with an appropriate amount of Nafion solution solution with ethanol as solvent, was spray deposited onto the diffusion layer. Porosimetry measurements were performed using a Carlo Erba Mercury Porosimeter md.2000. Micrographs were

obtained with a Cambridge Stereoscan 250 mk3 scanning electron microscope. The electrochemical measurements were carried out in H_2SO_4 1 M saturated with O_2 at 25 °C, electrode exposed area 1 cm^2 , by means of a potentiostat-galvanostat EG&G PAR 273A (cyclic voltammetry, galvanostatic polarisation) and an electrochemical interface Solartron Instruments mod.1287 connected to an impedance phase analyser Solartron Instruments mod.1260 for ac-impedance spectroscopy.

RESULTS AND DISCUSSION

Diffusion layer - Measurements were performed on PEFC electrodes with 0.1 mg Pt/ cm^2 . The diffusion layer had two distinctive pore distributions with boundary about 0.35 μm . To identify these different regions, we called micropores the pores with size lower than 0.35 μm and macropores the pores having size higher than 0.35 μm .

It was observed that electrode performance showed the same trend of the total porosity data for the electrode diffusion layer. PTFE 10 wt % electrode showed the greatest porosity of the diffusion layer, while 60 wt % ones gave the lowest porosity. Diffusion layer porosity can influence electrode performance for two main reason: high porosity increases the rate of mass transport of reactant gas on catalytic sites; high macroporosity allows a greater effective area of the catalytic layer deposited on the diffusion layer.

In the high current density range, the electrode is under diffusion control. So in this case, the contribute of total porosity, related to a larger amount of reactant gas on catalytic sites, is predominant on electrode performance. Regarding the low current density range region (1-5 $mA\ cm^{-2}$), where the electrode is under charge transfer reaction control, the electrode performance showed a different trend than high current density range. To explain this trend, it is necessary to take into account the influence of macroporosity on the electrode performance. The diffusion layer macroporosity and the porosity in a pore size range between 2-50 μm , as a function of PTFE loading. A minimum appear for a PTFE loading between 20 and 40 wt % (Fig.1).

A diffusion layer with a high macroporosity allows an higher effective catalytic area, because spray deposited catalyst can penetrate into the larger pore of the diffusion layer, so the triple contact zone Pt/Nafion/gas is increased.

This behaviour was confirmed by the straight line correlation between electrode potential and macroporosity in the range 2-50 μm . Exchange current density shows a minimum at 40 wt % PTFE, confirming the change in the electrode effective area.

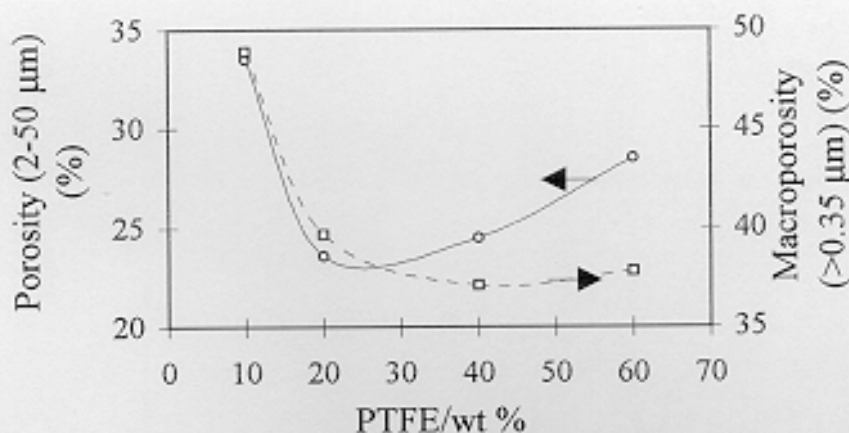


Fig.1 - Porosity in the range 2-50 μm and macroporosity of the diffusion layer as a function of PTFE content.

SEM micrographs of the diffusion layer on the carbon substrate, before the deposition of catalytic layer, for different PTFE loading electrode, seem to confirm these conclusions. At higher PTFE contents, it seems that the polymer covers all the surface of the layer. The presence of cracks, increasing with PTFE content, was also revealed. So the increase of PTFE loading, diminished the porosity and as a consequence, an oxygen transport limitation took place. The formations of cracks in number and size was also increased and this produced a change in the effective area of catalytic layer [9].

The change of effective electrode area with diffusion layer macroporosity is reflected only in a limited electrode potential vs. current density region, while the predominant effect of PTFE loading increase appears to be related to the decrease of oxygen amount on the catalytic sites. Such anomalous effect seen at low current density for electrode with different PTFE loading has been confirmed from electrochemical impedance spectroscopy data. Impedance spectra have been carried out on the gas diffusion electrode at various potentials. The Nyquist plots were obtained at electrode potential of 782 mV and 542 mV vs. NHE. They mainly consists of one semicircle characteristic of an electrochemical interface that can be simulated by a non linear regression with an equivalent electrical circuit $R_{\Omega}(R_p C_{dl})$. Where R_{Ω} is the sum of electrode and electrolyte resistance, R_p is the polarisation resistance and C_{dl} is the double layer capacity.

As electrode overpotential is increased the charge transfer resistance and the relaxation time of the charge transfer process decrease, whereas diffusion resistance increase and the R_{Ω} resistance is constant. The highest impedance has been measured for 60 wt % PTFE electrode. Fig.2 show R_p for different PTFE loading electrode at 782 mV vs. NHE and 542 mV vs. NHE.

The R_p trend is similar to that obtained from electrode potential vs. current density curves.

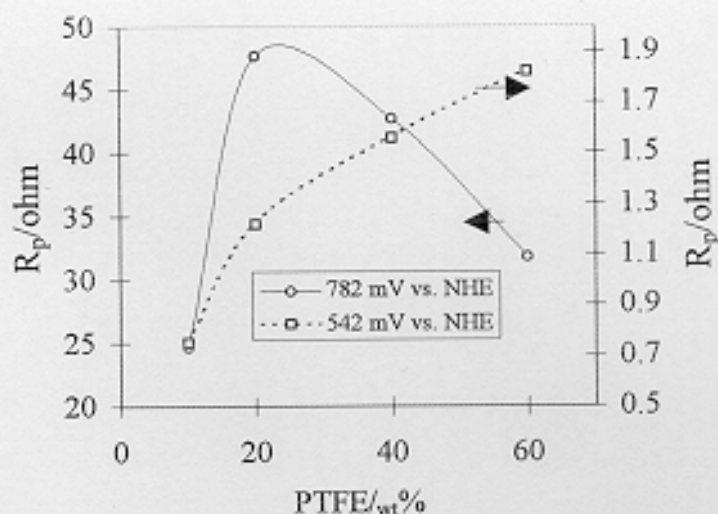


Fig.2 - Dependence of total polarisation resistance on PTFE content in the diffusion layer, at low (782 mV vs. NHE) and high (542 mV vs. NHE) overvoltage for oxygen reduction.

Fig.3 shows the double layer capacity obtained from impedance spectra at 782 mV vs. NHE; the curve is similar to that obtained from macroporosity data (Fig. 1) on the diffusion layer, showing a minimum value for a PTFE loading of 40%. The same trend as capacity, has been obtained for adsorbed hydrogen charge from cyclic voltammetry data (Fig.3).

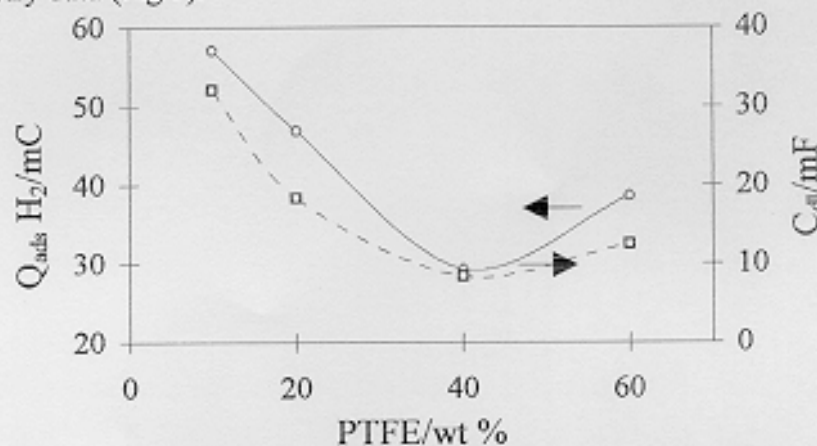


Fig.3 - Double layer capacitance from impedance and hydrogen absorption charge from cyclic voltammetry, as a function of PTFE content in the diffusion layer.

The PTFE content in the diffusion layer of PEFC cathodes changes the electrode microstructure. This change affects the electrochemical properties of the electrode. At high current density the negative influence of mass transport is reduced with low PTFE loading. At low current density the electrode performance goes through a minimum. The explanation of this phenomena is related to the

different porosity of the diffusion layer as a function of PTFE loading. The PTFE content has a direct influence on the diffusive layer because its increase reduces the total porosity and that limits the oxygen mass transport to the catalytic sites. The macroporosity, instead, has an indirect influence on the catalytic layer, because its increase allows to obtain an higher active area.

Catalyst Layer - Measurements were performed on PEFC electrodes with 0.2 mg Pt/cm^2 and 20 wt% PTFE. Fig.4 shows the electrode potential vs. Nafion loading in the catalytic layer, at two different current densities. Experimental data were obtained from polarisation plots of different electrodes and show clearly an influence of Nafion loading on electrode performance.

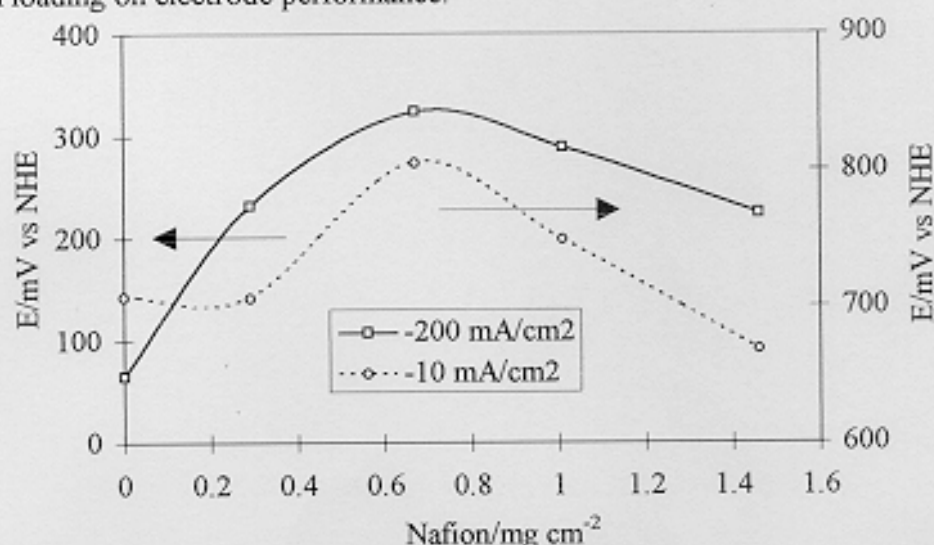


Fig.4 - Dependence of the electrode potential, during the oxygen reduction at 10 mA cm^{-2} and 200 mA cm^{-2} as a function of Nafion content in the catalytic layer.

SEM micrographs of the catalyst layer of these electrodes show a structure characterised by Pt/C agglomerates (about $5 \mu\text{m}$ diameter) and pores between agglomerates of size from $1.0 \mu\text{m}$ or less. Nafion exist in these pores covering the agglomerates surface [10]. The Nafion loading in the catalytic layer has to be enough to cover agglomerates uniformly with a thin layer. A too low Nafion content causes a poor proton conductivity and a low oxygen concentration on the catalyst sites. On the other side, an excessive Nafion loading produces flooding of pores and retardation of O_2 gas fed to the reaction sites. Two main phenomena, a reduction of the electrochemical active area and a decrease of O_2 and H^+ concentration are observed as a consequence of a Nafion loading change [11].

Hydrogen adsorption charge, obtained from cyclic voltammetry measurements, allowed to calculate the electrochemical active area vs. Nafion loading in the catalytic layer. Active area shows a maximum for a Nafion content of $0.6+0.7 \text{ mg/cm}^2$ (Fig.5).

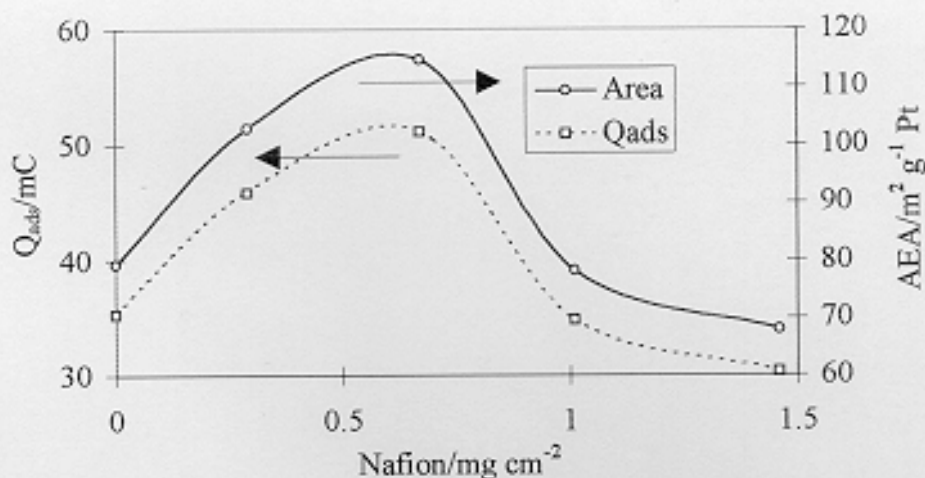


Fig.5 - Hydrogen absorption charge from cyclic voltammetry and active electrochemical area (AEA), as a function of Nafion content in the catalytic layer.

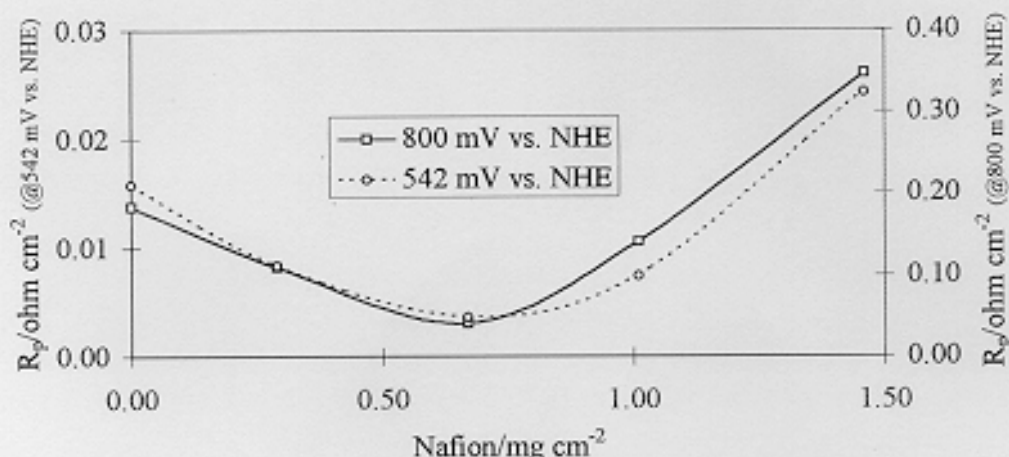


Fig.6 - Dependence of total polarisation resistance on Nafion content in the catalytic layer, at low (800 mV vs. NHE) and high (542 mV vs. NHE) overvoltage for oxygen reduction.

The Nyquist plot obtained at electrode potential of 800 mV and 542 mV vs. NHE allowed to obtain the polarisation resistance R_p . Fig.6 show R_p , normalised for the measured active area, for different Nafion loading electrode at these potential. The normalised R_p trend is similar to that obtained from electrode potential vs. current density curves and show an influence of Nafion loading on the electrode performances independent of electrode active area. Lowest R_p has been measured for 0.67 mg/cm² Nafion loading. The increase of the polarisation resistance for higher or lower values than the optimum polymer loading it is determined from a decrease in the concentration of reagent O₂ and/or H⁺ on the catalyst sites.

CONCLUSIONS

The PTFE content in the diffusion layer of PEFC cathodes changes the electrode microstructure in two ways: total porosity of the diffusion layer decreases with increasing PTFE content and the catalytic surface area being related to the macroporosity of the diffusion layer varies with PTFE loading. These changes affect the electrochemical properties of the electrode. On this basis the effect of PTFE loading on cathode performance depends on the current density region: at high current density (diffusion layer control), as a consequence of total porosity increase, the mass transport rate, as well as the performance, increased by decreasing PTFE loading; at low current density (catalytic layer control), as a consequence of macroporosity change, the performance went through a minimum, at about 20 wt % PTFE.

The content of Nafion affects the performance of the PEFC over the whole current density range. It exists an optimum Nafion loading related to the catalyst content. Higher or lower values than this optimum Nafion loading produce a decrease in the electrochemical active area and in the reagents concentration. The best Pt/C to Nafion ratio is 2:1.

REFERENCES

1. Proc. 1996 Fuel Cell Seminar, November 17-20, 1996, Orlando (USA)
2. Proc. 2nd International Fuel Cell Conference, February 5-8, 1996, Kobe (Japan)
3. T. Maoka, *Electrochim. Acta* **33**, 379 (1988)
4. M. Schulze, N. Wagner, G. Steinhilber, E. Gulzow, M. Wohn and K. Bolwin, Proc. 1996 Fuel Cell Seminar, November 17-20, 1996, Orlando (USA)
5. A.S. Aricò, V. Antonucci, V. Alderucci, E. Modica and N. Giordano, *J. Appl. Electrochem.* **23**, 1107 (1993)
6. V.A. Paganin, E.A. Ticianelli and E.R. Gonzalez, *J. Appl. Electrochem.* **26**, 297 (1996)
7. A. Fischer and H. Wendt, Proc. 1996 Fuel Cell Seminar, November 17-20, 1996, Orlando (USA)
8. E.A. Ticianelli, C.R. Derouin, A. Redondo and S. Srinivasan, *J. Electrochem. Soc.* **135**, 2209 (1988)
9. Giorgi, E. Antolini, A. Pozio, E. Passalacqua, 1997 Joint International Meeting (ISE/ECS), August 31 - September 5 1997, Paris, (France).
10. M. Uchida, Y. Aoyama, N. Edo, A. Ohta, *J. Electrochem. Soc.* **142**, 4143 (1995)
11. E. Antolini, L. Giorgi, A. Pozio, E. Passalacqua, Proc. GEI 1997, Giornate Elettrochimica Italiana, 17-20 Settembre 1997, Belgirate (Italy).