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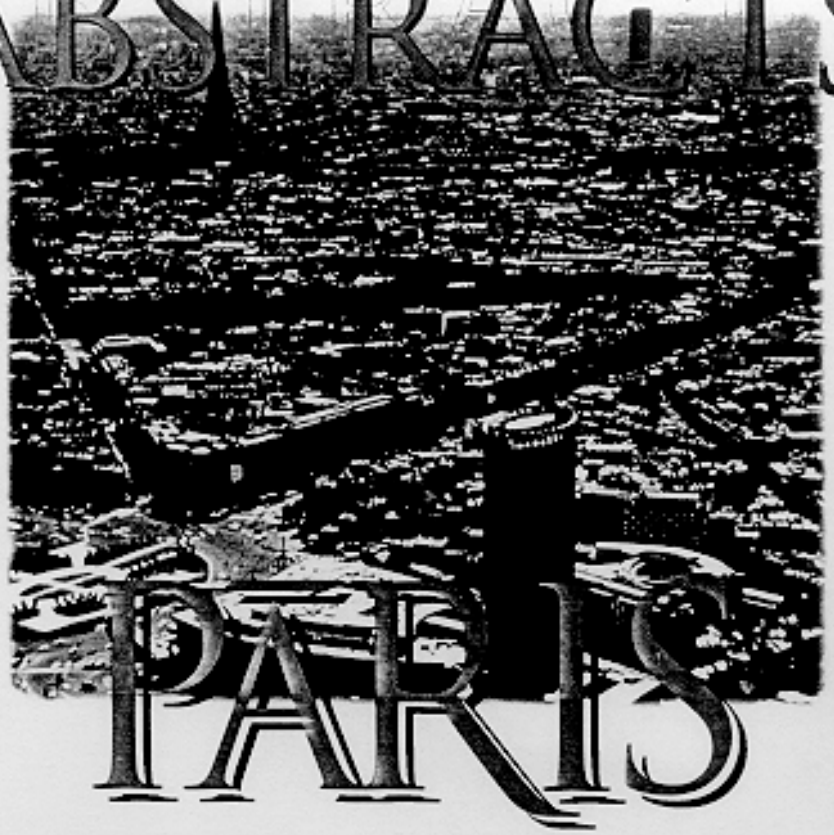
MEETING ABSTRACTS



PARIS

AUGUST 31 – SEPTEMBER 5, 1997

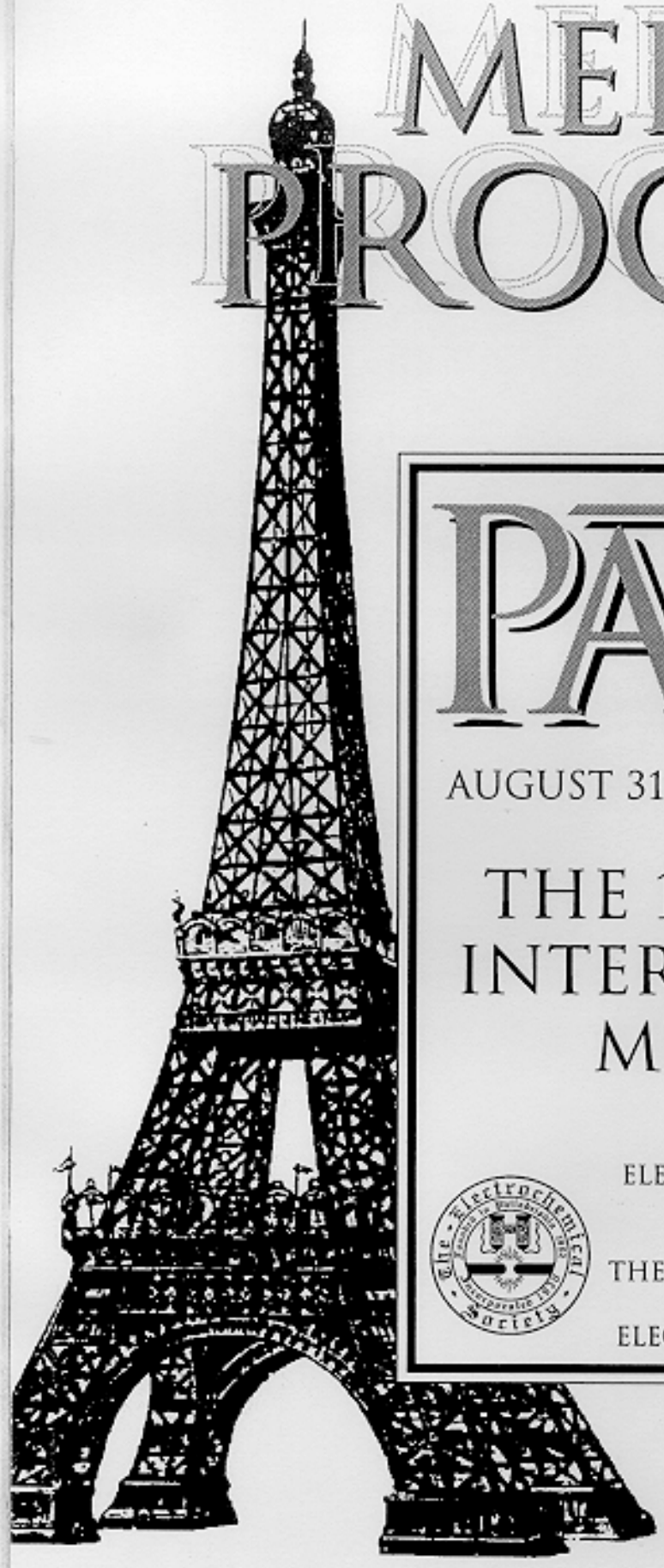
THE 1997 JOINT INTERNATIONAL MEETING

192nd Meeting

THE ELECTROCHEMICAL SOCIETY AND THE INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY

48th Annual Meeting

MEETING PROGRAM



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INFLUENCE OF THE TEFLON CONTENT IN THE DIFFUSION LAYER OF LOW-Pt LOADING ELECTRODES FOR POLYMER ELECTROLYTE FUEL CELLS

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Introduction

The influence of the composition (PTFE content) and structure of diffusional layer in low Pt-loading electrodes for Polymer electrolyte fuel cell) PEFC was investigated. The modification of electrode porosity and its on the catalyst activity for the cathodic reduction of oxygen was studied. Three layer low catalyst loading gas diffusion electrodes were prepared, using the spray technique for the deposition of both diffusion and catalyst layers.

Experimental

The 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}.

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 (35$_{wt}$% PTFE aqueous dispersion, Hostaflon 5033, Hoechst). The suspension was spray deposited onto a porous support (carbon paper Toray TGPH-090). 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 from the desired amounts of the Pt/C catalyst (20 % Pt/C, Electrochem Inc.), the glycerol and the Nafion solution (5$_{wt}$% Nafion 1100 EW, Aldrich) 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 at 25 °C by means of a potentiostat-galvanostat EG&G PAR 273A (cyclic voltammetry, galvanostatic polarization) and an electrochemical interface Solartron Instruments mod.1287 connected to an impedance phase analyzer Solartron Instruments mod.1260 for ac-impedance spectroscopy.

Results and Discussion

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 in 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 and the triple contact zone Pt/Nafion/gas is increased. To confirm this behaviour, by plotting the electrode potential vs. the macroporosity, in the range 2÷50 μm, we obtain a straight line (Fig.2). Exchange current density in shows a minimum at 40 wt % PTFE, confirming the change in the electrode effective area.

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 polymers covers all the surface of the layer, but the presence of cracks, increasing with PTFE content, is also revealed. So the increase of PTFE loading, diminished the porosity and as a consequence an oxygen transport limitation take place . The formations of cracks in number and size was also increased and this produced a change in the effective area of catalytic layer.

The change of effective electrode area with diffusion layer macroporosity, it is evident only in a limited electrode potential vs. current density region, while the predominant effect of PTFE loading increase, appear 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 plot obtained at electrode potential of 782 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 $R_\Omega(R_pC_d)$. Where R_Ω is the sum of electrode and electrolyte resistance, R_p is the polarization resistance and C_d 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. Highest impedance has been measured for 60 wt % PTFE electrode. Fig.3 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.4 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.4).

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.

CONCLUSIONS

The PTFE content in the diffusion layer of PEFC cathodes changes the electrode microstructure in two ways. First, total porosity of the diffusion layer decreased by increasing PTFE content; second, the catalytic surface area depended on the macroporosity of the diffusion layer, which 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 rate mass transport, 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.

References

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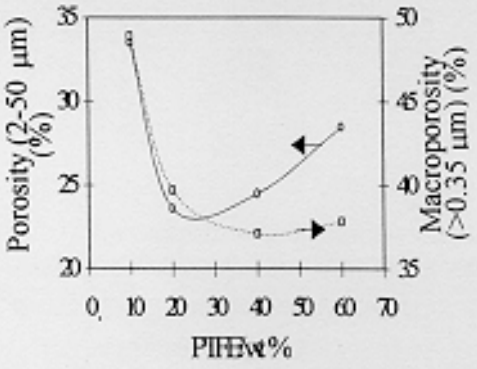

Fig.1 - Porosity in the range 2÷50 μm and macroporosity of the diffusion layer as a function of PTFE content.

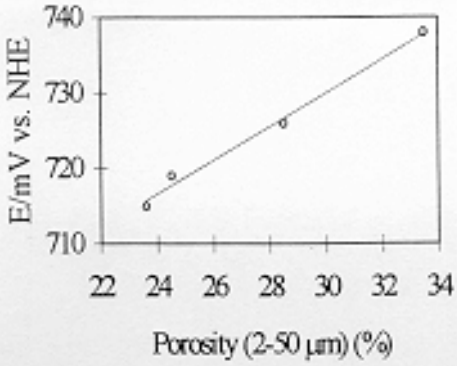

Fig.2 - Dependence of the electrode potential, during the oxygen reduction at 5 mA cm^{-2}, as a function of porosity in the range 2÷50 μm.

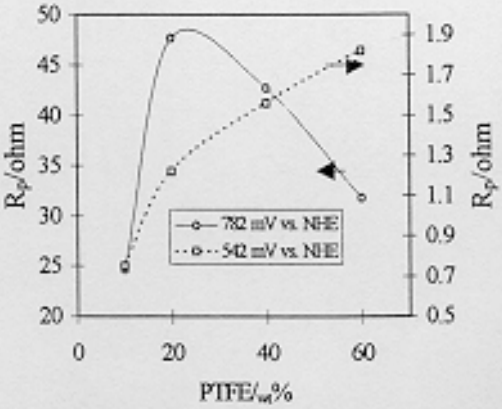

Fig.3 - Dependence of total polarization resistance on PTFE content in the diffusion layer, at low (782 mV vs. NHE) and high (542 mV vs. NHE) overvoltage for oxygen reduction.

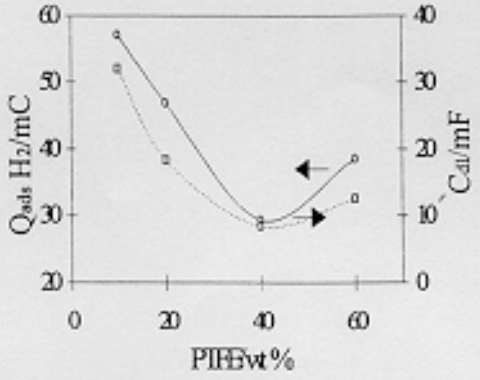

Fig.4 - Double layer capacitance from impedance and hydrogen absorption charge from cyclic voltammetry, as a function of PTFE content in the diffusion layer.