DIRECT LIQUID WATER HYDRATION OF FUEL CELL MEMBRANES

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Direct liquid water hydration of polymer electrolyte fuel cell membranes improves cell performance and has system advantages over conventional reactant humidification schemes. The liquid hydration of the membrane is accomplished in our case by wicking water from a supply in the anode flow-field through the otherwise hydrophobic anode gas diffusion backing directly to the membrane/electrode assembly. The liquid water can be provided to the anode plenum either by injecting droplets into the hydrogen cell inlet or by integrating water channels into the anode flow-field. Conventional carbon-cloth gas diffusion backings are modified to provide the anode wicking backing by sewing in fine multifilament wicking threads using a conventional sewing machine. This simple scheme is demonstrated to provide improved performance and good stability.

INTRODUCTION

One of the primary challenges in attaining the optimal performance of polymer electrolyte fuel cells (PEFCs) is in attaining effective hydration of the ionomeric structure. Less than full hydration results in a decrease in the ionomer protonic conductivity. In addition, the kinetics of the oxygen reduction reaction (ORR) at the cathode are also adversely affected by a decrease in water content. Maintaining a high hydration level at all times throughout the membrane/electrode assembly (MEA) is difficult in fuel cells for a number of reasons. For example, at low current densities or at open circuit, when little liquid water is produced by the ORR, the MEA hydration level will tend to drop even when the reactant gases are at saturated water vapor conditions because the water uptake of perfluorosulfonate membranes is less when vapor-equilibrated as opposed to liquid-equilibrated (1). On the other hand, at higher current densities, the electro-osmotic drag of water with the protonic flux from the anode to the cathode tends to dry out the anode. An additional problem is that the cathode side also then tends to flood because of the ORR generated water as well as the water dragged across. In general, it is difficult to maintain optimum hydration levels under all operating conditions.

Certainly, the simplest PEFC system would be one where no auxiliary humidification system is required. In principle, the water produced in the ORR reaction is sufficient to maintain adequate hydration of the fuel cell under certain conditions (2). Relatively high fuel cell performances have been demonstrated at near ambient pressures with no external humidification using thin ionomeric membranes at fairly low cell temperatures of around 50°C (3, 4). Another approach uses catalysts and hydrophilic fillers within the membrane to generate and retain water generated by the recombination of the reactants (5, 6). While attractive, these self-humidifying approaches may have some operational limitations. For example, the combination of low current density (i.e., high voltage efficiency), typical operating temperatures (e.g., 80°C), and near ambient reactant pressures is of much practical interest but would be quite difficult to maintain sufficiently hydrated.
In most PEFC systems, water is provided to the polymer electrolyte membrane in the vapor form by humidification of the reactants. A general approach to simplify reactant humidification entails some means of introducing humidification plates within the individual cells. In one particular approach, International Fuel Cells (South Windsor, CT) uses water permeable bipolar plates to both recover liquid water from the cathode plenum (7) and directly humidify the anode and cathode flow-streams within the cells (8).

In most other humidified reactant technologies, the reactant gas streams are humidified before entering the cell using either heated sparger bottles or humidification modules. In some stacks, the gas streams are humidified by flowing the reactants through a humidity exchanger integrated into one end of the stack. Accommodating the exchanger tends to increase stack size and system complexity. Control of the stack is also complicated if the cells are humidified via the reactant streams because the two systems then become coupled. Often, the optimal hydration level may not match the most effective reactant flowrate, and it may be difficult, for example, to switch-off the cathode humidification if the cell starts to flood, or to increase the humidification level at low current densities as the cell starts to dry out as less water is produced by the ORR. As mentioned above, this lack of water is further exacerbated by the membrane's tendency to take up less water when only vapor-humidified. For such reasons, it is difficult to provide optimal (and not excessive) hydration over all current densities with a particular set-up.

In general, the best way of decoupling hydration from the other subsystems and assure a liquid-equilibrated hydration level of the membrane is to introduce liquid water directly to the MEA, as has been done previously both by wicking from the periphery of the electrode through the ionomeric membrane and by injecting water from the periphery through miniature tubes formed in the membrane. In the former case, Watanabe et al. introduced liquid water to the membrane from a supply reservoir around the periphery of the membrane (9). Since the standard perfluorosulfonate membranes do not wick water particularly well, a composite layer component was added to the anode side of a conventional perfluorosulfonate membrane that consisted of recast ionomer for ionic conductivity and a wicking material to facilitate the transport of the water through the x-y plane of the membrane. Performance improvements over reactant humidification were demonstrated in small cells. In the other liquid hydration approach, researchers at Lynntech, Inc. formed miniature channels in perfluoroionomer membranes and injected water from the edge through the tubes thus formed (10, 11). In these configurations, it may be difficult to wick or pump the water a substantial distance, the membranes need to be relatively thick, and currently off-the-shelf membranes and MEAs can not be directly utilized. As a result, we are developing an approach to introduce liquid water directly through the anode gas diffusion backing from a water supply in the anode flow-field region. In this way, sufficient water should be readily available throughout the active area of a large cell.

EXPERIMENTAL

Anode Wicking Backing

The direct liquid hydration approach that we have adopted is a wicking configuration in which the liquid water is delivered to the MEA through the otherwise hydrophobic backing from a liquid water source in the anode plenum. In this manner, a near unlimited supply of
water can be provided over the entire active area because there are no water transport limitations as in the case of the membrane serving as the water conduit. In order to convey the water from the anode plenum to the membrane, the concept utilizes a two-part hydrophilic/hydrophobic backing structure. The simplest means that we have found to realize the two-part structure is to use a wicking thread sewn through a conventional hydrophobic gas diffusion backing to supply the hydrophilic wicking component as is shown in the exploded cross-section depicted in Figure 1 (not to scale). A number of materials could conceivably be used for the backing such as fluorocarbon/carbon black treated carbon paper (12), but we prefer to use a carbon black/PTFE filled carbon cloth gas-diffusion electrode such as non-catalyzed ELAT, from E-TEK, Inc. (Natick, MA). With a serpentine thread pattern with each stitch about 2 mm long and the rows separated by about 2 to 3 mm, about forty segments of the thread convey water in the z-direction for each square centimeter of electrode area. The actual region that is in contact with wicking thread is even greater because of the portion of the stitches that overlie the backing on both sides. This allows take-up and delivery of the liquid water over a greater area. The liquid water could be supplied from droplets in the gas channels or from separate water-filled channels in the anode plate that could be arrayed in a number of configurations. At less than 80 um in diameter, the wicking thread is readily impressed into the originally 350 um thick backing. Upon compression of the cell during assembly, the backings deform sufficiently to close the needle holes and accommodate the wicks to provide good interfacial contacts of the various materials.

In principle, the wicking thread can be sewn into conventional, catalyzed gas diffusion carbon cloth electrodes that are then impregnated with ionomer and hot-pressed to the membrane (13), although thin-film catalyzed membranes (or MEAs) are used in the experiments described here (14). As such, the platinum catalyst loadings of the membranes are in the neighborhood of 0.12 mg Pt/cm²/electrode. While loadings as low as 0.03 mg Pt/cm² are shown to be effective on the anode side, MEAs with symmetrical loadings are used in this case. If a catalyzed membrane or MEA is used, as here, the water supplied from the anode wick must traverse the catalyst layer to access the membrane. Even though the thin-film catalyst layers are not particularly hydrophilic structures, no special effort has been made to modify the anode catalyst structure for interfacing with the wicking backing.

The first cells used for comparing the anode wicking technique to conventional reactant humidification both used standard E-TEK gas-diffusion backings in conventional hardware. The only difference between the baseline comparison cells and the anode wicking cells is that wicking thread is sewn into the anode backing. The wick material we used is a 200 m/g continuous multifilament polyester thread that is less than 80 um in diameter available as U151 from Güntermann of America. The wicking backing is used only on the anode side because of the tendency of this side to dry out and the preponderance of water at the cathode side (due to the ORR) at higher current densities.

A membrane/electrode/gasket (MEG) assembly was used in the comparison cells that prevents condensate from contacting the membrane around the periphery of the electrode. If the MEG is not used, a certain amount of direct liquid hydration is achieved from the periphery in the small (5 cm²) laboratory cells. The use of the MEG thus provides a more relevant comparison between the humidification techniques and the direct water injection is found to have a much clearer advantage over the humidified reactants than in comparisons without the MEG assemblies.
RESULTS AND DISCUSSION

5 cm² Cells Operated with Water Injection

In the initial 5 cm² cell experiments, the water for the anode wicking backing was provided by injecting a droplet of water each second into the anode reactant inlet of the cell at a rather generous 1.5 ml/min. The water droplets were carried by the hydrogen flow through the conventional 5 cm² active area single-channel serpentine flow-field to provide contact with the anode wicking thread over the active area. No external humidification of the reactants was used with the water injection. Humidifier bottles, heated above cell temperature, were used for reactant humidification on the conventional comparison cells.

Figure 2 depicts polarization curves for two Nafion 115 membrane (DuPont) based fuel cells; one configured with an anode wicking backing using water injection and the other a standard cell with conventional reactant humidification. The cell with the wicking backing outperforms the conventional cell over the entire current density range even though the latter is using relatively aggressive humidification conditions (anode and cathode humidifiers at 110 and 90°C, respectively). Not only is the performance higher at the low current densities where it might be expected that the enhanced hydration conditions improves the ORR, but it is also greater at the higher ranges where the relatively dry cathode gases probably improve the mass transport situation within the cathode backing and flow-field.

The most dramatic difference in the two humidification techniques is shown in Figure 3, which depicts the high frequency (8 kHz) cell resistances for the two cells in Figure 2. As commonly observed, the resistance of the conventionally humidified cell is much greater at the higher current densities where the anode side of the MEA tends to dry out due to the electro-osmotic drag of water away from this side. The use of a relatively thick membrane such as Nafion 115 amplifies this effect compared to higher performance membranes which tend to allow a more effective back-diffusion of water. The run with water injection shows much more constant, and ultimately much lower, cell resistances. It appears that the droplets of injected water are contacting the plenum side of the wicking thread, where it is carried across the backing to supply the membrane directly with liquid water.

One of the difficulties with the off-the-shelf polyester thread used above was that it lost hydrophilicity with time in the cell. When examined afterwards under the microscope, the thread fibers appeared intact, as no damage or degradation was apparent. In all likelihood, the surface of the inherently hydrophobic polyester annealed, resulting in a loss of whatever surface functionality provided its original hydrophilic nature. The hydrophilicity of the polyester thread can be maintained by first passing the thread through 5% Nafion solution (Solution Technology, Inc., Mendenhall, PA). While Nafion is chosen for its chemical stability, other approaches, such as using other types of threads (e.g. cotton/polyester blends, rayon, etc.) or other coatings can result in more hydrophilic surfaces with greater wicking capacities. However, the products that are available and strong enough to provide very thin threads are limited and also would need to be tested for their long-term stabilities.

Additional cells were prepared using anode wicking backings with the Nafion solution treated threads. The 500 h life test performance of one such cell operated continuously at 0.5 V using a higher performance, developmental membrane from Dow is shown in Figure 4. Initially, the cell was operated using aggressive anode humidification (the use of
humidifier temperatures substantially higher than cell temperatures delivers considerable amounts of condensate to the cell) which was sufficient to maintain good hydration with the wicking backing. Direct water injection at 0.37 ml/min was eventually started at about 175 h whereupon the cell resistance, shown in Figure 5, did drop slightly. Less water injection appeared to be necessary to assure hydration using the higher performance membranes. After about 500 h, the life test was terminated due to difficulties with the hydrogen supply. As seen in Figure 4, a slight loss in current density was observed over the 500 hours. However, it was probably not due to cell humidification as Figure 5 demonstrates that the high frequency cell resistance only improved over this time, so the membrane appears to have been well hydrated throughout the run.

Carbon monoxide levels as low as 10 ppm in the hydrogen supply can have a detrimental effect on fuel cell performance because of CO's tendency to occupy the catalytically active sites at the anode. One strategy for improving the anode tolerance to CO is to increase the cell operating temperature considerably higher than the typical 80° C, whereupon the CO sticking coefficient (and surface coverage) is decreased, which frees up sites for the desired hydrogen oxidation reaction. With reactant humidification, however, the membrane tends to operate drier at elevated temperatures and the cell resistances are thus higher and the membrane more susceptible to failure. The performance obtained with a cell using the anode wicking backing and a developmental Dow membrane operating with direct water injection at 115° C is close to that of cells operating at 80° C, and the cell resistance remains likewise similar to the 80° C case (i.e., the roughly 0.08 Ω cm² as depicted in Figure 5), a result not normally attained with vapor-humidified cells at these higher cell temperatures.

Cells with Hydrogen / Water Anode Flow-Fields

The water injection experiments demonstrate the concept of providing direct liquid hydration of the membrane using a "hydrophilic/phobic" anode wicking backing. While the water injection technique might be viable in some situations, it would be difficult to implement in a stack and still assure uniform water distribution to each cell. The inability to do so would eventually lead to some cells becoming flooded and others drying out. Even within the individual cells, we assure a uniform distribution of water within the 5 cm² cells using water injection by the use of a single-channel serpentine flow-field. The use of multi-path flow-fields that are suitable for large active areas would invariably result in a poor distribution of the water droplets.

The general approach we then pursued for supplying a stable reservoir of water for anode wicking was to provide separate channels for the liquid water and for the anode gases, which can be done a number of different ways. Initially, sets of channels were formed into both sides of a thick, porous, electronically conductive carbon paper (Spectracarb from Spectracorp, Ltd., Lawrence, MA). The structure thus formed was somewhat similar to the porous channeled flow-fields used by IFC (8). The anode gases (i.e., hydrogen) and liquid water were manifolded to the opposing faces of the channeled paper, and the porous material was rendered either hydrophilic (if the water channels were on the current collector side) or hydrophobic (if the water channels were against the wicking backing). As such, the water was supplied to the anode wicking threads either through the hydrophilic paper flow-field ribs in the first case or through the water channels against the face of the wicking backing in the latter (where the hydrogen then accesses the electrode via the hydrophobic porous ribs). The former configuration tended to collect water in the hydrogen channels, which led to erratic performance whereas the hydrophobic
paper configuration provided results that were basically similar to those depicted for the anode wicking backing in Figures 2 and 3. For the former to have worked stably, it would probably have been necessary to control the paper pore size and the water/hydrogen pressure differential, as done by IFC in their scheme, to keep the two separated.

In any case, the two H₂/H₂O flow-field configurations described above resulted in awkward manifolding configurations and required a separate porous element in addition to the impermeable graphite composite component of the "bipolar" plate. A much simpler configuration that eliminates the porous element is to manifold separate hydrogen and liquid water channels within a conventional flow-field configuration. This also decreases the amount of space required for the anode flow structure, which decreases the pitch of the unit cell and increases the power density of the stack. Because it is difficult to provide the necessary channels on a 5 cm² scale and a demonstration using a larger active area was of interest, a graphite composite plate for a 50 cm² active area was machined with an H₂/H₂O anode flow-field that accommodates both reactant gas and water flow-channels as shown in Figure 6. Here, three channels are formed in a conventional serpentine arrangement, however, the middle channel is manifolded to carry water and the outer two to carry reactant gas. Flanking the water channel on both sides with hydrogen channels prevents the water channel from doubling back on itself. As such, the furthest diffusion pathway for the hydrogen to access the MEA is through the backing across a flow-field rib and halfway across a water-filled channel, a distance of slightly more than a millimeter.

In contrast to the water injection approach, the 50 cm² cell has a separate water manifold. In operation, a separate recirculation loop is thus provided for the water as is shown in Figure 7. A small pump is used as before to inject water into the cell, albeit to the separate H₂O manifold rather than into the hydrogen inlet. A needle valve (or a second back pressure regulator) is used on the stack effluent side of the water loop in order to slightly pressurize the water stream compared to the hydrogen reactant gas. This discourages the hydrogen from infiltrating into the higher pressure water channel in order to assure that the water channel remains continuously filled with liquid throughout. The water and hydrogen effluents both pass through a common back-pressure regulator to maintain the pressure within the cell at 3 atm. The water is collected in a combination trap and reservoir for re-introduction within the cell. In a practical system, the trap would be at cell pressure to minimize the water pump head and facilitate the recycle of hydrogen.

The polarization curves for two Nafion 115 based 50 cm² active area cells are compared in Figure 8. One is a standard cell with conventional reactant humidification, the other utilizes the separate water channel in the anode flow-field described in conjunction with an anode wicking backing. More realistic operating conditions are used in the 50 cm² cell compared to the 5 cm². For example, the cathode pressures are considerably lower (3 instead of 5 atm) and the stoichiometric airflows are more carefully controlled (about 2 X at 1 A/cm² instead of 4 X or more). However, as in the case of the smaller cells (Figure 2), the scheme that delivers liquid water directly to the MEA in the 50 cm² comparison (Figure 8) outperforms the otherwise similar conventional cell over the entire current density range. With the continuously filled water channel, it was necessary to pump only about 3 ml/min into the special plate, and even less would have sufficed if a fair amount of the water had not wicked over the ribs separating the water from the hydrogen channels. This can in principle be alleviated by selectively introducing the plenum side of the wicking threads only in those areas overlying the water channels (the wicking on the membrane side can conceivably still span the hydrogen channels to supply the liquid water in these areas). As the sewing piece is currently positioned by hand, it is too difficult to attain the required
accuracy. However, computer-controlled embroidery machines are available that could provide the desired wicking thread pattern (with accuracies close to 0.1 mm).

CONCLUSIONS

A very simple means is provided to maintain the polymer electrolyte membrane in direct contact with liquid water to assure optimal hydration over all types of conditions and current densities. It demonstrates effectiveness at higher operating temperatures and is probably beneficial under ambient pressure conditions. This approach results in a fuel cell hydration system that is low-cost, compact, simple, versatile (applicable to a variety of off-the-shelf membrane products and electrode technologies), and enhances performance.

Possibly more important than the increase in performance is the demonstration of a much simpler hydration approach from a system perspective. De-coupling the water and gas supply subsystems in principle simplifies the optimization of stack performance. Eliminating humidifier modules decreases system volume and improves response. This potentially low-cost, compact hydration system essentially requires only a pump and a water reservoir, which are required for most hydration schemes anyway. Conceivably, a stack system could be even further simplified by combining the stack cooling with the hydration system by pumping a sufficient amount of cooled water through the hydration channels in the anode plate to remove the excess heat generated by the fuel cell stack.

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FIGURES

Figure 1. Cross-section of a fuel cell incorporating an anode wicking backing.

Figure 2. Polarization curves for 5 cm² Nafion 115 cells comparing the performance of humidified reactant and anode wicking backing hydration schemes.
Figure 3. High frequency resistance curves for the cells portrayed in Figure 2.

Figure 4. Current density of a 500 h life test for an anode wicking backing cell using developmental Dow membrane.
Figure 5. High frequency cell resistance for the life test of the cell shown in Figure 4.

Figure 6. Anode block depicting the layout and manifolding of the serpentine H₂/H₂O flow-field channels.
Figure 7. Schematic of the hydration and anode flow scheme for the 50 cm$^2$ cell using the H$_2$/H$_2$O anode flow-field.

Figure 8. Polarization curves for 50 cm$^2$ Nafion 115 cells comparing the performance of humidified reactant and anode wicking backing hydration schemes.