PEM FUEL CELL STACK DEVELOPMENT BASED ON MEMBRANE-ELECTRODE ASSEMBLIES OF ULTRA-LOW PLATINUM LOADINGS

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We are attempting to scale-up our single cell technology, based on ultra-low platinum loadings, to develop a polymer electrolyte membrane (PEM) fuel cell stack for stationary power generation. We describe initial work on scale-up to a manifolded single cell based on a 100 cm² active area, with the intention of combining multiples of such cells to create stacks. The cells, which are fed by pressurized H₂ and air, utilize membranes catalyzed by ultra-low platinum loadings (0.14 mg Pt/cm²) and metal serpentine channel or screen flow-fields to minimize costs, while maintaining desirable power density. We describe some initial promising results from testing of stainless steel screens as flow-fields in such cells, achieving 0.5 W/cm² under mild flow and pressurization conditions.

INTRODUCTION

For some years, there has been substantial interest in PEM fuel cells for transportation applications. More recently, this interest has further extended to stationary power,¹⁻⁴ which has long been the domain of higher temperature fuel cell technologies such as phosphoric acid or molten carbonate. While there may be some efficiency losses in coupling the PEM fuel cell to a reformer system compared to its higher temperature counterparts, the perceived advantages of the PEMFC are its quick start-up, high current densities and non-corrosive electrolyte. To date, these systems typically utilize membranes with platinum loadings of 4 mg/cm²/electrode and areas greater than 200 cm². In order to compete in the stationary power market, costs would most likely need to be less than $1000/kW for an entire system. Lower platinum loadings are an important factor in meeting such cost projections. Using low-platinum loading technology developed at Los Alamos,⁵,⁶ we are attempting to produce moderately-sized stack components that provide sufficient power output at a fraction of the platinum content (and cost) of present-day PEM fuel cell stacks.

Most stationary applications will likely require relatively high power yields, which suggests the use of large active areas. On the other hand, some applications, such as uninterruptable power supplies (UPS), home-based stationary power¹ or private transportation systems, require the supply of high voltages but only modest power output. For this reason, as much as the desire to minimize materials and costs, a relatively modest active area of 100 cm² was chosen as the initial stage for this development effort. Additional strategies in this program include exploring the use of alternative flow-field materials and configurations to simplify fabrication and lower costs, minimize unit cell thickness for the same reasons, as well as to lower ohmic losses and system weight, and simplification and/or automation of cell fabrication.
EXPERIMENTAL

Membrane-Electrode Assemblies

We have experimented extensively with low platinum loading catalyzed membranes in small, single cells. These membrane-electrode assemblies (MEAs) are for the most part based on "thin-film" catalyst layers, in which an "ink" of catalyst and ionomer is applied directly to the membrane. The resulting catalyzed membranes are relatively robust and have been demonstrated on the small, single cell level to maintain high performances for thousands of hours and withstand numerous cycles of either start-up/shut-down or freeze/thaw conditions. In most cases, these MEAs have been fabricated by hand-painting the ink directly onto the membrane or onto hot-press decals.

The scale-up to cells much larger than our typical laboratory single cells prompted the development of an automated process to reliably and efficiently produce large catalyzed membranes. This was achieved by the use of a computer controlled standard X-Y analog chart recorder to apply the catalyst ink directly to a membrane or to decals that would later be transferred to the membrane by hot-pressing. Ink is supplied to the chart recorder pen by a pulse-free peristaltic pump drawing ink from a magnetically stirred vial. A schematic of the system is depicted in Figure 1.

To catalyze a membrane, the membrane is held in place on a heated vacuum table installed on the modified X-Y recorder. The pump and pen tubing are primed with ink. The operator interfaces with the computer program to align the pen settings properly. When given the approval, the program drops the chart recorder pen, starts the ink pump, and controls the pen to sweep over the desired electrode area in a serpentine pattern. When the pattern is complete, the pump turns off and the pen is raised. The amount of ink applied depends upon the pump speed, pen sweep-rate and size of the increment between sweeps. Total time to ink a 100 cm² area on one side of a membrane or one decal is about 2 minutes, which translates to an application of approximately 14 mg of platinum for a loading of about 0.14 mg Pt/cm².

Though both direct application of ink and the decal method produce comparable results, the decal method is preferable because it is much less time consuming and more convenient for producing large quantities of assemblies. Several decals can be inked in rapid succession, dried en masse in an oven and stored until needed for hot-pressing to a membrane.

When compared to other fabrication techniques we have experimented with, this simple process has several advantages such as 1) carefully controlled and uniform addition of the ink, 2) minimal wastage and cleanup (as compared to spraying or silk-screening), and lastly, 3) adaptability. Because the computer controls the printing area, the same unit can be adapted to any size or shape of electrode by varying the program.

Cell components

Although to this point we have experimented only with single cells, the hardware is designed for multiple cells with the requisite internal manifolding and sealing. The endplates and cell plates are rectangular to accommodate manifolding above and below the square 100 cm² active area in an effort to minimize unutilized space. The ratio of the active area to the endplate area is approximately 40%, which is reasonably high for the modest active area involved. The endplate dimensions are approximately 15 cm by 20 cm and are secured by 14 tie-bolts about the periphery in the conventional manner. A minimum
thickness of about 6 cm is required for the single cell, which includes endplates, current collector and cooling plates, and a unit stack cell (flow-fields, MEA, and seals).

We have used a variety of flow-fields in our scale-up work, including titanium or stainless steel serpentine-channel plates and stainless steel screens. Stainless steel screens were also used as cooling plates. The serpentine hardware consisted of metal sheets about 1.25 mm thick that were machined on one side with the serpentine open-faced channels. These were designed to be used back-to-back, sandwiching a stainless steel screen to form a combination bipolar/cooling plate. Typical MEAs consisted of catalyzed Nafion™ 112 (DuPont) situated between E-TEK (Natick, MA) carbon-cloth gas diffusion style backings. In general, the catalyzed membranes were prepared using the decal method described above. The inks used contained 5% Nafion solution (1100 eq. wt. from Solution Technologies, Mendenhall, PA), 20% platinum on Vulcan XC-72 (E-TEK), and any of a number of appropriate solvents.

Cell testing

The test station for the 100 cm² cells contains a Hewlett-Packard 6050A load box with two 120 amp modules, a 208 V power supply to bias the cell against the load box such that low cell voltages can be attained, reactant humidification equipment, gas flowmeters, back-pressure regulators, temperature controllers, and control relays for actuating the cell's heating and cooling equipment. The test station also contains internal safety features that will shut down the cell under various conditions (loss of gas flow, or extreme cell temperatures, for example). Additionally, the load boxes are interfaced to a Macintosh (Apple) computer so that experimental data, such as polarization curves, may be obtained using programs written with Labview (National Instruments) software.

The cells were typically operated on H₂/air at 3/3 atm (30/30 psi). Air flow-rates were approximately two times stoichiometric (i.e. 50% utilization) at 1 A/cm². Hydrogen flow varied but was typically slightly over stoichiometric at maximum current density. Occasionally, oxygen was used as a diagnostic aid. To provide water to the cell, the gases were externally humidified at temperatures ranging from 90 - 115°C for H₂ and 40 - 100°C for air. The cell temperature was generally maintained between 70 - 80°C to obtain optimum performance. For the majority of single cell work, the cell was air-cooled by an external fan. Multiple cells necessitated the use of internal water cooling. Water was circulated through the cell via a cooling plate and upon exiting the cell was circulated through a fan-cooled radiator to maintain proper temperature.

RESULTS AND DISCUSSION

Initial development work was conducted using serpentine channel flow-fields because we obtain our highest performances in our conventional LANL test cells (5 cm² and 50 cm²) using such flow-fields machined into graphite blocks. Pressure drop is a concern in large-scale systems with their higher gas flows, thus the single channel pattern typically used in the small test cells was expanded to a 7-channel pattern (Figure 2). The seven channels are arranged in a parallel flow scheme and are close to equal in length, as is advocated by Ballard. This general type of configuration should minimize water accumulation in the flow-channels while permitting a relatively low pressure drop. Pressure drops measured across the 7-channel plate at the 2 x stoichiometric flow-rate were 0.25 atm (4 psi) or less. Compared to previous work, it should be mentioned, however, that the 7-channel scheme is not an optimized flow-field configuration.
Titanium was chosen as the original flow-field material because of its high conductivity, the possibility of nitriding the surface to make it corrosion resistant and its availability in thin sheets, which could be machined with various patterns. It may also be of interest for transportation applications because of its relative lightness. In single 100 cm$^2$ cells with acid-etched titanium serpentine flow-fields and MEAs of ultra-low platinum loadings, current densities of 1.1 - 1.15 A/cm$^2$ (110 to 115 A) were attained at 0.5 V as shown in Figure 3. The high frequency resistances of these cells were approximately 0.09 Ω cm$^2$. This compares rather favorably with the 5 cm$^2$ laboratory cells, where the lowest resistances attained with thin-film catalyzed Nafion 112 MEAs are on the order of 0.065 Ω cm$^2$. Typical current densities at 0.5 V for the 5 cm$^2$ test cells are at best 1.4 A/cm$^2$ with Nafion 112 MEAs at H$_2$/air = 3/3 atm. Though some loss in performance occurred with scale-up, the results obtained with the 100 cm$^2$ titanium cell were very encouraging. In particular, the ultra-low platinum, titanium serpentine plate cells produced 0.5 W/cm$^2$ at 0.7 V or 0.2 W/cm$^2$ at 0.8 V, which is within the range of stationary power requirements. Maximum performance of the cells was obtained with surprisingly high humidifier temperatures of about 115/80°C for the anode/cathode. Despite the high humidification levels and the observation that the polarization curve in Figure 3 starts to drop at relatively low current densities, flooding of the cathode compartment was not otherwise apparent.

Though acid-etched titanium proved to be a reasonable flow-field material in terms of short-term performance, there were many practical obstacles to continuing its use in the cells. Because titanium is a very hard material, it was not possible to machine the plates without first annealing the metal. Even with annealed plates, machining the intricate seven-channel serpentine pattern was extremely time consuming and costly (end mills kept breaking due to the material's hardness). The machining cost of the titanium flow-fields was approximately $750 per plate. Clearly, this is not acceptable for practical applications. Additionally, the annealing process creates an oxide layer on the titanium that must be removed by acid etching to attain acceptable contact resistances.

We then replaced the titanium with stainless steel. Researchers elsewhere have reported the use of stainless steel as a replacement for graphite in fuel cell stacks. They report no significant differences in cell performance in switching from graphite to stainless steel flow-fields. Additionally, they observed no corrosion of the stainless steel after 1000 hours of testing. Thus, for stationary power applications, where stack weight is not as critical as for transportation, the ruggedness of stainless steel as well as its low cost relative to graphite or titanium, make it an attractive material for practical use.

On the other hand, we observed a loss in performance in changing from titanium to stainless steel serpentine flow-fields. As also shown in Figure 3, at 0.5 V, current densities ranged from 0.90 - 1.0 A/cm$^2$ and performance in the kinetic region of the polarization curve dropped off from 0.85 V at 0.1 A/cm$^2$ for titanium to 0.82 V for stainless steel. While the loss of current density at 0.5 V was apparently due to higher resistances with the switch to un-etched stainless steel, the reasons for the loss of kinetic activity were not clear.

Even though the stainless steel flow-fields performed adequately, machining the narrow serpentine channels proved to be nearly as difficult and as expensive as for titanium. While lower cost alternatives to machining of the stainless steel are worth considering, we were interested in pursuing some alternative flow-field schemes such as porous or screen materials. Researchers at Sandia Livermore Laboratory (CA) and

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elsewhere\textsuperscript{10} have experimented with the use of simple metal screens as flow-fields. As mentioned above, our original cooling plate design was based on a stainless steel woven screen. The combination of its apparent success and the previous work inspired us to pursue the use of screens as flow-fields. Among the advantages screens possess are that they require no special machining, are readily available in a variety of thicknesses and mesh sizes, and are inexpensive. To attain a bipolar plate structure, 0.25 mm (10-mil) thick stainless steel "barrier" plates would be used to separate the anode and cathode screen flow-fields in adjacent cells within a stack. In the single cells the same plates were used to protect the gold-plated copper current collector plates from indentation by the screens.

The use of the screen flow-fields presented new challenges in optimizing the gas flow pattern through the screen, sealing the cell, and attaining enough compressive force on the backings to achieve good interfacial contacts. Some idea of the uniformity of gas flow through a screen flow-field was obtained by appropriately fixturing a stainless steel screen and an E-TEK backing in a clear Plexiglass test fixture. Humidified air at 3 atm was flowed through the cell at the equivalent rate of two times stoichiometric at 1 A/cm\textsuperscript{2}. Water vapor tended to condense on the relatively cool Plexiglass such that the flow-field appeared cloudy. Large droplets from condensation and slugs of water that had accumulated in the feed line would occasionally pass through the flow-field and temporarily clear the condensate from the face of the Plexiglass. In this manner, stream lines would become apparent that would reflect the general reactant flow. The streamlines suggested that gas flow accessed all parts of the stainless steel screen fairly uniformly. In addition, we observed that water channeled directly through the flow-field without extensive pooling or flooding. Lastly, the pressure drops necessary to attain the desired flows and water removal were less than those required with the 7-channel serpentine flow-fields. In general, the behavior of the stainless steel screen flow-field as observed in the Plexiglass test fixture was much better than we had expected.

When installed into the electrochemical cells, the screen flow-fields initially provided poor performances. One of the difficulties was that the applied cell compression forced the E-TEK backings into the screens, which caused not only unacceptable pressure drops, but also compromised the integrity of the backing structures. The solution was to employ a combination of screens. The backing was protected from the large mesh size, relatively thick screen that served as the actual flow-field by a fine stainless steel screen. Pressure drops of 0.15 atm (2 psi) for air and < 0.07 atm (1 psi) for H\textsubscript{2} at the standard flow-rates were obtained. Even with the additional screens, the unit cell thicknesses were still less than 3 mm. Further changes in sealing of the MEA to prevent cross-over and acid-etching of the stainless steel before use to remove oxide coatings improved the cell performances to 1.0 A/cm\textsuperscript{2} at 0.5 V, as is depicted in Figure 4. Somewhat high cell resistances of 0.14 Ω cm\textsuperscript{2} were obtained, which may account for an excessive voltage drop of about 50-70 mV at 1 A/cm\textsuperscript{2}. This resistance is high compared to the titanium serpentine cells and primarily arises from the numerous stainless steel interfaces in the cell. On each side, there are interfaces between the collector plates and the barrier plate, as well as three more interfaces between the two screens and the backing. As in the case of the stainless steel serpentine hardware, however, the 100 mA/cm\textsuperscript{2} cell voltage was lower than with the titanium serpentine flow-fields. The kinetic losses are apparent in the iR corrected polarizaton curves of Figure 4. Otherwise, the screen flow-fields provided near equal performance to the serpentine hardware, suggesting that the reactant access throughout the active area was equally effective. While it is conceded that our serpentine channel design is probably far from optimized, the relative performance of the simple screen configuration is...
very encouraging and offers much promise for this simple flow-field scheme. One of the challenges, though, will be to obtain and maintain good interfacial conductivities.

If it is eventually possible to maintain a performance of roughly 50 W at 0.5 V per cell output in a stack, a thickness of approximately 3 mm per unit cell (flow-fields, seals, MEA and cooling plate) would result in a 1 kW stack of 20 cells that is only 6 cm thick, not including endplates. The maximum power density of this configuration would be about 1kW/liter. Naturally, including the endplates and the corresponding increase in footprint lowers this value substantially. For example, a 5 kW stack would then yield about 0.4 kW/liter.

CONCLUSIONS

Ultra-low platinum loading of large surface area membranes was achieved by the use of a computer-controlled chart recorder to apply a uniform layer of catalyst "ink" to the membrane surface or a decal. Advantages of this method include the controlled application of the ink to reproducibly catalyze membrane surfaces with a certain desired platinum loading and the adaptability to catalyze different sizes or shapes of electrodes.

Combining the use of low-platinum loaded MEAs with titanium serpentine flow-fields, produced cells that yielded 0.5 W/cm² at 0.7 V, which is within the realm of practical use for stationary power applications. A major barrier to the continued development of the titanium cell is the difficulty in machining the 7-channel serpentine flow-field pattern and relatively high associated costs. Though similar flow-fields made from stainless steel did not perform quite as well as the titanium plates, it may be possible to improve their performance by pretreating the metal to lower contact resistance. Additionally, newer fabrication technologies based on state of the art lithography techniques may provide plates that are inexpensive to produce on a mass-production scale.

Cells based on stainless steel screen flow-fields, in combination with low-platinum loaded MEAs, produced outputs of about 50 W at 0.5 V, which compared favorably with the titanium serpentine plate cells (55 W at 0.5 V). Though there was some loss in performance, the advantages gained by the use of screens (availability in various thicknesses and mesh sizes, low cost, elimination of machining, lighter weight, etc.) are attractive as a practical alternative to serpentine plates. With a maximum power density of about 50 W/cell at 0.5 V, the screen flow-fields provide a relatively inexpensive and lightweight PEM fuel cell configuration. Further refinements of the system should increase the maximum power and also improve the power densities at cell voltages of more relevance to stationary power applications.

Future work will include further single cell development with an emphasis on improving interfacial conductivities, improving backing components and implementing higher activity Pt alloy catalysts. In addition, multiple cell development, building on the results obtained above, will be initiated. Particular areas of concern in stack work will be the ease of fabrication of cell components and improving humidification schemes. Additional concepts to improve system efficiency, such as dead-ended H₂ feeds or low pressure cathodes, will also be explored.
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FIGURES

Figure 1. Computer controlled process for applying a uniform layer of catalyst ink to either a membrane or a decal blank positioned on a heated vacuum table.
Figure 2. 7-channel serpentine flow-field design machined into about 1.25 mm thick metal plates. Channels are ca. 0.8 mm wide and 1.0 mm deep with 0.8 mm wide ribs.

Figure 3. Polarization curves comparing the performances of fuel cells with 100 cm² titanium (Ti) and stainless steel (SS) serpentine channel flow-fields. Conditions are $H_2/air = 3/3$ atm, $T_{cell} = 80^\circ C$, 50% air utilization at 1 A/cm², and MEAs with 0.14 mg Pt/cm²/electrode.
Figure 4. Cell and iR corrected polarization curves comparing the performances of titanium (Ti) serpentine channel and stainless steel (SS) screen flow-fields. Conditions are the same as in Figure 3.