HIGH PERFORMANCE ELECTRODES FOR HYDROGEN/AIR PEMFC OPERATING AT ATMOSPHERIC PRESSURE

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Proton Exchange Membrane Fuel Cells (PEMFCs) are in an advanced state of development. However, the weight, volume, and cost of this type of systems are still limiting factors to their commercialization. In order to overcome some of these constraints, work has been conducted to attain high performances in hydrogen/air PEMFC, working at atmospheric pressure. The electrodes were prepared by either the spray or the dry method, and contained a platinum loading varying between 2 and 6 mg/cm². The influence of the PTFE content in the electrode, both for the anode and cathode, as well as of the concentration of platinum supported on carbon on the PEMFC performance were investigated. The optimization of the composition and structure of the electrode catalyst layer led to performance such as 0.35 W/cm² at cell voltage of 0.7 V.

INTRODUCTION

High power density and high energy efficiency PEMFC development has been the objective of many investigations during the last 15 years and PEMFC power plants are now very close to reaching this goal as well as commercialization. The increased interest in this type of power source is due to its potential for meeting the power requirements needed for electric traction. However, further decreases of the weight and volume of the fuel cell stacks and auxiliaries are required. One way to decrease the weight and increase the specific power of such system is to operate it at atmospheric pressure, but without significant loss of performance. This would eliminate auxiliaries, such as a compressor, and also would lead to a lighter stack. The aim of this work is to develop high performance electrodes for PEMFCs, which can operate at current densities higher than 0.3 A/cm² at cell voltage of 0.7 V, with hydrogen and air as reactants and at atmospheric pressure. Previous investigations at the Center for Electrochemical Systems and Hydrogen Research (1, 2) indicate that such PEMFC performance could be achieved by using electrodes with a high percent of platinum content on the carbon support, by optimizing the electrode structure, and by minimizing the ohmic losses in the proton conducting membrane electrolyte.
EXPERIMENTAL

Methods of Electrode Preparation

Two methods of electrode preparation were used. The first one - the spraying method consists of spraying a suspension of uncatalyzed or catalyzed carbon particles in water/alcohol mixtures to form the gas-diffusion and active layers respectively on the heated, Teflonized carbon cloth substrate (3). The second one - the dry method consists in casting the dry powdered materials on the carbon cloth, and subsequently cold pressing of this powdered material/carbon cloth composite to form the electrode.

Membrane and Electrode Assembly (MEA) Preparation

These electrodes (hydrogen and oxygen) were impregnated with Nafion 117 solution (5 wt % in alcohol) by brushing. The amount of proton conducting polymer deposited in the electrodes was about 0.6 mg/cm². The Nafion impregnated electrodes were hot pressed onto the proton conducting membrane. The membranes, used in this work, were Aciplex S 1104, Nafion 115 and Nafion 112. The thickness of the first two membranes in the dry state was approximately 120 μm, the thickness of the third membrane was 50 μm.

Single Cell Electrochemical Tests

The performances of all MEAs were investigated in 5 cm² geometrically active area single cells. Those cells were connected to the fuel cell test stations, equipped with controls for the current density, cell voltage, electrode potentials, gas pressures, and cell temperature, as well as gas humidification bottles. All experiments were performed at constant gas flow. The steady state current-voltage dependencies were recorded by using a computerized data acquisition facility. The experiments were carried out at 70 °C cell temperature and at atmospheric pressure of the reactant gases unless otherwise specified.

RESULTS AND DISCUSSION

Power Density Limiting Factors

Most of the limitations of a PEMFC operating at atmospheric pressure are due to (i) the low concentration of O₂ in the gas phase which reduces further the cell voltage, (ii) the slow diffusion of O₂ dissolved in the electrolyte, to the electrocatalyst particles in the active layer, and/or (iii) O₂ diffusion through the substrate diffusion layer which in all
probability contains water droplets or films and a nitrogen blanket. In order to overcome these problems, previous studies have shown that the thickness of the active layer should be reduced and the electrocatalyst loading of the electrode increased. This goal can be achieved by using a higher concentration of platinum supported on the high surface area carbon. Another way of improving the electrode performance is to vary the PTFE content in order to optimize the water management in the active layer.

Influence of Methods of Preparation

The effect of the different methods of electrode preparation on the PEMFC performance is illustrated in Figure 1. The platinum loading of the electrodes was 2.5 mg Pt/cm². The gas-diffusion layers consisted of 4 mg/cm² of acetylene black Teflonized with 30% PTFE. Four different ways of preparation of the active layer were used: (i) spraying of Pt/carbon catalyst/30% FEP suspension, drying and rolling (spray); (ii) spraying of initially Teflonized Pt/carbon catalyst suspension, drying, and pressing (Teflonized spray); (iii) spraying of Pt/carbon catalyst mixed with Teflonized (30% PTFE) acetylene black, drying and pressing (spray/dry); (iv) dry-casting of Pt/carbon catalyst mixed with Teflonized (30% PTFE) acetylene black and pressing (dry). The results showed that there is no significant influence of the method of electrode preparation on the electrode performances for current densities up to 800 mA/cm². Thus it was decided to use the dry method of preparation for subsequent experiments because this method is relatively easy to use, fast, and without any loss of the platinum electrocatalyst during fabrication.

Influence of Platinum Loading

The influence of the platinum loading in the electrode on the PEMFC performance was studied by using supported platinum on carbon electrocatalysts consisting of 40, 60 and 80 wt % platinum. The amount of supported electrocatalysts was kept constant at 6.6 mg/cm², while the platinum loading of the electrodes were 2.64 mg/cm² (40% Pt/C), 3.96 mg/cm² (60% Pt/C), and 5.12 mg/cm² (80% Pt/C). The particle sizes of the platinum and the related estimated thickness of the active layers of the electrodes are presented in Table I. The PEMFC performances are shown in Figure 2. The highest and lowest Pt-loaded electrodes have the same electrochemical activity at low current densities (less than 100 mA/cm²) but at the high current densities the highest platinum loaded electrode gave the best results. The electrode with 3.96 mg Pt/cm² had the highest electrochemical activity and the same slope in the linear region as the electrodes with the smallest amount of platinum loading. The slope in the linear region was lower for the PEMFC with electrode containing 5.12 mg Pt/cm². These results can be better explained by the Tafel plots for the PEMFC in the three cases (Figure 3) and the resulting electrode kinetics, mass transport, and ohmic parameters (Table II) estimated using a non linear least square fit of the experimental data to the empirical equation [1] (5).
\[ E = E_0 - b \log(i) - R i - m \exp(n i) \]  

where \( E \) is the cell potential, \( i \) the current density, \( R \) the ohmic resistance and \( m \) and \( n \) are parameter describing the mass transport effects in the PEMFC. The electrode with the 60% Pt/C has the highest electrochemical activity, while the electrochemical activities of electrodes with 80% Pt/C and 40% Pt/C are significantly lower. Because the weight of the active layer in the electrode was maintained constant (8 mg/cm²), its thickness was different and depended on the specific gravity of the supported catalyst; the thickness of the active layer decreased in the order 40% Pt/C, 60% Pt/C, 80% Pt/C. The amount of Nafion impregnated in the active layer was practically constant (0.6 mg/cm²) and the extent of Nafion penetration into the active layer was also constant. The thickness of the impregnated layer and the surface area of the Pt-catalyst (Pt particle size) are the main factors which determine the platinum utilization in the electrodes (6). The highest electrochemical activity is obtained in electrodes with 60% Pt/C catalyst, showing that this is the best compromise "thickness/Pt utilization/Pt particle size". In the case of electrodes with 40% Pt/C, the lower electrochemical activity is due to a lower Pt utilization, caused by a thicker active layer (insufficient Nafion penetration into the active layer). In the case of electrodes with 80% Pt/C the electrochemical activity can be explained by the lower surface area of platinum particles (Table I). At higher current densities, PEMFCs with electrodes having thicker active layers, exhibit higher slopes in the linear region of cell potential (E) versus current density (i) plot, which is probably caused by the higher ohmic resistance in the Nafion impregnated active layer. On the contrary, electrodes with 80% Pt/C catalyst (thinner active layer) show a better conductivity, leading to a lower slope of the PEMFC E vs. i plot. These results illustrate that it is possible to design PEMFC electrodes, by varying the Pt concentration on carbon, to attain high power densities and cell potentials.

**Influence of PTFE Content in Active Layers of Electrodes**

The amount of PTFE in the electrodes was varied by using different ratio of Pt supported on carbon electrocatalyst/Teflonized acetylene black. The latter has 30% Teflon. For total active layer weight of 8 mg/cm², the ratios 4:1, 7:1 and 9:1 parts by weight 60% Pt/C : 30% Teflonized acetylene black were investigated. These ratios correspond to 6.00%, 3.75%, and 3.00% of PTFE in the entire active layer respectively. The goal of these experiments was to investigate the effect of PTFE content which was lower than 10%, which amount was found to be optimal from a previous investigation (4). In Figure 4 are shown the E vs. i plots for MEAs with different PTFE contents. The results show that decreasing the PTFE content below 6% leads to a poorer performance, caused, probably, by higher gas diffusion hindrance in the active layer of the electrode. This can be explained by the decreased volume of the hydrophobic, reactant gas permeable, porous regions in the active layer, which has a
negative influence on the electrode performance, especially when air at atmospheric pressure is used as the cathodic reactant.

Influence of Proton Conducting Membrane on PEMFC Performance

The influence of the proton conducting membrane on the performance of PEMFCs is illustrated in Figure 5. These results are in good agreement with results, obtained earlier (6). The thinnest membrane, Nafion 112, provides the best performance because of its lower ohmic resistance. On the other hand, the E vs. i plot for PEMFC with the Aciplex S membrane is better than that with Nafion 115 membrane despite the thickness being the same in both cases. This is due to the lower equivalent weight of Aciplex S membrane (EW=1000) compared to the Nafion 115 membrane (EW=1100) and hence the higher ionic conductivity of the Aciplex-S material. It must also be noted that the PEMFC with the Nafion 112 membrane shows a departure from linearity in the E vs. i plot at a considerable higher current density than in the PEMFCs with Nafion 115 and Aciplex-S membranes, confirming our previous conclusions that mass transport of protons and/or water can also explain the region of the E vs. i plot in which there is a departure from linearity.

CONCLUSIONS

This study is still at an early stage, but interesting results have already been obtained, showing that the optimization of the structure of the electrode and the composition of the active layer could lead to significant improvements in cell performance. The attained performance so far is 0.7 A/cm² at cell voltage of 0.65 V with air at atmospheric pressure as reactant. This demonstrates that, it is possible to reach power density of 0.5 W/cm² at an efficiency close to 60 % based on the lower heating value (LHV) of the hydrogen/oxygen reaction in a PEMFC operating with air at atmospheric pressure. Concerning the catalyst, this study was conducted with very high platinum loading (up to 6 mg Pt/cm²). We expect that further optimization of the electrodes will lead to a decrease of Pt loading, to less than 2 mg Pt/ cm², without loss of performance.

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REFERENCES

1. E.A. Ticianelli, C.R. Derouin, A. Redondo, and S. Srinivasan, J. Electrochem. Soc. 135, 2209 (1988)
2. S. Srinivasan, D.J. Manko, H. Koch, M.A. Enayatullah, and A.J. Appleby, J. Power Sources, 29, 367 (1990)
3. R. Mosdale, P. Stevens, Solid State Ion., 61, 251 (1993)
4. R. Mosdale, M. Wakizoe, and S. Srinivasan, In Press
5. J. Kim, S-M Lee, S. Srinivasan and C. Chamberlain, In Press J. Electrochem. Soc.
6. M. Wakizoe, O.A. Velev, and S.Srinivasan, Electrochimica Acta, 40, 335 (1995)

Table I Dependence of Pt particle size and active layer thickness of electrode on percent of Pt in supported electrocatalyst and Pt loading

| Catalyst type Pt/C, % | Electrode Pt loading [mg Pt/cm²] | Pt particle size [nm] | Active layer thickness, µm |
|------------------------|------------------------|----------------------|--------------------------|
| 40                     | 2.64                   | 3.9                  | 17                       |
| 60                     | 3.96                   | 8.8                  | 10                       |
| 80                     | 5.12                   | 25                   | 8.0                      |

Table II Electrode kinetic, mass transport and ohmic parameters for PEMFCs with electrodes with different Pt loading. Parameters were calculated using the empirical equation [1] which shows excellent fit of experimental E vs i data (5)

| Pt loading | E₀, mV | R, Ω | b, mV/dec | m, mV | n      |
|------------|--------|------|-----------|-------|--------|
| 5.12       | 933    | 0.266| 48        | -3.89 | 0.00008|
| 3.96       | 1051   | 0.209| 48        | 73.02 | 0.001  |
| 2.64       | 950    | 0.298| 63        | 0.40  | -0.004 |
Figure 1 Cell potential vs. current density plot for PEMFCs with electrodes prepared by different methods. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1]

Figure 2 Cell potential vs. current density plot for PEMFCs with electrodes containing different platinum loading. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1]
Figure 4: Cell potential vs. current density plot for PEMFCs using electrodes with different PTFE content. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1].

Figure 3: Tafel plot for PEMFCs, using experimental data in Figure 2.
Figure 5 Cell potential vs. current density plot for PEMFCs with different proton conducting membranes. Electrode Pt loading 3.96 mg/cm², cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1]