ABSTRACT

The proton exchange membrane fuel cell (PEMFC) is one of the most promising electrochemical power sources for space and electric vehicle applications. The wide spectrum of R&D activities on PEMFCs, carried out in our Center from 1988 to date, is as follows (1) Electrode Kinetic and Electrocatalysis of Oxygen Reduction; (2) Optimization of Structures of Electrodes and of Membrane and Electrode Assemblies; (3) Selection and Evaluation of Advanced Proton Conducting Membranes and of Operating Conditions to Attain High Energy Efficiency; (4) Modeling Analysis of Fuel Cell Performance and of Thermal and Water Management; and (5) Engineering Design and Development of Multicell Stacks. The accomplishments on these tasks may be summarized as follows:

1. A microelectrode technique was developed to determine the electrode kinetic parameters for the fuel cell reactions and mass transport parameters for the H₂ and O₂ reactants in the proton conducting membrane.

2. High energy efficiencies and high power densities were demonstrated in PEMFCs with low platinum loading electrodes (0.4 mg/cm² or less), advanced membranes and optimized structures of membrane and electrode assemblies, as well as operating conditions.

3. The modeling analyses revealed methods (i) to minimize mass transport limitations, particularly with air as the cathodic reactant; and (ii) for efficient thermal and water management.

4. Work is in progress to develop multi-kilowatt stacks with the electrodes containing low platinum loadings.

INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) is one of the most promising electrochemical power sources for space and electric vehicle applications. As illustrated in Figure 1, this type of fuel cell has the best prospects for attaining high energy efficiencies and high power densities. The other advantages are:

1. It's a low temperature fuel cell system, and, thus, the start-up time could be quite fast.

2. It uses a polymeric electrolyte (a perfluorinated sulfonic acid membrane) which is made conducting, by the absorption of only water.
3. This type of fuel cell has very good prospects for long lifetimes, as has been demonstrated by a 100,000 hour lifetime in single cells.

The wide spectrum of R&D activities on PEMFCs, carried out in our Center from 1988 to date, is represented in the flow chart. In the following sections, presented are the highlights of the work which has been carried out to date and also in progress.

ELECTRODE KINETICS AND ELECTROCatalysis OF OXYGEN REDUCTION

The slow kinetics of the oxygen reduction reaction is the main cause of efficiency losses in fuel cells. This loss in efficiency also has an effect of reducing the attainable power density. However, in order to have a viable power system, a minimum efficiency (in terms of power density) of 40% to 50% is desirable. To elucidate the electrode kinetics of oxygen reduction at the platinum Nafion interface, a microelectrode technique (1) was developed in our Center. The schematic of the cell is shown in Figure 2. This technique was used to determine the electrode kinetic parameters for oxygen reduction on platinum as well as of the diffusion coefficients and of the solubilities of oxygen in the electrolyte. The results showed that the Tafel behavior for oxygen reduction is very similar to that in aqueous acid electrolytes but that the exchange current densities were higher at the platinum proton exchange membrane interface. As in the case of aqueous electrolytes, reaction order for the reaction with respect to oxygen is unity. The studies at different temperatures yielded the activation energy for the reaction which was again of the same order as the aqueous electrolytes. This study also was shown to yield the diffusion coefficient and solubilities of oxygen in the membrane. It was found that the diffusion coefficients about an order of magnitude lower in the polymer electrolytes, but the solubilities are, however, considerably higher. However, the product of the diffusion coefficient times solubility is higher in the polymer electrolytes than in the aqueous electrolytes, thus accounting for lesser mass transport problems in the proton exchange membrane fuel cells. An interesting aspect of the microelectrode study is that the electrode kinetic parameters which were obtained on the smooth platinum microelectrode were within an order of magnitude of those obtained on the high surface area electrocatalyst in the fuel cell electrodes in PEMFCs.

In a separate study, platinum alloy electrocatalysts were evaluated for the oxygen reduction reaction in proton exchange membrane fuel cells. This involved comparison of the electrocatalytic activity for oxygen reduction reaction (ORR) on carbon supported binary platinum alloys (Pt/Cr, Pt/Mn, Pt/Fe, Pt/Co, Pt/Ni) with that of a conventional Pt/C electrocatalyst (all electrodes containing the same Pt loading, 0.3 mg/cm²). Figure 3 shows the iR corrected Tafel plots indicating the enhancement in electrocatalytic activities towards ORR exhibited by all the binary platinum alloys (2). In addition to the electrode kinetic studies in proton exchange membrane fuel cells, in situ X-ray absorption spectroscopic studies were conducted to determine the electronic and geometric properties of the alloys at potentials in the fuel cell operating range. Of all the alloys, the platinum chromium alloy has shown the highest enhancement in electrocatalytic activity. The results of the electrochemical and X-ray absorption spectroscopic studies showed correlations between the electrocatalytic activities and the geometric as well as electronic properties of the alloys, i.e. Pt-Pt bond distances and Pt d-band vacancies (Pt 5d orbitals) in the form of volcano type relationships.

OPTIMIZATION OF STRUCTURES OF ELECTRODES AND OF MEMBRANE AND ELECTRODE ASSEMBLIES

Following the work of Srinivasan and co-workers at Los Alamos National Laboratory from 1985 to 1988, a wide variety of studies were carried out in our Center to enhance the performance of
proton exchange membrane fuel cells for space and electric vehicle applications. These studies consisted of:

1. A determination of the effect of the platinum content on the fuel cell performance.
2. Preparation of electrodes with different Teflon contents in the active and diffusion layer and their evaluation in fuel cells.
3. Changing the conditions of hot-pressing during the preparation of the membrane and electrode assemblies.

The effect of increase of platinum content on the performance is akin to that of increase of pressure and can be attributed to the increase in electrocatalytic activities. However, the performances obtained even with a very ultra low platinum loading of 0.1 mg/cm² was quite good. The effective utilization of the platinum with the ultra low platinum loading was quite high (3). Figure 4 illustrates the effect of platinum loading on the power density vs. current density plot. This figure shows that at current density of about 500 mA/cm² the amount of platinum required per kilowatt is only 1.2 grams per kilowatt while with the state-of-the-art electrodes it is about 10 times this value. Optimization of the Teflon content in the diffusion layer and the catalytic layer is therefore of vital importance. The Teflon content of about 50% in the active layer and 40% in the diffusion layer showed the best performance in our studies (4).

In respect to the optimization of the conditions for the preparation of the membrane and electrode assemblies, it was found that a high temperature is more favorable for attaining a better performance in fuel cells. The temperature also depends on the glass transition temperature for the membrane. With some experimental membranes from the Asahi Chemical Company, it was found that even though the glass transition temperature is around 140° hot-pressing at about 155 - 160° produces a better behavior.

SELECTION AND EVALUATION OF ADVANCED PROTON CONDUCTING membranes AND OF OPERATING CONDITIONS TO ATTAIN HIGH ENERGY EFFICIENCIES AND HIGH POWER DENSITIES

A detailed study of the effect of the membranes and of the operating conditions was carried out using DuPont's Nafion®, Dow experimental and Asahi Chemical's Aciplex®-S membranes (5). A comparison of the performance of fuel cells with the three types of membranes is shown in Figure 5. The results of the studies such as the one as shown in this figure as well as those at different temperatures and pressures have been analyzed. Correlations have been drawn with the physicochemical properties of the membranes. A typical example is shown in Table I. One of the most important physicochemical parameters is the water content of the membrane. (The membranes with higher water contents have higher sulfonic acid contents and thus show better performances in PEMFCs.) The conductivity is directly related to the water content of the membrane and attaining the maximum conductivity is essential from the point of view of reducing the slope of the linear region in the current potential plot.

MODELING ANALYSIS OF FUEL CELL PERFORMANCE AND OF THERMAL AND WATER MANAGEMENT

One of the toughest challenges in developing proton exchange membrane fuel cells is to reduce the mass transport overpotentials particularly when air is used as the cathodic reactant. For space applications there is hardly any choice other than using pure hydrogen and pure oxygen as reactants but for terrestrial applications air is the unique choice for the cathodic reactants. A comparison of the performances of PEMFCs with H₂/O₂ and H₂/air as reactants illustrates the
significant problems when air is used. Further, for terrestrial applications such as electric vehicles, it is essential to work at very low pressures (ideally at 1 atm pressure). Mass transport overpotentials have an effect on the slope of the linear region of the cell potential vs. current density plot and also can cause the departure of this plot from linearity at low current densities. A systematic study was conducted in our Center to elucidate other problems causing these effects (6). In this study, where O2/He, O2/Ar and O2/N2 gas mixtures were used, the cell potential current density plot with these gas mixtures is shown in Figure 6. This figure shows that with a lighter inert gas, He, the mass transport effects are somewhat less than with Ar or N2. Ar, N2 and air exhibit the same type of current potential behavior. The mathematical analysis of this behavior showed that the increase of the slope in the linear region is due to the mass transport problem in the catalyst layer while the departure from linearity is caused by problems by films of water or droplets of water in the diffusion layer.

A problem which is related to the mass transport problem is also thermal and water management. At the present time, the fuel cell performance is quite satisfactory at low to intermediate current densities, but with the need for operating the fuel cells at relatively high power densities, it is necessary to operate at higher current densities. As stated in the previous section, the proton conducting membrane operates most satisfactorily when the water content has its maximum value. In the fuel cells which have been developed to date, the humidification of the membrane has been shown to be important. At the higher current density, it is also necessary to remove a considerable amount of heat. For instance, if the fuel cell were to operate at about 2 A/cm², the electricity generation corresponds to 1.2 watts/cm² while the heat generation rate is about 1.8 watts/cm². A modeling analysis was carried out of the thermal and water management problems (7). Different methods of cooling (air cooling, liquid cooling and evaporative cooling) were examined. The results showed that when air is used as the cathodic reactant, the evaporative cooling method appears to be most beneficial (Table II).

ENGINEERING DESIGN AND DEVELOPMENT OF MULTI-CELL STACKS

During the period from about 1984 to date, considerable progress has been made in attaining high power densities and high energy densities in single cells. The work at Ballard Power Systems, Inc. has also demonstrated that high levels of performance could be obtained in multi-cell stacks. At Ballard, the fuel cells have been developed using electrodes with high platinum loading. At the present time, the toughest challenge is of an engineering nature, i.e. developing multi-cell stacks with low platinum loading electrodes and also finding solutions to the mass transport problems and thermal and water management. Our Center is currently engaged in the development of multi-cell stacks (1 and 10 kW) using electrodes made in-house. The electrodes which would be used will be fabricated either using the rolling or the spraying method. Due consideration of the flow patterns in the bipolar plate, humidification of the reactant gases and of the operating conditions (temperature, pressure, flow rate) will be taken into account. Modeling analysis of the multi-cell stack in respect to the electrochemical performance, thermal and water management are also being carried out. For the 1 kW stack, the electrode area will be 150 cm², whereas for the two 10 kW stacks, the electrode areas would be either 300 or 600 cm².

CONCLUSIONS

The accomplishments on these tasks may be summarized as follows:

1. A microelectrode technique was developed to determine the electrode kinetic parameters for the fuel cell reactions and mass transport parameters for the H2 and O2 reactants in the proton conducting membrane.
2. Three fold activity enhancements for ORR have been demonstrated with Pt/cr alloys electrocatalysts. Studies using in-situ XAS spectroscopy have revealed important fundamental insights into ORR electrocatalysis.

3. High energy efficiencies and high power densities were demonstrated in PEMFCs with low platinum loading electrodes (0.4 mg/cm² or less), advanced membranes and optimized structures of membrane and electrode assemblies, as well as operating conditions.

4. The modeling analyses revealed methods to (i) minimize mass transport limitations, particularly with air as the cathodic reactant; and (ii) for efficient thermal and water management.

5. Work is in progress to develop multi-kilowatt stacks with the electrodes containing low platinum loadings.

ACKNOWLEDGEMENTS


REFERENCES


### Table I. Physico-chemical Characteristics of Perfluorinated Sulfonic Acid Polymer Membranes for PEMFCs

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Equiv. Weight, g/mols SO\textsuperscript{-3}</th>
<th>Thickness in dry state, (\mu\text{m})</th>
<th>Water Content, %</th>
<th>Conductivity, (\Omega^{-1}\text{cm}^{-1})</th>
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<tr>
<td>Dow</td>
<td>800</td>
<td>125</td>
<td>69</td>
<td>0.118</td>
</tr>
<tr>
<td>Aciplex\textsuperscript{®}-S</td>
<td>1000</td>
<td>120</td>
<td>43</td>
<td>0.108</td>
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<tr>
<td>Nafion\textsuperscript{®}</td>
<td>1100</td>
<td>100</td>
<td>34</td>
<td>0.059</td>
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</table>

### Table II. Mass Flow of Ambient Air Required for Cooling PEMFC

<table>
<thead>
<tr>
<th>Membrane</th>
<th>(E_0, \text{V})</th>
<th>Tafel slope, mV/dec</th>
<th>Resistance, (\text{\Omega cm}^2)</th>
<th>(i_{900}\text{mA/cm}^2)</th>
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<tr>
<td>Dow</td>
<td>0.983</td>
<td>62</td>
<td>0.106</td>
<td>25</td>
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<tr>
<td>Aciplex\textsuperscript{®}-S</td>
<td>1.017</td>
<td>63</td>
<td>0.111</td>
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<tr>
<td>Nafion\textsuperscript{®}</td>
<td>0.990</td>
<td>52</td>
<td>0.168</td>
<td>40</td>
</tr>
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</table>

### Table II. Mass Flow of Ambient Air Required for Cooling PEMFC

<table>
<thead>
<tr>
<th>Current Density</th>
<th>Cell Potential (V)</th>
<th>Heat to be Removed</th>
<th># of Stoichiometric Mass of Air</th>
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<tr>
<td>200</td>
<td>0.702</td>
<td>3.488</td>
<td>1.42</td>
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<tr>
<td>400</td>
<td>0.604</td>
<td>8.384</td>
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<tr>
<td>600</td>
<td>0.513</td>
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<td>2.71</td>
</tr>
<tr>
<td>800</td>
<td>0.426</td>
<td>21.881</td>
<td>3.00</td>
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<tr>
<td>1000</td>
<td>0.340</td>
<td>30.430</td>
<td>3.40</td>
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</table>
Electrode Kinetics and Electrocatalysis

Optimization of Electrode Structure and Membrane Electrode Assembly

Membrane Evaluation and Optimization of Operating Conditions

Multi-cell Stack Development (1 to 10 kW)

Mass Transport Analysis and Thermal & Water Management

Figure 1  Flowchart of Activities on Proton Exchange Membrane Fuel Cell Project at Texas A&M University.
Fig. 2. Schematic of a micro-electrode set up for evaluation of mass transport and electrode kinetic parameters in a PEM environment.
Figure 3  $iR$-corrected Tafel plots for oxygen reduction in proton exchange membrane fuel cells at 95°C and 5 atm pressure for Pt (ETEK) and Pt alloy electrocatalysts (JMRC). Pt loading on electrodes, 0.3 mg/cm². Pt/C (Δ), Pt/Cr (♦), Pt/Mn (⊕), Pt/Fe (▽), Pt/Co (■) and Pt/Ni (●).
Figure 4. Effect of Pt loading in the electrode on power vs current density in PEMFC (○) 0.090 and (●) 0.145 mg Pt/cm²-CESHR; (▲) 0.4 mg Pt/cm² ETEK, Inc.; (▼) 5 mg Pt/cm²-Johnson & Mathey at 95°C and 5 atm.
Fig. 5. Comparison of Dow Nafion and Aciplex-S membrane in a PEM fuel cell environment
Effect of different gas compositions: pure oxygen, air, 20% oxygen in He, Ar and N₂, on the performance of a proton exchange membrane fuel cell at 70°C and 1 atm pressure.