JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 1-7

Thin-film catalyst layers for polymer electrolyte fuel cell electrodes

M. S. WILSON, S. GOTTESFELD

Electronics Research Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

Received 7 February 1991

New structures for the Pt/C catalyst layer of polymer electrolyte fuel cell electrodes have been developed that substantially increase the utilization efficiency of the catalyst. Fabricating the catalyst layers and gas diffusion backings separately makes it possible to formulate each structure with the properties that are most suitable for its function. In the case of the catalyst layer, the optimal properties are hydrophilicity, thinness, uniformity, and the proper ratio of ionomer and supported catalyst. The catalyst layers are cast from solution as thin films that utilize the ionomer itself as a binder. The thin films are hot pressed directly onto the ionomer membranes, and the hydrophobic gas diffusion backings are inserted when the cells are assembled. The performances of fuel cells based on the thin film catalyst layers are comparable with those of gas diffusion electrode designs that utilize several times as much platinum, thus the specific activities of the Pt catalysts in the new structures are significantly higher.

1. Introduction

The advantages inherent in polymer electrolyte membrane (PEM) fuel cells for applications such as transportation are mitigated by the high costs associated with the use of platinum or platinum-rich alloy catalysts that are kinetically necessary in a cell with an acid electrolyte and a relatively low operating temperature (about 80° C). The economic future of PEM fuel cells is contingent upon lowering the costs of the ionomeric membranes and the catalysts. The former may be accomplished by simple economies of scale, but the latter can be reduced only by more efficient utilization of the platinum.

In this work we address some of the problems inherent in achieving high catalyst utilizations in PEM fuel cells and describe a new philosophy for the structure of the catalyst layer in gas diffusion electrodes. We utilize novel electrode fabrication techniques to prepare electrodes with the desired morphology.

2. Electrode structures

2.1. *Morphology of a conventional Teflon bonded electrode*

In recent years, work in our laboratory on PEM fuel cells was devoted to the replacement of membrane/electrode assemblies based on Pt black catalysts of high loadings ($4\,\mathrm{mg\,cm^{-2}}$) by assemblies of high performance based on supported Pt/C catalysts of only $0.4\,\mathrm{mg\,Pt\,cm^{-2}}$ [1]. The structure of the supported platinum fuel cell electrodes was adapted from phosphoric acid fuel cells. The catalyst layer of a typical gas diffusion electrode of this type consists of 2 nm diameter platinum particles supported on carbon black. This layer sits on top of a base layer of carbon black, which is spread over carbon cloth or carbon paper. The entire structure is bonded together with 25 to 50 wt % Teflon (DuPont). In phosphoric acid fuel cells, the liquid electrolyte seeps into the hydrophobic catalyst layer to provide ion access to the catalyst sites. In the case of PEM fuel cells, access of the ionomer electrolyte to the platinum particles within the catalyst layer is achieved by impregnating [2] the active (catalyzed) side of the electrode with a solubilized form of the ionomer Nafion (DuPont). Impregnation is carried out by brushing or spraying the recast solution onto the front side of the electrode.

This mode of construction introduces several difficulties in the case of the PEM fuel cell. For example, the erratic thickness of a typical catalyst layer, combined with variations in the impregnation depth of the recast ionomer, result in areas where the catalyst layer is not fully impregnated and areas where the ionomeric additive could extend into the electrode further than the catalyst layer, thus introducing an unnecessary transport barrier to the diffusion of gas through the backing. Not surprisingly, it is difficult to match the impregnation depth exactly with the depth of the catalyst layer in an electrode of this construction.

Although Teflon is effective as a binder and imparts hydrophobicity to the gas diffusion regime of the electrode, no particular advantage is realized by the presence of Teflon in the immediate vicinity of the catalyst sites. This statement is counter to the prevailing philosophy that the Teflon is necessary to provide hydrophobic regions within the catalyst layer through which the gas can access the catalyst. An ideal gas conduit would be a pore lined with only a thin coating of Teflon (for hydrophobicity) to allow a passageway for the gas. However, in practice, discrete and dense clumps of Teflon are formed because the melt does not

0021-891X/92 $03.00 + .12

wet the carbon particles uniformly. Thus, when the recast ionomer is applied to the electrode later in the impregnation step, much of the carbon surface is already covered with Teflon and many of the pores are blocked.

Even if the Teflon is evenly distributed throughout the pores, the advantages normally associated with Teflon cannot be capitalized upon to improve the performance of the catalytic layer. The high solubility of oxygen in Teflon [3] is useful only to those catalyst particles at the interface of Teflon and the carbon support. However, sites that are totally enveloped by Teflon are denied proton access and cannot contribute to the electrochemical process. This is demonstrated in liquid electrolyte by the decrease in catalyst active area with the increase of Teflon weight percent in gas diffusion electrodes [4]. Incidentally, Teflon is no more efficient in transporting oxygen than either the ionomer or water. The permeabilities of oxygen through hydrated Nafion and through water are both considerably greater than through Teflon [5]. Therefore, a pore filled with the former materials will transmit oxygen at a higher rate than a solid pore filled with Teflon (note: permeability = solubility × diffusivity, and the diffusivity of oxygen in Teflon is very low [3]). In summary, Teflon can increase the diffusivity of gases only in the sense that it provides hydrophobicity to an open pore to prevent it from being clogged with water. Although this property is desirable in the gas diffusion portion of an electrode, a penalty is paid in the catalytic region due to the lack of utilization of the catalyst in completely dry and/or Teflon-coated pores.

2.2. *Thin film catalyst layers*

A catalyst site must satisfy three criteria for it to contribute to the electrochemical reaction in a fuel cell. The criteria are proton access, gas access, and electronic path continuity. The structure and composition of an electrode can affect all three of these parameters in varying degrees. To maximize catalyst utilization, it is desirable to satisfy these three criteria for as many of the catalyst sites as possible.

The new electrode structure presented here attempts to improve upon the previous construction by significantly increasing the contact area between the polymer electrolyte and the platinum clusters. This increase is achieved in two ways. First, the supported catalyst and the ionomeric additive are cast together to form the catalytic layer. This assures that the thickness of the catalyst layer coincides with the depth of the ionomer. Second, the contact area between the ionomer additive and catalyst is increased by completely eliminating the Teflon component and by improving the dispersion of the ionomer throughout the catalyst layer. The latter is accomplished by blending the solubilized ionomer and the platinized carbon into an homogeneous "ink", from which the thin film catalyst layer of the electrode is cast.

The gas diffusion portion of the electrode consists of a separate Teflonized carbon cloth backing that is stacked behind the thin film to provide support and to provide a hydrophobic distribution network for the gases. This two-part construction of the electrode – hydrophobic backing and hydrophilic catalyst layer – allows each of the two regions to be fabricated separately with the properties that best suit the function of each region.

The thickness of the catalytically active region is usually determined by the depth of proton penetration, which is a function of the specific protonic conductivity, the volume fraction and the distribution of the ionomeric electrolyte within the electrode structure. However, increasing the volume fraction of the ionomeric electrolyte also increases the thickness of the electrode and, hence, the mass transport barrier and the electronic impedance of the electrode, both of which are detrimental effects. Thus, above a certain optimum, the potential drop across the catalyst layer increases with the volume fraction of the ionomer.

The last of the three criteria is the access of gas. In the new type of thin film catalyst layer, the gas is not provided with a network of hydrophobic pores within the catalyst layer; thus, gas diffusing through the catalyst layer must traverse pores filled with water and/or ionomer. However, the permeability of oxygen through recast ionomeric films is sufficient such that a 5 μm diffusion pathway through the ionomer to the catalyst particles will not introduce significant oxygen transport losses on the cathode side of the fuel cell [6]. Consequently, a Teflon-free thin film catalyst layer with an effective tortuosity thickness of 5 μm or less should in principle be able to sustain current densities equivalent to a much thicker electrode that uses an extensive network of gas distribution pores.

The effects of proton penetration and thin layer gas diffusion, as well as the relationship between volume fraction of ionomer and potential drop within the layer, indicate that the optimal catalyst layer should be very thin and possess a high volume density of small catalyst particles, with the remainder of the volume completely filled with ionomer. The presence of voids or unfilled pores in the film would only lower the ionic and electronic conductivities. Furthermore, since gas diffuses nearly as readily through hydrated ionomer as through water pockets, it is more advantageous for voids to be filled with the former material than the latter.

3. Experimental details and results

3.1. *Preparation of the catalyst layer inks and electrodes*

A Nafion/Pt-C/glycerol ink is prepared from a commercial solubilized Nafion solution (5% solution from Solution Technology, Inc., Mendenhall, Pennsylvania) and from 19.8 wt % platinum on carbon (Prototech Co., Newton Highlands, Massachusetts) combined with glycerol and water and then thoroughly mixed by ultrasound. The addition of glycerol and water results in a mixture that is relatively viscous and holds the

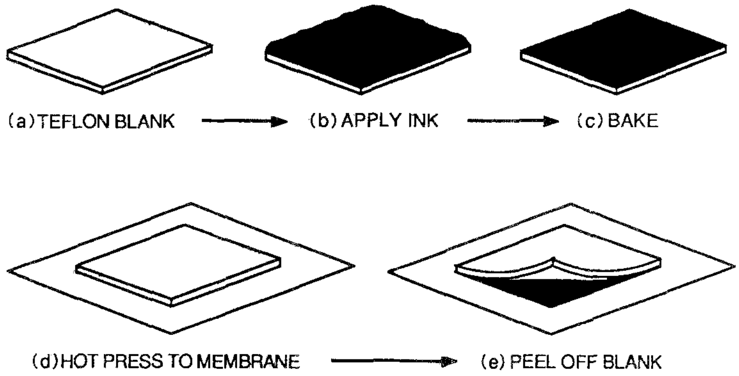

Fig. 1. Primary steps in the fabrication of a thin film catalyst layer bonded to an ionomeric membrane.

carbon particles in suspension and minimizes their agglomeration once the ink is extensively ultrasounded. The ink does not readily dry out or segregate, and it is easily painted onto a surface in a thick continuous coat. When the applied layer is baked at about 135° C, the mixture provides a very uniform film.

The following is a typical preparation protocol:

1. Combine solubilized Nafion (5 wt %) and 19.8% Pt on carbon and mix. A weight ratio of 1 : 3 for the Nafion (dry)/Pt-C is preferable.
2. Add water and glycerol such that the weight ratios are approximately 1 : 5 : 20 for carbon/water/glycerol.
3. Mix and ultrasound extensively. Although the mixture is initially not uniformly viscous, it will eventually thicken. If the alcohols from the Nafion solution are allowed to stay in the mixture (i.e. the container is capped), the ink will dry more quickly in the oven.
4. A blank of Teflon film (Fig. 1a) is thoroughly cleaned and coated with a thin layer of premium fluorocarbon spray (mold release). The blank is painted with a layer of the ink (Fig. 1b) and is baked in a forced convection oven at 135° C until dry (Fig. 1c). If necessary, additional layers are added to achieve the desired catalyst loading, although it is desirable to minimize the overall baking time.
5. The coated blank, a polymer electrolyte membrane, and a counter electrode are hot-pressed together in the conventional manner (Fig. 1d). The assembly is inserted into the hot press at 100° C and a light load is applied until the press heats up to 125° C (for Nafion 117) or 145° C (for membrane "C", a product of Chlorine Engineers, Inc., Japan) at which point the assembly is pressed at 70–90 atm for 90 s.
6. The membrane/catalyst assembly is removed from the press and allowed to cool, then the Teflon blank is peeled away from the membrane, leaving the thin film adhering to the membrane (Fig. 1e).
7. An uncatalyzed Teflon-bound electrode (Prototech) can be used as the gas diffusion backing for the thin film catalyst layer. The backing is merely inserted in place during installation of the membrane assembly into a fuel cell housing (that is, no hot press or other cementing is done).

3.2. *Experimental results*

All the ink formulations were prepared using Pt/C catalysts supplied by Prototech, consisting of 19.8 wt % platinum on XC-72 carbon powder. This allowed direct comparison with conventional Teflon-bonded electrodes fabricated by Prototech for use in our PEM fuel cells using the same supported catalyst. The experimen-

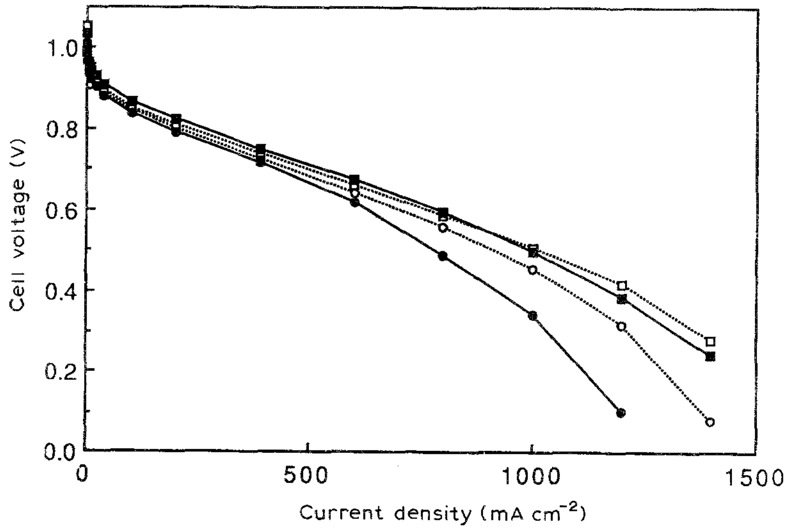

Fig. 2. Polarization curves for 0.20 and 0.35 mg $\mathrm{Pt\,cm^{-2}}$ "thin film cathodes" in cells with Nafion 117 membranes. Conditions: T (cell) = 80° C; T (humidifiers) = 105° C; anode/cathode pressures = 3/5 atm. Key: (○) 0.20 air, (□) 0.20 oxygen, (●) 0.35 air and (■) 0.35 oxygen.

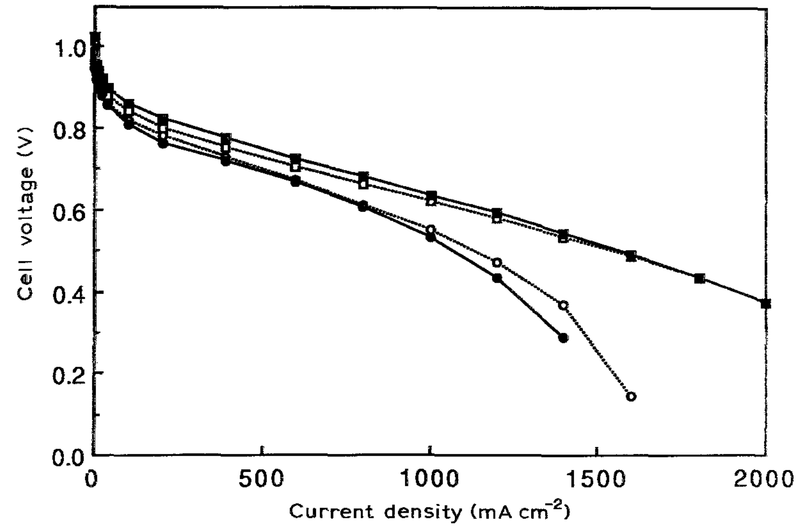

Fig. 3. Polarization curves for 0.15 and 0.22 mg Pt cm^{-2} "thin film cathodes" in cells with membrane "C". Conditions: as in Fig. 2. Key: (○) 0.15 air, (□) 0.15 oxygen, (●) 0.22 air and (■) 0.22 oxygen.

tal thin film electrodes were used only at the cathodes in the fuel cells tested, because the electrochemical process of oxygen reduction at the cathode is the more important electrocatalysis challenge. Conventional Prototech electrodes were used on the anode side (0.35 mg Pt cm^{-2} plus 50 nm Pt sputter coat [7] for a total of 0.45 mg Pt cm^{-2}) to supply a consistent reference for comparisons of the performance of cells based on thin films and on conventional Prototech cathodes. Once installed in the testing hardware, fuel cells based on thin film electrodes take longer than conventional assemblies to reach their eventual peak performance. The delay is most likely caused by the slow process of rehydrating the ionomer within the catalyst layer that had been subjected to relatively extensive baking during fabrication.

Figure 2 depicts the voltage against current density curves for 0.20 and 0.35 mg Pt cm^{-2} thin film cathodes in cells with Nafion 117 membranes and conventional Prototech anodes. At the lower current densities, the cell voltages on neat oxygen for the thicker catalyst film are slightly higher than those for the thinner film, but they drop somewhat more rapidly as the currents increase until the thinner electrode eventually yields the better performance. The higher platinum loading achieved in the form of a thicker catalyst layer thus improves the performance in the kinetic regime, but as the current density is increased and the active region of the catalyst layer narrows, less of the layer is utilized and mass transfer effects through the catalyst layer become more important. The differences are even more pronounced when the fuel cells are run on air where the thinner film consistently outperforms the thicker one.

Fuel cells utilizing membrane "C" (Chlorine Engineers, Inc., of Japan) were also assembled with thin film cathodes. Figure 3 depicts voltage/current density curves for both air and neat oxygen from two fuel cells utilizing 3 : 1 Pt-C/Nafion cathode catalyst layers with loadings of 0.15 and 0.22 mg Pt cm^{-2}. The performances of these electrodes approach those of conventional Prototech electrode assemblies with two or three times as much platinum (0.45 mg Pt cm^{-2}). Although the behaviour of the two thin film cathodes are similar, the cell voltages with the 0.22 mg cm^{-2} cathode loadings are slightly higher at the lower current densities, whereas the performance of the 0.15 mg cm^{-2} cathode approaches (and in the case of air, consistently exceeds) that of the thicker catalyst layer at the higher current densities. These results are consistent with the examples using Nafion 117 cells. A similar effect is also observed when varying amounts

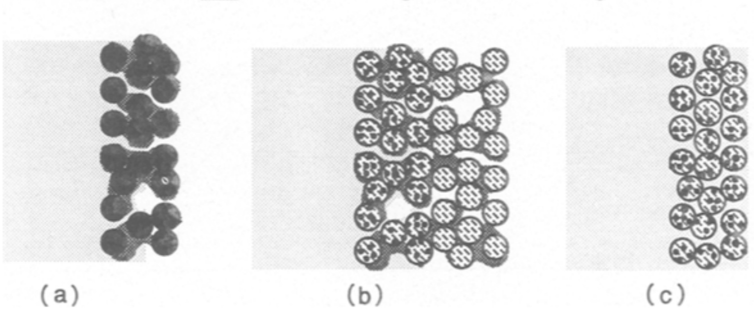

Fig. 4. Cross-sectional schematics of the ionomer/electrode interface for three constructions. (a) GE/HS-UTC style based on unsupported Pt catalyst bonded to the ionomeric membrane. (b) Prototech carbon cloth electrode incorporating Pt/C catalyst hot-pressed onto the ionomeric membrane (catalyst layer thickness 50–100 μm). (c) Thin catalyst film electrode in which a thin Pt/C-Nafion catalyst layer is hot-pressed directly onto the ionomeric membrane (catalyst layer thickness 50–100 μm).

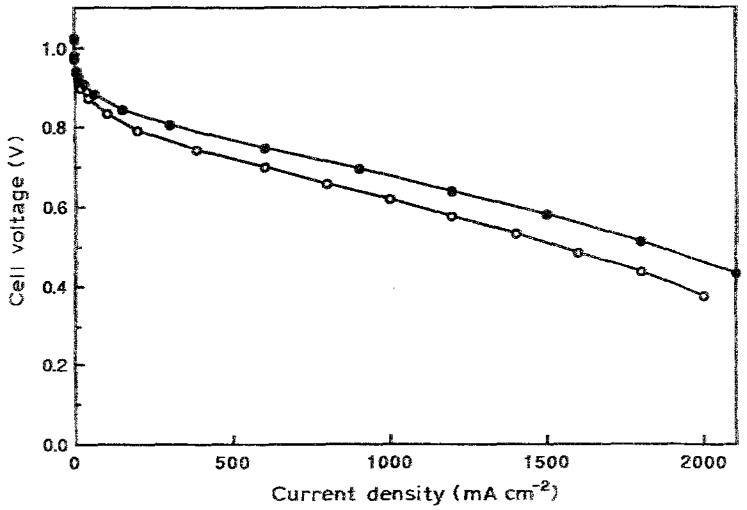

Fig. 5. Comparison of cell voltage against current density performances for H_2/O_2 cells with Prototech and thin film cathodes. Conditions for membrane "C" as in Fig. 2. Key: (○) thin film 0.15 mg Pt cm^{-2}, (●) Prototech 0.35 mg cm^{-2} + 50 nm Pt.

of Nafion are impregnated into conventional gas diffusion electrodes, in that the higher Nafion loadings provide better performance at low current densities and the lower Nafion loadings perform better at the higher current densities [8].

4. Discussion

4.1. *Optimal catalyst layer thickness*

The results obtained with the two kinds of membranes as a function of platinum content (that is, the catalyst layer thickness) and cathode gas (air or neat oxygen) illustrate the importance of the thinness of the films with respect to the proton penetration and gas accessibility which together define the active region. As the current density increases, the active region narrows. Therefore, the thinner electrodes would provide better performance on air down to a thickness roughly equivalent to that of the active region at a particular current density. In these electrodes, based on 19.8 wt% Pt/C, reasonable performance is obtained down to about 0.10 to 0.15 mg Pt cm^{-2}, after which it falls off as the amount of catalyst is decreased. Thus, the thickness associated with 0.1 mg Pt cm^{-2}, which is somewhat less than 4 μm, roughly defines the thickness of the catalytically active region at the higher current densities.

On the other hand, a higher loading of catalyst is observed to increase the fuel cell performance at lower current densities by virtue of the increase in the active area. Consequently, one could possibly maximize the overall performance of a thin film electrode by increasing the Pt concentration in an even thinner catalyst layer while maintaining a roughly equal average platinum particle size (of approximately 2 nm).

4.2. *Nafion as a binder*

In the absence of Teflon as the binder in the thin film catalyst layer, the recast Nafion provides the structural integrity. Unfortunately, Nafion is not melt processable as supplied, hence, recast films do not possess the structural integrity of commercial fluoropolymer ionomeric membranes. However, the recast can be toughened by heating to elevated temperatures for moderate amounts of time, which causes a certain amount of acid-catalyzed discoloration and degradation. The approximately thirty minutes at

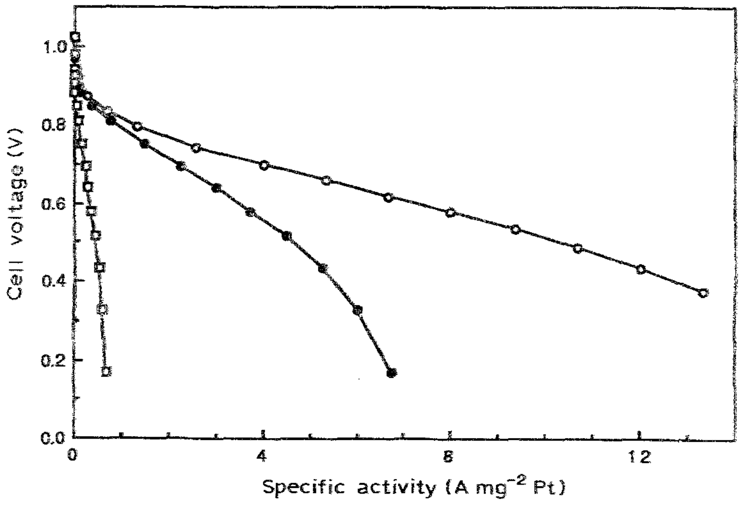

Fig. 6. Comparison of H_2/O_2 cell voltages against specific cathode activities for the three electrode constructions depicted in Fig. 4. Key: (○) thin film 0.15 mg Pt cm^{-2}; (●) Prototech 0.35 mg cm^{-2} + 50 nm Pt; (□) GE/HS-UTC style, 4 mg Pt cm^{-2}.

135° C required to dry a coat of glycerol based ink may degrade a significant fraction of the sulphonic acid active groups (that is, the concentration of sulphonic acid groups is decreased as determined by ion-exchange). Consequently, the degraded Nafion in this case is not as hydrophilic as undegraded recast Nafion. However, the lesser hydrophilicity and greater robustness of the partially degraded Nafion may be beneficial, especially in the cathode where flooding is often a concern.

On the other hand, the loss of active groups effectively decreases the ionic conductivity of the thin film. For this reason, catalyst layers utilizing undegraded Nafion may be more advantageous. Thus, high-quality thin film electrodes using undegraded Nafion have also been prepared to see if any improvement is evident. One method of protecting the recast Nafion is to convert the H^+ form of solubilized Nafion into the Na^+ form, which does not degrade substantially even at 200° C. A Nafion/Pt-C slurry has been prepared as before and undegraded thin films are obtained despite the elevated temperatures. However, an undegraded recast Nafion hot press film swells in water to such an extent that it is greatly weakened. In another approach, the Na^+ to H^+ conversion step is avoided by baking the H^+ Nafion/Pt-C inks in a vacuum oven at a sufficiently low temperature (90° C) that the amount of degradation is minor.

In both of these undegraded ionomer fabrication techniques, complete transfers of the thin film to the membrane are not consistently obtained during the hot press. When tested in fuel cells, the assemblies constructed with undegraded recast Nafion have not performed as well as the ones based on partially degraded thin films, have not been as stable in operation, and display symptoms of flooding. The relatively fragile undegraded catalyst layers are believed to be swelling from the formation of water in the operating cell to such an extent that water pockets and localized ruptures in the film cause discontinuities in the electronic and ionic paths. Thus the trade-off between robustness and a high concentration of intact sulphonic acid groups in the thin film fabrication technique is biased at this point towards film robustness for optimal performance.

The use of Nafion as a binder introduces certain structural advantages over conventional electrodes that utilize a rigid support with respect to the bonding of the electrode to the PEM. Upon hydration, the dimensions of a hydrophilic ionomer membrane increase a fair amount and the swelling from the osmotic forces exert substantial forces [9]. In a PEM fuel cell with a large cross-sectional area, the relatively rigid Teflon-bonded carbon matrix of a conventional electrode structure cannot easily accommodate variations in the swelling of the membrane if the membrane water content varies substantially. The stress is most probably relieved by the electrode partially delaminating from the membrane or by cracking in the electrode. Thus, startup and shutdown (hydration/dehydration) cycles decrease the longevity of the cell.

The thin film catalyst layer of this work is more securely bound to the membrane than its predecessor and will, itself, swell an appreciable amount upon hydration because of the high concentration of ionomer. Consequently, the integrity of the interface between the membrane and catalyst layer is more readily maintained. In addition, the two-part construction of the thin film electrodes (that is, catalyst layer and backing) allows relief of the strain at the thin film/backing interface since the two surfaces are not physically bonded.

4.3. *High performance PEM assemblies*

The evolution of high performance PEM fuel cells began with high Pt loading (4 to 10 $mg\,cm^{-2}$) Teflon-bonded unsupported catalyst layers that were directly applied to the ionomeric membrane, as developed by General Electric and later by Hamilton Standard-United Technologies Co. [10]. The gas diffusion backings were inserted during assembly of the fuel cell stack. Lower Pt loadings and performances nearly as high were subsequently accomplished using carbon supported platinum particles in a catalyst layer that was integral to the gas diffusion electrode structure. Finally, we have demonstrated here thin film catalyst layers, consisting of supported Pt catalyst, that are bonded directly to the membrane, with a separate gas diffusion structure used as a backing. Thus, the evolution has come full-circle and some of the attributes of the earlier techniques are combined to further increase the catalyst utilization. Cross-sectional schematics of the ionomer/electrode interfaces for the three constructions are portrayed in Fig. 4.

The thin-film catalyst layer structure (Fig. 4c) depicts an idealized membrane-electrode interface in the sense that the electrolyte is continuous across the interface. This continuity can also be achieved with electroless platinum deposition technqiues [11, 12], in which platinum clusters are formed directly in the membrane. Although the electroless processes provide optimal catalyst-membrane interfaces, the catalyst utilization efficiencies of the relatively large platinum clusters thus formed are very low. The thin-film catalyst layer fabrication process attempts to emulate this structure, and, by using supported catalyst, also improve the platinum utilization efficiency.

In our laboratory hardware, the performances of fuel cells based on Prototech (0.45 $mg\,Pt\,cm^{-2}$) and on thin film (0.15 $mg\,Pt\,cm^{-2}$) electrodes that utilize the same type of catalyst (20 wt % Pt/C from Prototech) are quite similar (Fig. 5). For comparison of the catalyst utilization efficiencies, the cell voltages are plotted in Fig. 6 as a function of the specific activites of the cathodes ($A\,mg^{-1}$ Pt). Included in this figure are also specific activities calculated from the performance of a Ballard fuel cell stack [13] that uses 4 $mg\,Pt\,cm^{-2}$ electrodes of the GE/HS-UTC type. It should be noted that the conditions, membrane type (Dow), and hardware in this latter case are different from those in the other two curves and its inclusion is merely illustrative. The differences in the specific activities for each type of electrode are dramatic and, clearly, the thin-film supported catalyst construction is the most viable for high platinum utilization.

5. Conclusion

This limited series of experimental efforts illustrates the potential benefits of exploring alternative polymer electrolyte fuel cell electrode structures in increasing catalyst utilization. Whereas the catalytic regime of an electrode of conventional design is fairly porous and hydrophobic with numerous voids, the approach presented here suggests that the optimal structure for high catalyst utilization is a catalyst layer that is as dense and as thin as possible, with an appropriate mixture of Pt-C and ionomer. These structures have been prepared from solution using a heat-modified ionomer as both the bonding agent and the ionic conductor.

Acknowledgement

This work was supported by the U.S. Department of Energy, Office of Conservation and Renewable Energy.

References

[1] I. D. Raistrick, in J. W. Van Zee, R E. White, K. Kinoshita and H. S. Burney (Eds), 'Proceedings of the Symposium on Diaphragms, Separators, and Ion Exchange Membranes', The Electrochemical Society (1986) p. 172.
[2] I. D. Raistrick, U.S. Patent No. 4876115 (1989).
[3] R. A. Pasternak, M. V. Christensen and J. Heller, *Macromolecules* **3** (1970) 366.
[4] D. Rocco de Sena, E. A. Ticianelli and E. R. Gonzalez, in Program Abstracts, 1990 Fuel Cell Seminar, Phoenix AZ (1990) p. 391.
[5] T. Sakai, H. Takenaka and E. Torikai, *J. Electrochem. Soc.* **133** (1986) 88.
[6] S. Gottesfeld, I. Raistrick and S. Srinivasan, *J Electrochem. Soc.* **134** (1987) 1455.
[7] E. A. Ticianelli, C. R. Derouin and S. Srinivasan, *J. Electroanal. Chem.* **251** (1988) 275.
[8] E. A. Ticianelli, C. R. Derouin, A. Redondo and S. Srinivasan, *J. Electrochem. Soc.* **135** (1988) 2209.
[9] K. K. Pushpa, D. Nandan and R. M. Iyer, *J. Chem. Soc., Faraday Trans. 1* **84** (1988) 2047.
[10] A. J. Appleby and E. B. Yeager, *Energy* **11** (1986) 137.
[11] H. Takenaka, E. Torikai, Y. Kawami and N. Wakabayashi, *Int. J. Hydrogen Energy* 7 (1982) 397.
[12] P. Millet, M. Pineri and R. Durand, *J. Appl. Electrochem.* **19** (1989) 162.
[13] K. Prater, *J. Power Sources* **29** (1990) 239.