



Characterization of Proton Exchange Membrane Fuel Cells with Catalyst Layers Obtained by Electro spraying

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Electrospraying of Pt/C-Nafion-alcohol dispersions was employed as a new method to deposit catalyst layers on Nafion membranes for hydrogen/oxygen(air) fuel cells. It is shown that single cells with catalyst layers obtained by electro spraying exhibit good initial performance (*ca.* 1 A/cm²@ 700mV) at 80°C and 300 kPa without the need for hot-pressing of the electrode layer. Analysis of polarization losses reveals a significant contribution of mass-transport losses to the fuel cell performance for hydrogen/air fuel cells. We suggest that control of electro spray processing parameters can lead to tailored electrode structures where such mass transport losses are mitigated.

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Electrostatic polymer processing (electro-spraying, electro spinning, and combinations of the two) represents a new and highly versatile approach for the fabrication of polymer-based electrochemical device components.^{1,2} Electro spraying and electro spinning can afford particles and fibers with diameters of 100 nm or less, suggesting that nanostructured electrolytes and electrodes may be obtained by judicious choice of materials and electrostatic processing parameters. Moreover, these electrostatic processing approaches may have applicability to a wide variety of polymer-based electrochemical devices, including fuel cells, batteries, capacitors, and electrochromic and electroluminescent displays. We believe that electrostatic processing could be used for the construction of an entire proton-exchange membrane fuel cell (PEMFC), including the membrane, electro-catalyst layers, and gas diffusion layers. Particularly appealing is the potential ability to control composition, porosity, and wettability of these fuel cell components.

As a first step in the development of this technology, Nafion was electro sprayed from solution to afford thin films and subsequently characterized as having physical properties (water uptake, dimensional changes, electrical conductivity) similar to those of Nafion 117 films.¹ Following that, electrochemical properties of half-cells with commercial Nafion 117 and catalyst layers obtained by electrostatic processing were characterized.²

The present research is focused on evaluation of PEM single cells with catalyst layers obtained by the electro spraying technique on commercial Nafion 112 films.

Experimental

Electrospraying setup.—The electro spraying experimental setup is shown in Fig. 1. It consists of (1) a high-voltage power supply, (2) a syringe pump, (3) a 5 mL syringe containing Pt 'ink' (see below) with 21-gauge electropolished (as described in Ref. 3) injection needle that served as an anode, and (4) a grounded aluminum plate (made from aluminum foil) that served as a cathode. The aluminum plate was placed on top of an acrylic plastic plate and Nafion 112 film (5) was placed on top of this plate. The polymer film was exposed to the spray through a Teflon mask that had square opening (3.2 × 3.2 cm²) in the center. After applying a high voltage (with respect to a grounded electrode) to the syringe needle, Pt ink droplets were ejected from the tip of the needle toward the counter electrode.

Pt ink preparation.—To prepare Pt ink, 107.8 mg of 20% platinum on Vulcan XC-72 carbon (E-TEK) was mixed with 1 mL of 5% Nafion solution (Aldrich) and 4 mL of ethyl alcohol, and was ultrasonically dispersed for 2 h.

MEA preparation.—Nafion 112 membranes (from DuPont) were cleaned by heating in 5% H₂O₂ (Aldrich) solution at 70°C for 1 h followed by rinsing in high purity (Milli-Q) water. The film was treated then in 0.5 M H₂SO₄ (Aldrich) at 70°C for the same time duration. To remove traces of sulfuric acid from the membrane, it was heated repeatedly in water.

Electrospraying of the Pt ink was performed with the following parameters: spraying voltage, 20 kV, distance from the membrane to the tip of the syringe needle, 5 cm, ink flow rate, 5 mL/h. After electro spraying, the membrane with a catalyst layer on both sides was dried in the oven for 1 h at 80°C to remove residual alcohols. The final film consisted of 70% of Pt/Vulcan XC-72 and 30% of Nafion (dry base). Pt loading was confirmed by inductively coupled plasma optical emission spectroscopy (Galbraith Laboratories, Knoxville, TN).

Electrochemical measurements.—Single cell tests were performed with 890C Fuel Cell Test System (Scribner Associates, Inc.). Catalyst coated membrane with 10 cm² active area was placed between ELAT nontatalyzed diffusion layers (E-TEK) and mounted into a single cell test fixture (Fuel Cell Technologies, Inc.). The anode served as both a reference and counter electrode, and cathode was a working electrode. To achieve the best level of performance, the cell was preconditioned as follows. First, the cell was maintained under open-circuit potential for 1 h while being purged with humidified hydrogen and oxygen. After that, the temperature was raised to 60°C and multiple cycling of potential was performed until stable

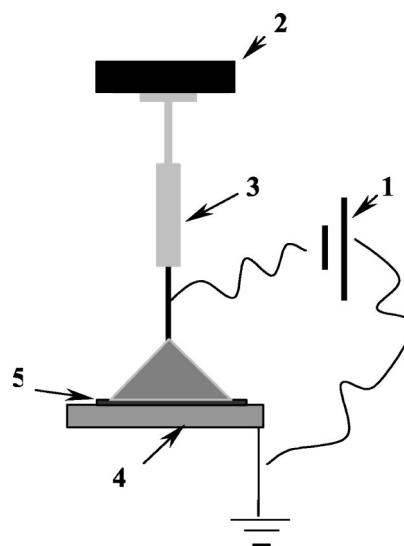


Figure 1. Electro spraying set-up: (1) power supply, (2) syringe pump, (3) syringe needle, (4) grounded aluminum plate, and (5) membrane.

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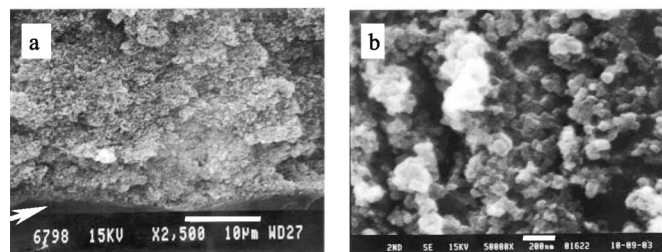


Figure 2. SEM of the catalyst layer/Nafion 117 cross-section obtained with resolutions of (a) 2500 and (b) 50000. The arrow in Fig. 2a shows location of Nafion 117.

cyclic voltammogram was obtained. Measurements were performed on cells operating at 80°C and 100% relative humidity with stoichiometric H₂/O₂(air) flows of 2/9.5.² Anode/cathode loadings were 0.2/0.09 and 0.2/0.36 mg_{Pt}/cm².

Hydrogen crossover current was determined as it was suggested in Ref. 4; the value of 4.8 mA/cm² for 80°C and 300 kPa was obtained.

Impedance measurements.—Cell resistance at constant current was determined from high-frequency impedance measurements performed using a 1260 SI impedance analyzer (Solartron, Inc).

Microscopy.—Scanning electron microscopy (SEM) of freeze-fractured cross-sections of catalyst coated membranes was performed with JEOL JSM-820 microscope.

Results and Discussion

Microscopy.—SEMs of an electrocatalyst layer on Nafion 117 obtained by electrostatic processing are shown in Fig. 2. As seen in Fig. 2a, catalyst particles are well dispersed and the catalyst layer appears to be reasonably homogeneous throughout its thickness. In addition, adhesion of the catalyst layer to the Nafion film appears to be uniform. Figure 2b shows individual support particles (typically 40-50 nm in diam) bound to each other with Nafion. The catalyst layer has a porous structure that is expected to facilitate gas access to the catalyst particles. Porosity of the cathode catalyst layer was estimated as the ratio of void volume to the total volume of the catalyst layer. For two cathode loadings 0.09 and 0.36 mg_{Pt}/cm² porosity was found to be 84 and 77%, respectively.³ Considering the error in thickness determination, we can assume that porosity of the catalyst layer does not depend on loading for our technique of fabrication of catalyst layers. Compared to other techniques described in the literature,^{6,7} electrospraying affords the prospect of fabrication of electrodes with higher porosity. For example, the porosity value from an air-brush spray technique was found to be 67%,⁶ while for the state of the art GM electrodes fabricated by the decal technique, the value of ~30% was reported.⁷

Evaluation of initial fuel cell performance.—Figure 3 shows performance of hydrogen/oxygen and hydrogen/air single cells for two cathode loadings. As seen from the figure, a 4x reduction in cathode loading results in 60-80 mV and greater voltage reduction both for oxygen and air over entire current density range. Switching from oxygen to air dramatically decreases fuel cell performance indicating significant diffusion limitations in the course of oxygen reduction.

At 1 A/cm² H₂/O₂ single cells with loading 0.2/0.36 mg_{Pt}/cm² yield voltage of 0.74 V which is ~30 mV less than performance of

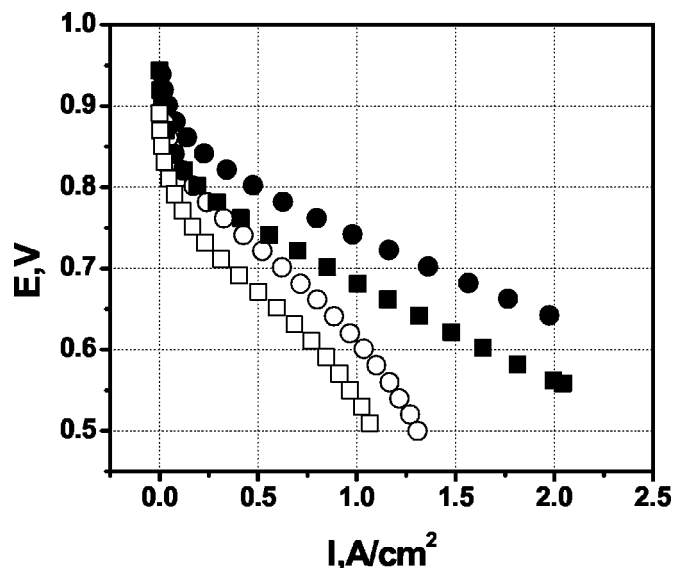


Figure 3. Stationary polarization curves for H₂/O₂ (solid symbols) and H₂/air (open symbols) single cells utilizing Nafion 112 membrane for two different cathode loadings-0.09 (square symbols) and 0.36(circles) mg_{Pt}/cm². 80°C, 300 kPa and 100% RH.

the state-of-the art fuel cells produced by GM.^{5 b}

Contributions of different losses in the performance of single cells were analyzed according to⁵

$$E_{\text{cell}} = E_{\text{eq}} - \eta_{\text{ORR}} - \eta_{\text{HOR}} - \eta_{\text{ix}} - IR \quad [1]$$

where E_{eq} is equilibrium potential for reaction of water generation which depends on temperature and partial pressure of oxygen and hydrogen; η_{ORR} and η_{HOR} are overvoltages for oxygen reduction and hydrogen oxidation reactions, respectively; η_{ix} is concentration polarization and R stands for ohmic cell resistance that includes protonic resistance of the membrane and ionomer in the catalyst layer and electronic resistances of diffusion layers, catalyst layers and interfaces between catalyst-diffusion layers and diffusion layers-bipolar plates. The overvoltage of the hydrogen oxidation reaction is considered negligible due to the fact that exchange current density for hydrogen oxidation reaction is five orders of value higher than for ORR.⁸

The ohmic resistance of a single cell was determined by direct impedance measurements; in the current range of 0.1-2 A/cm² the value of resistance was almost constant and changed from sample to sample from 60 to 90 mOhm cm².

Figure 4 depicts IR-corrected cell voltage vs. current density, corrected for hydrogen-crossover current, extracted from curves presented in Fig. 3. As seen from the figure, all curves have a linear portion that ranges up to 1 and 0.1 A/cm² for hydrogen/oxygen and hydrogen/air conditions, respectively. The slopes of the lines (72 and 69 mV) obtained for two different loadings suggest that slow kinetics of ORR is the rate-determining step in these regions of current densities. The Tafel slope values are close to the theoretical value $2.303 \cdot RT/F = 69.9$ mV (at 80°C) and are in agreement with the values of 60-70 mV observed for ORR in PEM fuel cells.⁴

The difference in cell voltage between H₂/O₂ and H₂/air fuel cells in the kinetic region at a given current density can be estimated on the basis of⁴

³It was supposed that density of Nafion, carbon and platinum was 2.0, 1.8, and 21.45 g/cm³, respectively.⁵

^bConditions -80°C, 270kPa_{abs}, 100% RH.

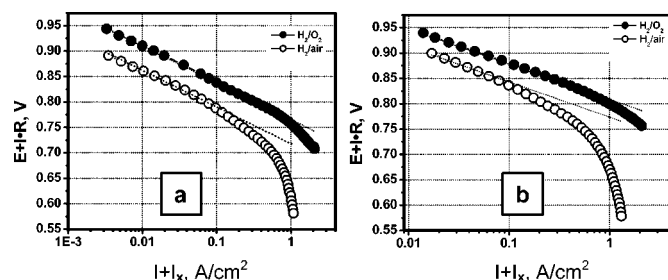


Figure 4. Polarization curves corrected for both IR losses and hydrogen crossover for H₂/O₂ and H₂/air single cells at two different cathode loadings: a – 0.09 mg_{Pt}/cm²; b – 0.36 mg_{Pt}/cm². 80°C, 300 kPa and 100% RH. I_x-hydrogen crossover current.

$$\Delta E_{O_2/air} = E_{O_2} - E_{air} = 2.303m \frac{RT}{F} \log \left(\frac{p_{O_2}}{p_{air}} \right) \quad [2]$$

where m is reaction order for the ORR. Assuming that $m = 1$,^{9,10} $\frac{p_{O_2}}{p_{air}} = 4.76$ and $2.303RT/F = 69.9$ mV, a value of 47.3 mV was obtained for $\Delta E_{O_2/air}$ and is consistent with experimental values of 50 and 40 mV, observed for two cathode loadings 0.09 and 0.36 mg_{Pt}/cm², respectively.

Comparison of the corresponding curves for oxygen and air in Fig. 4a and b shows that the voltage difference due to an increase in cathode Pt loading (at given current) results in 45 and 50 mV increases in resistance-corrected voltage in the kinetic region for oxygen and air, respectively. Theory (see Eq. 9 in Ref. 5) predicts ~42 mV increase in voltage for a 4x increase in cathode loading assuming that mass-specific electrochemically active surface area of the catalyst does not depend on loading.

As seen from Fig. 4, when the current density increases, at some point the polarization curves begin to deviate from Tafel behavior. This is an indication of mass-transport limitations that are caused by slow oxygen diffusion to the surface of the catalyst. The reason for this might be poor water management resulting in electrode flooding. It is obvious, that diffusion limitations should be more pronounced in air compared to pure oxygen. For state-of-the art electrodes^{4,5} diffusion limitations are eliminated up to 1.8 A/cm² in hydrogen/oxygen fuel cells and up to 0.2 A/cm² in H₂/air fuel cells, while for our technique of fabrication of electrodes, diffusion limitations are more pronounced. A deviation from linearity begins at

current densities higher than 1 and 0.1 A/cm² for H₂/O₂ and H₂/air single cells, respectively. Therefore, our future efforts will be concentrated on the analysis of the nature of diffusion limitations, and current work is focused on the reduction of thickness of diffusion layer by switching to higher Pt loadings in the Pt/C catalyst.

Conclusions

An electro spraying technique was employed to obtain catalyst coated membranes for hydrogen/oxygen (air) fuel cells. It was shown that single cells with catalyst layers obtained by electrostatic processing exhibit good initial performance at an operating temperature of 80°C and pressure of 300 kPa without optimization of electro spraying parameters. Kinetic regions for oxygen reaction were observed up to 0.2 and 1 A/cm² for hydrogen/air and hydrogen/oxygen fuel cells, respectively. Analysis of polarization losses revealed significant contribution of mass-transport losses to the fuel cell performance for hydrogen/air fuel cells. Current efforts are focused on analysis of the nature of diffusion limitations and characterization of microstructure of catalyst layers.

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References

1. E. H. Sanders, K. A. McGrady, G. E. Wnek, C. A. Edmondson, J. M. Mueller, J. J. Fontanella, S. Suarez, and S. G. Greenbaum, *J. Power Sources*, **129**, 55 (2004).
2. O. A. Baturina and G. E. Wnek, Paper 990 presented at The Electrochemical Society Meeting, Orlando, FL, Oct 12-16, 2003.
3. B. Hoyer, G. Sorensen, N. Jensen, D. B. Nielsen, and B. Larsen, *Anal. Chem.*, **68**, 3840 (1996).
4. S. Kocha, in *Handbook of Fuel Cells-Fundamentals, Technology and Applications*, W. Veilstich, A. Lamm, and H. Gasteiger, Editors, Vol. 3, p. 538, Wiley, Weinheim (2003).
5. H. A. Gasteiger, W. Gu, R. Makhata, M. F. Mathias, and B. Sompalli, in *Handbook of Fuel Cells-Fundamentals, Technology and Applications*, W. Veilstich, A. Lamm, and H. Gasteiger, Editors, Vol. 3, p. 593, Wiley, Weinheim (2003).
6. J. Itonen, F. Jaouen, G. Lindbergh, A. Lundblad, and G. Sundholm, *J. Electrochem. Soc.*, **149**, A448 (2002).
7. H. A. Gasteiger, J. E. Panels, and S. G. Yan, *J. Power Sources*, **127**, 162 (2004).
8. N. M. Markovic, B. N. Grgur, and P. N. Ross, *J. Phys. Chem. B*, **101**, 5405 (1997).
9. U. A. Paulus, T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, **495**, 134 (2001).
10. S. Mukerjee and S. Srinivasan, *J. Electroanal. Chem.*, **357**, 201 (1993).