NEW CONCEPTS FOR POTENTIALLY LOW COST FLOW-FIELD AND ELECTRODE BACKING COMPONENTS FOR POLYMER ELECTROLYTE FUEL CELLS

Mahlon S. Wilson, Thomas E. Springer, John R. Davey, and Shimshon Gottesfeld
Materials Science and Technology Division,
Los Alamos National Laboratory, Los Alamos, NM 87544

New concepts for potentially low cost flow-field and electrode backing components for polymer electrolyte fuel cells are investigated. The primary motivation for the new configurations is to enhance cell performance on air by minimizing the oxygen diffusion barrier. This is accomplished with the use of porous flow-fields and unusually thin backers.

INTRODUCTION

Current flow-field technology for polymer electrolyte fuel cells (PEFCs) typically consists of grooved, serpentine flow-fields through which the gaseous reactants flow. A cross-section schematic is shown in Figure 1a. In order to bridge the open faced channels of the flow-field, a relatively rigid structure is required to facilitate the transition from the flow-channel to the catalyst layer, while ensuring gas transport uninhibited by excessive liquid water. This component is frequently described as the gas diffusion layer and will be referred to here as the backing. In an air electrode, the oxygen must diffuse through the backing in order to reach the catalyst layer. As the current density of the fuel cell is increased, this diffusion barrier lowers the effective concentration of oxygen at the catalyst layer and the performance of the electrode suffers. If the ribs in the flow-field are themselves non-porous, then the reactants must also diffuse laterally through the backing to reach the catalyst in the regions centered over the rib. It can be appreciated that two strategies can be implemented that would minimize the diffusion pathway. The first is to use much narrower ribs in the flow-field, which essentially suggests the use of a macroporous network for the flow-field, and the second is to minimize the thickness of the gas diffusion layer so the barrier to oxygen diffusion is minimized. The combination of the two concepts is shown in Figure 1c. Another possibly useful configuration is basically a compromise of the two and it is shown in Figure 1b. We describe here our recent efforts to implement the use of thin backings and/or macroporous materials in these two configurations.

Cost is another motivation for exploring alternative flow-field and backing components. Currently, fuel cell gas diffusion structures are made by hand in small quantities at relatively high costs. While automation would decrease the cost, the use of carbon papers or cloths in the structures will always add a component of complexity to the process. On the other hand, substantial quantities of thin, carbon black/polymer composite films are manufactured very cheaply for a large variety of uses by a number of companies on automated machinery. It should be only a matter of optimizing the components and processes to potentially attain very inexpensive, mass produced, backing materials based on such composite films.
The conventional technology for fuel cells consists of (machined) graphite bipolar plates. Efforts are being made to replace this expensive component with lower cost, more easily formed materials such as Kynar/carbon black composites which can be molded directly into the shape of a bipolar plate, given a suitable design. Unfortunately, this last material is, like graphite, relatively brittle and a certain amount of breakage may occur, especially in the case of thin unit cells. Perhaps some of these difficulties could be alleviated with the use of macroporous flow-field materials that are relatively durable and low cost and would not require extensive machining. It should be mentioned that metal hardware is attracting greater attention and some of our efforts in this regard are discussed elsewhere in this volume.1

THIN BACKINGS

Conventional PEFC backings

The hardware and electrode structures discussed here are primarily relevant for catalyzed ionomeric membranes, such as those we describe as "thin-film" catalyzed membranes.2 These are low platinum loading (typically 0.12 to 0.18 mg Pt/cm² or even less at the anode) 5 - 7 µm thick catalyst layers formed by the application of a catalyst/ionomer solution "ink" to the membrane. Catalysts are 20 wt% Pt on Vulcan XC-72 from E-TEK (Natick, MA). With these catalyst layers, the backing materials used are microporous, hydrophobic, electronically conducting structures similar to "gas-diffusion" electrodes, except that they are un catalyzed. Our conventional backing material is ELAT from E-TEK which is effectively a carbon black/PTFE impregnated carbon-cloth approximately 350 - 450 µm thick. Other commercially available gas diffusion-type structures are based on carbon paper instead of carbon cloth, but we typically obtain better performance with the latter. The role of our backings is to a certain extent analogous to that of the PTFE/carbon paper3,4,5 typically used to back wet-proofed PTFE/Pt-black electrodes such as those originally developed by GE for PEFCs. Both types of backings supply electronic contact and gas access to the respective catalyst layers. However, in the case of the hydrophilic (non-PTFE) thin-film catalyst layers,2 the backings serve the important additional function of a microporous water barrier. If a macroporous (ca. 30 µm pore size) PTFE/carbon paper backing is used in conjunction with the thin-film electrodes, a "flooding" situation quickly occurs. Some results and possible explanations for the dissimilar thin film and PTFE/Pt-black backing requirements are provided in Ref. 6. In any case, the need of a backing structure significantly affects the transport losses in fuel cells operating on air.7 We are interested in minimizing these losses in order to maximize fuel cell performance on air, possibly at lower pressures.

Porosity and tortuosity: possible backing performance enhancement

Modeling of fuel cell performance is useful to understand the limitations of the conventional backings and to predict what performance enhancements are possible. The most relevant parameters are the porosity and the tortuosity. A rough estimate of the porosity, ε, of the conventional backing using the material density and eventual geometry provides a value of about 0.4. The Carman tortuosity factor, τ, is defined as the square of the ratio between effective tortuous gas path length and backing thickness, and can be derived from ac impedance measurements. The low frequency loop in the ac impedance of an air electrode results from the dynamic lag of the oxygen partial pressure in the cathode catalyst layer with respect to changes in current density. The characteristic frequency, ωₜ,
of the backing can be measured as the frequency of the maximum imaginary component for this spectral feature, and can be shown\textsuperscript{8} to be equal to:

$$\omega_B = \frac{D_{ON}}{\tau \ell_B^2}$$

where $D_{ON}$ is the O$_2$-N$_2$ binary diffusion coefficient and $\ell_B$ is the effective backing thickness (with geometry taken into account\textsuperscript{8}).

Because the backing portion of the impedance spectrum is well separated from the higher frequency loop determined by kinetic and ionic resistance and condensed phase diffusion effects, the estimate of backing layer tortuosity is not dependent on estimates of these latter parameters.\textsuperscript{8} Rather, the tortuosity estimate is only dependent on $D_{ON}$ and the gross geometry of the backing. In this manner, we determine the tortuosity factor of the E-TEK backing structure from ac impedance spectra to have a value of around 7. The diffusion pathway is then $\tau^{1/2}$, or about 2.6 times as great as the backing thickness. While this is a relatively high value, one might expect significant tortuosity from the microporous backing as it primarily consists of a hot-pressed and sintered mixture of relatively high surface area carbon black and colloidal PTFE solution. Many of the gas passages formed are likely to be dead-ended, bottle-necked, or severely convoluted.

With knowledge of the porosity and the tortuosity, it is now possible to predict what sorts of effects much thinner backing layer structures could potentially have on cell performance. Figure 2 is a simulation of the increase in performance that could be obtained if a conventional backing with a 300 µm effective thickness is replaced by one only one tenth as thick. Both of the thicknesses are for uniform reactant access across the backside of the backings, so the effects would be somewhat different for channeled flow-fields. As can be seen, the mass transport limitations are significantly less with the thinner backing resulting in higher limiting current densities. Even in the maximum power region (about 0.5 V), significant improvement is evident. Other factors that are not addressed in this figure are possible improvements in performance that might occur with the thinner backing when the cells are operated at low pressure, or relatively close to stoichiometric flow, or if the reactant distribution is not perfectly uniform throughout the cell. A caveat to the performance improvements promised by Figure 2 is that it assumes that the properties of the conventional backings will be replicated on the much thinner scale.

**Bilayer backings used with conventional flow-fields**

The use of thin backings with conventional, serpentine channel flow-fields is problematic because the thin materials do not have the structural integrity or rigidity to span our 0.8 mm wide channels. In addition, the gas permeation to those areas of the backing covered by the ribs will be severely limited by the narrow diffusion path through the thin backing material. A compromise that partially provides the benefits of a microporous structure and sufficient structural integrity to span the ribs is to combine a thin microporous backing layer with a thicker, more rigid, macroporous structure to form a bilayer backing. A cross-section schematic of this configuration is shown in Figure 1b. The structural component will unfortunately add thickness to the structure, but the value of its tortuosity factor should be close to unity, so a 300 µm thick open layer should effectively present a gas transport barrier similar to that of a 100 µm thick microporous structure. However, this simple picture is not a completely accurate portrayal of the conditions in the operating fuel cell. The above model and simulations do not account for effects of liquid water...
permeation through and accumulation in the backings. We have reason to believe that the primary difficulty in the bilayer backing occurs at the interface between the micro- and macroporous structures. Water that has squeezed through the microporous structure may tend to accumulate at the interface in the much larger pores. The hydrophobic/hydrophilic nature of the macroporous support material may then be expected to affect the accumulation of the water.

In Figure 3 are shown polarization curves for test cells with bilayer backings on the cathode side that consist of thin microporous films combined with 250 μm thick Spectracarb 2050 (Spectracorp, Lawrence, MA) carbon paper. In one case, the carbon paper is hydrophobized with FEP120 (DuPont) and the other one is hydrophilized with 2% diluted Nafion™ solution (Nafion is a product of DuPont, 5% Nafion solution is from Solution Technology, Mendenhall, PA). Both cells are run under identical humidification conditions of anode/cathode humidifier temperatures of 105/70°C. The limiting current density of the cell with the hydrophilic backing support is somewhat greater than that of the hydrophobic support, whose rapid voltage decay suggests a "flooding" condition. We suggest that the "flooding" is primarily attributable to water trapped at the bilayer interface, and is thus corrected to a certain extent when the macroporous support is hydrophilic. This conjecture is further supported by the observation that the limiting current densities for both cells increase and are similar when the cells are poorly humidified. However, the lower current density performances are sufficiently erratic and poor with low humidification that such conditions are not desirable for normal cell operation. Optimization of the components of such bilayer backings may provide an attractive alternative to conventional backings from the aspects of reproducibility, performance and cost. Nevertheless, in order to obtain the minimal transport-loss suggested by the simulation in Figure 2, a support/flow-field structure is required that eliminates the diffusion barrier due to the structural component, which suggests the use of porous flow-fields.

POROUS FLOW-FIELDS

Damiano9 introduced the use of porous flow-fields in place of ribbed flow-fields in phosphoric acid fuel cells. Relatively thick layers of fibrous carbon paper or bonded particles are incorporated into the design of the gas-diffusion electrodes conventionally used in phosphoric acid fuel cells. The thicker carbon paper component serves as the flow-field because the reactants are forced to flow laterally through this component, not unlike Figure 1c. There is no remaining need for a machined serpentine flow-field. In this way, the strategies listed above for minimizing the reactant diffusion pathway are realized for phosphoric acid fuel cells.

For our macroporous flow-field structures, we typically use resin bonded carbon papers such as provided by Toray (Japan) or Spectracorp. These are roughly 70% porosity, 30 μm mean pore diameter fiber boards of various available thicknesses that can withstand as much as 20 atm of compression without crushing. Possible other "porous" flow-field structures may consist of carbon or metal foams or sintered particles. Although not discussed here, we have also experimented with woven metal screens,1 based on work done at Sandia Livermore and elsewhere.10

One of the difficulties with macroporous flow-fields is the inherently high pressure drop that is generated when appreciable amounts of gas are forced through relatively thin and long porous flow-fields with pores only about 30 μm in diameter. To this point, the
solution has been to use thick porous flow-fields. There are a couple of drawbacks to this approach. First, the use of thicker flow-fields results in thicker unit cells and hence lower stack power densities. Furthermore, the gas flows more readily channel, especially in the case of PEFCs where water may accumulate and block off regions. Lastly, the high current density region is concentrated along the edge where the reactant stream enters the cell. Since the majority of heat is generated in this region, cooling a stack becomes more problematic and the high current density regions tend to flood.

Radial porous flow-fields

As mentioned above, one of the difficulties with porous flow-fields is that the pressure drop incurred from forcing the gas reactants through relatively small pores (about 30 μm diameter) of the flow-field is considerably greater than through grooved channels. Another difficulty with using macroporous flow-fields in single cell hardware is in providing the manifolding that allows the reactants to be channeled through the structure without short-circuiting around the periphery of the flow field.

We circumvented both of these difficulties in early experimentation by using a radial flow geometry, in which inner and outer rings are machined into the standard graphite blocks and reactant flow is passed between the rings through a circular porous flow-field. The scheme is shown in Figure 4. Because the gases must flow through the overlying flow-field to reach the other ring, no short-circuiting around the flow-field is possible and the only gasketing required is around the periphery of the flow field. Pressure drops are also relatively low because of the relatively short distance through which the flow must traverse. Further advantages of the radial flow scheme are that the electrode region subjected to the "fresh" (oxygen rich) air is distributed around the periphery, and hence the regions of higher current density and water production are also widely distributed. In the case of the square flow-field mentioned above, the high current production would only be along the front edge, leading to excessive heat build up and/or flooding in this area. Unfortunately, the radial flow-field design is not very amenable to stacks, because manifold penetrations are needed that run up through the center axis, and also the low pressure drop is obtained only up to a certain size. The design has some utility for portable, low-power, ambient-pressure, fuel cell stacks.

Flow-field pressure tests

The primary factors in flow-field design are uniformity of reactant flow and magnitude of cell pressure drop. A trade-off occurs with the latter in that the uniformity of the reactant flow in a two-phase flow system is often improved in designs with a high pressure drop. In addition, an even flow distribution across many parallel cells in a stack is more readily attained with higher cell pressure drops. However, high pressure drops are undesirable because of the increase in compression costs and correspondingly lower system efficiency.

In order to quantify the level of the pressure drop and to visualize the dynamics of the accumulation of water in the macroporous flow-fields, a test rig was fabricated. The rig consisted of Plexiglas plates into which manifolds for a 50 cm² cell were machined. Air flows equivalent to 2 times stoichiometric flow at a current density of 1 A/cm² were fed to the rig for various thicknesses and types of flow-field material. A back pressure regulator was used to maintain the down stream pressure at 3 atm (30 psig). The air feed was sparged through a humidifier bottle upstream of the test rig and heated to 70°C in order to simulate the two-phase (gas/water) flow often encountered in actual cell
Immersion of the rig in a room temperature bath resulted in substantial condensation of the humidified stream in the rig. The behavior of the two-phase system could be visually monitored through the clear Plexiglas plates. The pressure drop across the cell was measured using a Magnehelix differential pressure gauge.

The pressure drop over a 1.5 mm (60 mil) thick Spectracarb 2050 flow-field using the humidified feed was on the order of about 0.06 atm (1 psi) as shown in Figure 5. When the flow-field was suddenly subjected to slugs of water that tended to collect in the inlet plenum, the pressure drop might momentarily spike several times higher. One of the apparent difficulties with the relatively thick flow-field was that water would collect in various areas and force the reactant flow to channel, typically down one side. One possibility we explored to alleviate this difficulty was to use thinner flow-fields. Not only would these increase the flow shear force to prevent water accumulation, but a thinner unit cell could be realized. With the use of a 0.25 mm (10 mil) thick flow-field of the standard Spectracarb 2050 material, the amount of channeling decreased, but was not eliminated, and the corresponding pressure drops increased to about 0.34 atm (5 psi), as is shown in Figure 5. Pressure drops should probably be somewhat less than 0.1 atm in practical systems to minimize compression losses. On the other hand, higher cell pressure drops simplify balancing the flows over many cells in a stack.

**Hydrophilic flow-fields**

We realized when we first started work on porous flow-fields that water accumulation would be a difficulty, as was evident in the channeling we saw in the Plexiglas test rig. One approach to minimize water clogging areas of the flow-field was to hydrophilize the flow-field material in order to wick water away before it could accumulate. The hydrophilization process used for pressure drop testing was to polymerize either aniline or pyrrole in situ on the flow-field material. In some formulations, the polyaniline (PANI) rendered the flow-fields quite hydrophilic and these could withstand several hours of boiling in water with no weight loss or loss of hydrophilicity. When hydrophilized flow-fields were examined in the test rig, the amount of water accumulation was substantially suppressed and, most interestingly, the pressure drops across test cells would also decrease, by about 10% to as much as 40% for some material/thickness combinations (some of the data are shown in Figure 5). Conceivably, the addition of the hydrophilizing material allowed the water to move through the finer, wicking component of the structure without accumulating and blocking the flow-channels. Because the polymerization process was not highly reproducible, we eventually resorted to hydrophilizing the flow-fields by dipping the material in 2% Nation solution as mentioned in an earlier section. Flow-fields treated with the Nation solution are interesting in that they are not "instantaneously" hydrophilic as are the polyaniline or pyrrole structures. However, when in the presence of water for some time, they eventually attain a hydrophilic state. This may possibly be beneficial in that the flow-field structure may initially resist trapping water, but if it does, it eventually wicks it away.

**Interdigitated macroporous flow-fields**

A possible solution to lowering the high pressure drops is to combine the macroporous flow-field with channels in such a manner as to provide the optimal compromise of the two flow-field configurations. This can be achieved by using interdigitated channels to deliver the reactant gases throughout the macroporous flow-field structure, which overlays the channeled substrate. The general scheme is depicted in Figure 6. The channels are formed as a series of interdigitated fingers, with one set of
fingers supplying the reactants and the second set removing the exhausted gas. In order to get from one set of fingers to the other, the reactants must pass through the macroporous flow-field, thus achieving the advantages provided by such structures. One can readily appreciate that the pressure drop can be decreased substantially, and that much larger active areas can be accommodated with only minimal pressure drop increases.

Figure 5 also shows the decrease in pressure drop achieved with interdigitated (ID) channels. The experimental conditions were the same as described previously. The distances used between the interdigitated fingers for the 0.25 mm thick porous flow-fields were 3, 5, and 10 mm. The interdigitated channels were machined directly into the relatively thick porous flow-field. This configuration may have cost and simplicity advantages in practical cells. As can be seen, merely introducing the interdigitated channels lowered the pressure drops by at least an order of magnitude. Decreasing the finger separation from 10 to 3 mm further lowered the pressure drop about a factor of two. When viewed in the clear Plexiglas test rig, the flow appeared to be uniform, although the visual test is not the best indication of uniform reactant distribution. Curiously, the pressure drops increased in the two cases in Figure 5 where the macroporous material was hydrophilized with PANI. If no channeling was occurring in the non-coated cases, then hydrophilizing the flow-fields may only serve to increase the water uptake and effectively decrease the porosity. Figure 5 shows that in the case of the 1.5 mm thick porous flow-field, the introduction of interdigitated channels decreased the pressure drop to a very low value.

There may be other possible advantages to interdigitated flow-field schemes. For example, from the perspective of stack design, it would be desirable to achieve uniform current densities throughout the active area. This is not easily accomplished because the region around the reactant inlet will provide the highest current densities. In the interdigitated scheme, the high and low current density regions are centered on the widely distributed feed and effluent fingers, respectively. This may help to alleviate large variations in the temperature and water content distributions.

**Interdigitated flow-fields with thin backings**

In addition to the transport improvement attained by the elimination of the non-porous ribs of serpentine flow-fields, porous flow-fields have the additional advantage of supporting the backing material across its entire surface as is shown in Figure 1c. While this has advantages with conventional gas diffusion backings by providing uniform pressure against the membrane/electrode assembly, Figure 1c demonstrates that it becomes possible to support a very thin backing.

A 10 cm² cell with a 0.25 mm thick hydrophilic porous flow-field overlying interdigitated channels and a 25 µm thick hydrophobic gas diffusion backing was tested with a thin-film catalyzed developmental Dow membrane. In Figure 7, this cell is compared to a 5 cm² cell with standard backings (effectively about 300 µm thick) and serpentine flow-fields. All other conditions are similar (approximately 0.13 mg Pt/cm² thin film catalyst layers on developmental. Dow membrane, etc.) As can be seen, the limiting current density with the thinner backing is substantially greater. If the curves are iR corrected (Figure 8), the low current density performances of the two are roughly equal, and the thinner backing gains a substantial advantage in the important mid-range area. The lower current density performance in this cell was not particularly good because the cell with the thinner backing tended to dry out. This difficulty is hopefully due to the backing...
material properties, and not to its thinness. This belief is somewhat supported by results obtained when as-received thin backings of this type are treated in a number of ways before use.

CONCLUSION

The use of catalyzed membranes separates the functions of catalyst layer and backing and thus permits a greater degree of flexibility in backing and flow-field components. One possibility discussed here is the use of unusually thin backings which promise increased reactant transport in air electrodes and, hence, higher performances. While yet further development of the thin backing materials is required for optimal performance, substantially higher limiting current densities are demonstrated. When thin backings are used in a bilayer configuration in combination with a more open, structural component, performances of conventional backings are attained with materials that are machine made and very inexpensive compared to conventional gas-diffusion-type backings.

The thin backings should, however, provide optimal performance when used with macroporous flow-field structures so as to minimize the diffusion barrier. While porous flow-fields provide uniform support and reactant access across the backing, the use of such materials often result in uncomfortably high pressure drops and poor reactant flow distributions. One solution, described here, is to use interdigitated channels in conjunction with the porous flow-field to lower pressure drop and improve the reactant distribution. Channels formed in the macroporous material would eliminate the need for machined graphite bipolar plates. Hence, macroporous flow-fields may cost advantages in addition to possible performance advantages.

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Figure 1. Cross-section schematics depicting a) conventional flow-field with gas-diffusion style backing, b) conventional flow-field with a bilayer (micro- and macroporous) backing, and c) macroporous flow-field supporting a thin microporous backing.

Figure 2. Simulations depicting the increase in performance that might be expected if the effectively 300 μm thick conventional backing is replaced with one one-tenth as thick with similar properties. Simulation conditions: \( \text{H}_2/\text{air} = 3/5 \text{ atm, } T_{\text{cell}} = 80°C \).
Figure 3. Bilayer backing configuration with conventional, serpentine flow-fields. Cell conditions: $5 \text{ cm}^2$, $\text{H}_2/\text{Air} = 3/5 \text{ atm}$, $T_{\text{cell}} = 80^\circ \text{C}$, 0.18 mg Pt/cm$^2$ thin film catalyst layers on a developmental Dow membrane.

Figure 4. Single cell radial flow hardware for experimentation of porous flow-fields. Configuration provides low pressure drop and simplified sealing.
Figure 5. Pressure drops over 50 cm² macroporous flow-fields with no channels (NC) or interdigitated channels (ID). "t" = macroporous material thickness, "w" = spacing between channels. Polyaniline (PANI) renders the flow-fields hydrophilic.

Figure 6. A schematic for a reactant flow-field scheme that combines the use of interdigitated flow-channels with an overlying macroporous flow-field structure.
Figure 7. Experimental comparison of cells with conventional and with thin backings. The respective hardware are 5 cm$^2$, serpentine flow-fields and 10 cm$^2$, interdigitated porous flow-fields.

Figure 8. iR corrected polarization curves of the cells described in Figure 7.