

Improvement in the diffusion characteristics of low Pt-loaded electrodes for PEFCs

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Abstract

Low Pt loading electrodes have been obtained by the direct mixing of electrocatalyst and Nafion[®] ionomer (for catalyst layer) and by the introduction of an intermediate hydrophobic carbon layer to optimize gas distribution. The influence of Teflon[®] content in the carbon layer has been studied and an optimum content of 20 wt % has been found. The behaviour of the improved electrodes as a function of temperature (70–95 °C) and gas (H₂ and air) pressure (1–5 bar) has been evaluated in a 50 cm² single cell. In air operation at 5 bar absolute pressure and 95 °C a maximum in the power density of about 450 mW cm⁻² has been obtained.

1. Introduction

Recently, different electrode preparation methods for polymer electrolyte fuel cells (PEFCs) have been developed to obtain high power density with low Pt loading [1, 2], based on the impregnation of the traditional gas diffusion electrode with a soluble form of an ionic conductor. An increased contact region between catalyst, electrolyte and reactants is obtained extending the three-dimensional reaction zone [3]. With this method a decrease in platinum loading in the electrode from 4 to 0.4 mg cm⁻² has been obtained without loss in power density [1]. Subsequently it has been found that the sputtering of a thin film of about 50 nm of Pt on the front of the electrode surface further improves the cell performance [2]. Recently, alternative methods have been developed, based on the direct mixing of Pt with the ionomer proton conductor, to obtain an improvement in catalyst utilization [4]. The ionomer in the catalyst 'ink' acts as binder for Pt/C particles, realises a good integrity of catalyst layer and increases the reaction zone, the ionic conductivity and the catalyst utilisation. The same authors have made further improvements in the electrode preparation procedure, with

the objective of optimising the deposition of the catalyst layer on the electrodes or directly on the membrane, and improving the stability of long-term performance [5]. Very recently, similar technology has been used from several other groups to simplify the fabrication procedure of electrodes and membrane electrode assemblies (MEAs) [6–8].

Little work has been carried out on the composition of the diffusion layer of these electrodes, studies being limited to the optimisation of the carbon layer characteristics when carbon cloth was used as substrate [6, 9].

In this paper progress in low Pt loading electrodes on carbon paper with improved structure able to deliver high performance in H₂/air is described. The introduction of an additional hydrophobic carbon layer between the carbon paper and the catalytic layer has shown a beneficial effect in the cell performance. The new electrode formulation has been compared with a standard electrode and the influence of Teflon[®] content in the carbon diffusion layer has been investigated. Comparative studies have been made on the optimised electrode at temperatures up to 95 °C and pressure from 1 to 5 bars.

2. Experimental details

2.1. Electrodes preparation

The standard electrode (SP1) was prepared by applying an electrocatalyst layer composed of 20 wt % Pt/Vulcan XC-72 (Electrochem Inc.) and 30 wt % PTFE (polytetrafluoroethylene) directly on a wet-proofed carbon paper (Toray TGPH090) of 0.3 mm thickness. The catalyst layer of this electrode was impregnated with a Nafion[®] solution (5 wt % from Aldrich) and dried at 80 °C, the final Nafion loading was about 0.9 mg cm⁻². The standard electrode was compared with an alternative electrode (AP1) where the catalyst 'ink' was obtained by mixing the Nafion[®] solution, glycerol and the Pt/C electrocatalyst with a catalyst/Nafion[®] ratio of 3 : 1 (wt % dry) and a Nafion solution/glycerol ratio of 1 : 1. The catalyst slurry obtained was sprayed on a diffusion layer, composed from carbon (Vulcan XC-72) and 40 wt % PTFE, previously sprayed on the wet-proofed carbon paper and heat treated at 350 °C. The SP1 and AP1 electrodes were prepared with a Pt loading of 0.49 and 0.41 mg cm⁻² respectively.

A series of electrodes with low Pt loading (0.1 mg cm⁻²) was prepared following the alternative procedure by varying the PTFE content in the carbon layer from 10 to 60 wt %. The electrodes characteristics of the prepared electrodes are summarized in Table 1.

The MEAs were obtained using the same electrodes for anode and cathode and Nafion[®] 117 (DuPont) as membrane, previously purified in 5 wt % H₂O₂ solution at 80 °C for 1 h and followed from another treatment in H₂SO₄ 1M. The MEAs were made by hot pressing electrodes and membrane at 130 °C for 3 min under 50 kg cm⁻² pressure.

2.2. Electrochemical characterizations

For the electrochemical tests a 50 cm² single cell incorporated in a GlobeTech, Inc. test station from Bryan Texas USA was used. The fuel cell test station was equipped with humidification chambers, temperature controllers (model Cal 9900, Cal Controls), back-

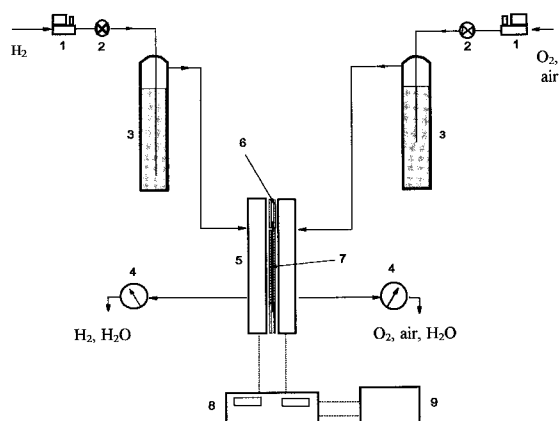


Fig. 1. Fuel cell test station: (1) mass flow controller, (2) shut off valve, (3) humidification bottle, (4) back-pressure regulator, (5) fuel cell, (6) gasket, (7) membrane-electrode assembly, (8) electronic load and (9) data acquisition.

pressure regulators, mass flow controllers (model 1159, MKS Instruments, Inc.). A schematic diagram of the set up is reported in Figure 1. Cell potential-current density characteristics were obtained in galvanostatic mode using a programmable Electronic load (HP 6060B, Hewlett Packard) interfaced via computer for data acquisition. Measurements were carried out at cell temperatures from 70 to 95 °C, and pressures from 1 to 5 bars absolute for cathode side and from 1 to 3 bars on the anode side. The gas flow rates were kept constant at 1.5 and 3 times the stoichiometric value calculated at current density of 1 A cm⁻² for fuel and oxidant, respectively. During the tests the gas humidification temperatures were of 5 and 15 °C higher than that of the cell for air (or O₂) and H₂, respectively.

3. Results and discussion

The two different electrode configurations (SP1 and AP1) are compared in Figure 2, where the cell performance is reported for H₂/O₂ and H₂/air operation at 70 °C. The alternative procedure (AP1 electrode) produces a significant rise in cell potential at all current densities in O₂ and mostly at high current density in air. This improvement is associated with both the optimization of the catalyst and diffusion layer. The direct mixing of the catalyst with ionomer conductor enhances Pt utilisation [4, 5] and the introduction of the intermediate hydrophobic carbon layer improves the gas and water management [10].

From these preliminary results it is evident that the carbon layer in the AP electrode configuration and, its morphological characteristics, play an important role in the gas diffusion limitation [10]. Starting from these

Table 1. Basic structural characteristics of the electrodes investigated

Sample	Carbon layer /mg cm ⁻²	PTFE content /%	Pt Loading /mg cm ⁻²
SP1	no layer	–	0.49
AP1	2	40	0.41
AP2	2	10	0.10
AP3	2	20	0.10
AP4	2	40	0.10
AP5	2	60	0.10

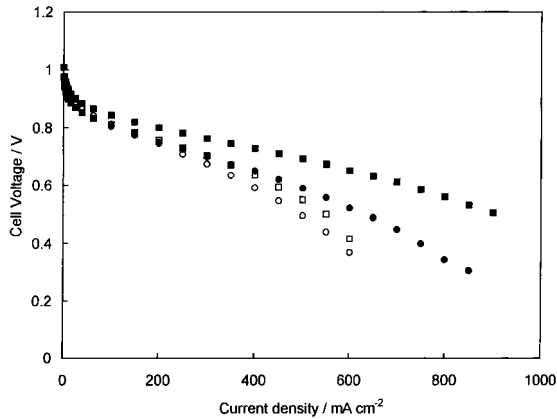


Fig. 2. Air and oxygen polarization curves for standard and alternative electrodes. Anode/cathode pressure 2.5/3.0 bar, $T_{\text{cell}} = 70^\circ\text{C}$, $T_{\text{humidifiers}} = 85/75^\circ\text{C}$. Key: (○) air SPI; (□) air API; (●) O₂ SPI; (■) O₂ API.

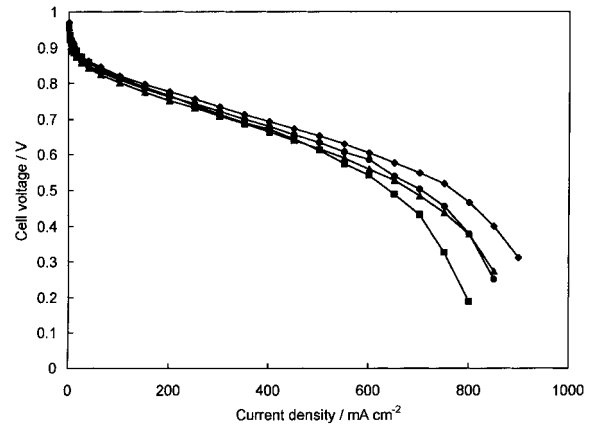


Fig. 4. Influence of PTFE content (wt %) in carbon layer on cell voltage vs current density for AP2, AP3, AP4 and AP5 electrodes. H₂/air at 2.5/3.0 bar, $T_{\text{cell}} = 70^\circ\text{C}$. Key: (■) 10%; (◆) 20%; (●) 40% (▲) 60%.

considerations the effect of varying the percent of PTFE in the carbon layer was investigated using 10, 20, 40 and 60 wt % PTFE in electrodes with low Pt loading with other fabrication parameters constant (Table 1).

In Figures 3 and 4, the cell performance obtained at 70°C with different PTFE content in carbon layer is shown in H₂/O₂ and H₂/air, respectively. The best performance was obtained with a diffusion layer containing 20 wt % of PTFE. The difference between the investigated polymer content is more evident in H₂/air operation (Figure 4) where the presence of a nitrogen blanket, together with product water, causes enhanced diffusion limitations due to the microporosity and/or to the hydrophobicity of the carbon diffusion layer.

The results obtained in H₂/air at 70°C are compared in Figure 5 at four different current densities as a

function of PTFE content. At low current density (100 mA cm^{-2}) the effect is negligible, while at high current densities ($500\text{--}700\text{ mA cm}^{-2}$) the influence is more pronounced, showing a maximum at 20 wt % of PTFE with a successive decrease in cell voltage with increase in PTFE content. These results are in agreement with the conclusions drawn from galvanostatic polarisation and impedance measurements [11] and can be explained by consideration that a low content of PTFE improves water transport with a consequent better humidification of the polymer electrolyte. The low performance for the 10 wt % PTFE electrode (AP2) is probably due to the lower hydrophobicity which improves the conductivity of the carbon and catalyst layer but which is not able to efficiently remove the water generated in the cell.

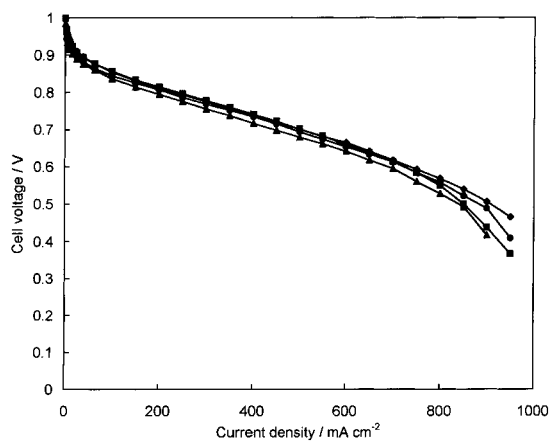


Fig. 3. Influence of PTFE content (wt %) in carbon layer on cell voltage vs current density for AP2, AP3, AP4 and AP5 electrodes. H₂/O₂ at 2.5/3.0 bar, $T_{\text{cell}} = 70^\circ\text{C}$. Key: (■) 10%; (◆) 20%; (●) 40%; (▲) 60%.

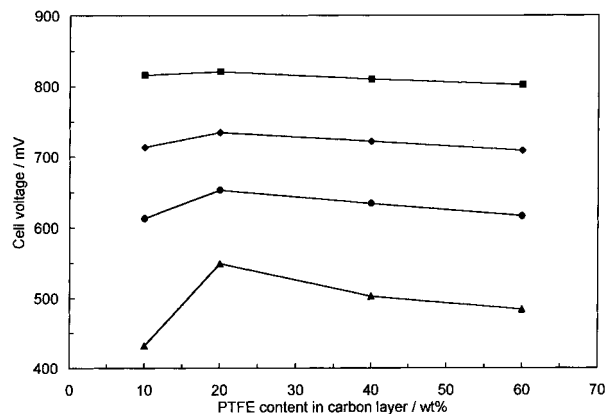


Fig. 5. Cell voltage as a function of PTFE content (wt %) in the carbon layer at different current density. H₂/air operation at 2.5/3.0 bar, $T_{\text{cell}} = 70^\circ\text{C}$. Current densities: (■) 100; (◆) 300; (●) 500 and (▲) 700 mA cm⁻².

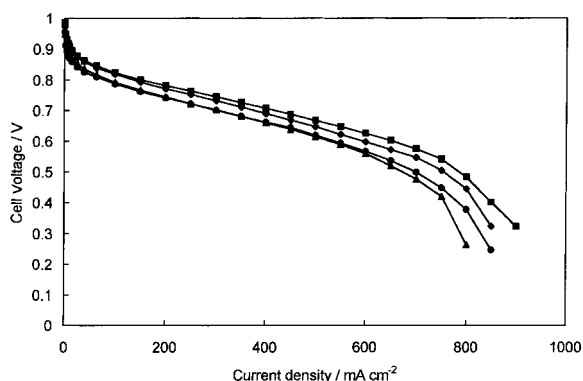


Fig. 6. Influence of H₂/air pressure on the cell performance using AP3 electrode at 70 °C. Key: (▲) 1/1 bar; (●) 1.5/1.5 bar; (◆) 2.5/3 bar; (■) 3/5 bar.

The optimized structure (AP3) containing 20 wt % PTFE in the carbon layer has been investigated by varying the operating conditions. The effect of air pressure on the cell performance in the range 1 to 5 bar absolute at 70 °C and with an air utilization of about 30% is reported in Figure 6. As expected, the cell performance increases with increasing air partial pressure but mass transport limitations are still visible at higher current density. The enhancement in cell potential when the gas pressure is increased from 1/1 to 3/5 bar for H₂/air is about 100 mV at 0.7 mA cm⁻². Power densities of 330 and 390 mW cm⁻² were obtained at 0.6 V for 1 and 5 bar air pressure, respectively.

The effect of temperature on the fuel cell behaviour for the optimized electrode at 70, 80 and 95 °C and 3/5 bar H₂/air pressure is shown in Figure 7. The increase in limiting current with increasing temperature indicates that diffusion problems are less important when the cell operates at 95 °C. In the same figure the cell power density at the three different temperatures is shown. Very high power densities of about 450 mW cm⁻² at 0.5 V and 430 mW cm⁻² at 0.6 V at 95 °C are achieved.

4. Conclusions

An alternative and efficient method of electrode fabrication has been achieved for H₂/air polymer electrolyte fuel cells. The direct mixing of catalyst with the ionomer provides a very high performance by enhancing conductivity and Pt utilization in the catalyst layer. The introduction of an intermediate carbon layer, between catalyst and carbon paper substrate, produces a micro-porous hydrophobic layer that is believed to achieve improved gas and water management in air operation.

The optimization of the PTFE (20 wt %) content in the carbon layer for low Pt loading (0.1 mg cm⁻²) has

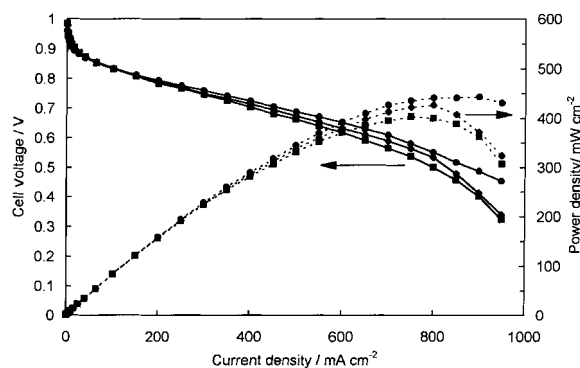


Fig. 7. Influence of temperature on (—) cell voltage and (- - -) power density for the optimized electrode (AP3) with 20 wt % of PTFE in H₂/air at 3/5 bar of pressure. Key: (■) 70 °C; (◆) 80 °C; (●) 95 °C.

produced a maximum performance of 450 mW cm⁻² in H₂/air operation at 95 °C.

The cell voltage/current density performance obtained with the new electrode structure is temperature and pressure sensitive, though the influence of pressure in the present study is less notable than that in the work of other authors [4, 8]. Power densities of 330 mW cm⁻² at 0.6 V at atmospheric pressure and at 70 °C represent an interesting result for possible application of PEFCs for electric vehicles.

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