

## Proton Exchange Membrane Fuel Cell R&D at Texas A&M University

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### SPECTRUM OF R&D ACTIVITIES

Research efforts in the area of proton exchange membrane fuel cells (PEMFC) at the Center for Electrochemical Systems and Hydrogen Research (CESHR), Texas Engineering Experiment Station (TEES), Texas A&M University System (TAMUS) involves multifaceted fundamental and applied approaches. Among the main goals in this effort are the attainments of high power densities and energy efficiencies and long lifetimes in PEMFCs with low Pt loading electrodes. Our efforts comprise of (1) microelectrode and single cell investigations for the determination of the electrode kinetic, mass transport and ohmic parameters as well as membrane characteristics such as ionic conductivity and oxygen solubility and diffusion coefficient and (2) the use of x-ray techniques such as XANES and EXAFS to understand the role of geometric and electronic factors in the electrocatalysis of oxygen reduction by the Pt-C and by binary alloys of Pt with base transition elements. In addition, are the efforts to optimize the membrane electrode assemblies to attain high catalyst utilization and lower mass transport losses. Besides these, are the engineering-related efforts towards improved water and thermal management in 50 cm<sup>2</sup> cells and the modeling studies of the membrane electrode assemblies and of multicell stacks. The knowledge gained from these investigations are being incorporated in the current projects for the development of multicell stacks, with performance capabilities acceptable for space and terrestrial (electric vehicles) applications. The progress made in the above-mentioned areas of research and development are briefly summarized in the following sections.

### MICROELECTRODE TECHNIQUE TO DETERMINE ELECTRODE KINETIC, MASS TRANSPORT AND OHMIC PARAMETERS

A novel microelectrode technique was developed to carry out these determinations at the platinum microelectrode/proton exchange membrane interface. An illustration of the experimental set-up for these measurements, as a function of temperature and pressure, is represented in Fig. 1. Cyclic voltammetric, chronoamperometric and AC impedance spectroscopic techniques were used. The purity of the system was assessed from the cyclic voltammograms at a sweep rate of 100 mV/s. The electrode kinetic parameters for oxygen reduction were obtained from the mass transfer corrected Tafel plots, as obtained from the current versus potential plots recorded on the microelectrode at low sweep rates (< 10 mV/s). The analysis of chronoamperometric plots yielded the diffusion coefficients and solubilities of oxygen in the membrane. The results of the AC impedance studies lent insight on (i) specific resistance of the membrane; (ii) the grain boundary resistance and capacitance of the membrane; and (iii) the charge transfer resistance of the oxygen reduction reaction and the double layer capacitance as a function of potential. These parameters were determined as a function of operating temperature and pressure. A detailed study was carried out using DuPont's Nafion® membranes. Studies are in progress with the Asahi Chemicals Aciplex®-S membranes. The results to date provide clear evidence for the better electrode kinetic and mass transport rates for oxygen reduction at the interfaces of platinum with proton exchange membrane rather than with aqueous acid electrolytes, such as sulfuric or perchloric acid.

### OPTIMIZATIONS OF STRUCTURES AND COMPOSITIONS OF ELECTRODES AND OF MEMBRANE AND ELECTRODE ASSEMBLIES TO ATTAIN HIGH ENERGY EFFICIENCIES, HIGH POWER DENSITIES AND TO ENHANCE PLATINUM UTILIZATION

Considerable progress was made in these areas during the last five years at TAMU. Firstly, high energy efficiencies and high power densities were achieved with low platinum loading or (about 0.4 mg/cm<sup>2</sup>) electrodes using H<sub>2</sub>/O<sub>2</sub> or H<sub>2</sub>/Air as reactants. Secondly, the platinum utilization was significantly enhanced in PEMFCs (Fig. 2) with electrodes containing only about 0.1 mg/cm<sup>2</sup> prepared in-house by the rolling method. It was also demonstrated that the platinum

utilization can be increased by using alloy electrocatalysts (Pt-Cr, Pt-Co, Pt-Ni). Thirdly, performance improvements were made possible by optimization of the Teflon contents in the active and diffusion layers.

The alternate approach to attain high energy efficiencies and power densities is to use perfluorinated sulfonic acid membranes with higher water contents and specific conductivities. Previous studies by Srinivasan and his co-workers at Los Alamos National Laboratory and at Texas A&M University have demonstrated the considerably better performances with the Dow membranes than with Nafion®. Our studies, since 1992, have revealed high levels of performances with Asahi Chemicals Aciplex®-S membranes. These studies also demonstrated the advantages of increased temperature for hot-pressing of the membrane and electrode assemblies to considerably higher values (say by about 20°C) than the glass-transition temperature.

#### X-RAY ABSORPTION TECHNIQUES TO ELUCIDATE ROLE OF ELECTRONIC AND GEOMETRIC FACTORS ON THE ELECTROCATALYSIS OF OXYGEN REDUCTION BY BINARY PLATINUM ELECTROCATALYSTS

The x-ray absorption studies (XAS) were conducted at Brookhaven National Laboratory (BNL) by McBreen and Mukerjee. The combination of both XANES (x-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure) provide a powerful tool, especially because of the *in situ* capabilities, to elucidate the mechanism of electrocatalysis of oxygen reduction on the alloy electrocatalysts (Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe and Pt-Mn). The XAS studies were made both in the transmission and fluorescent modes using the National Synchrotron Light Source at BNL. XAS measurements were made at the Pt L<sub>2</sub> and L<sub>3</sub> edges as well as the K edge of the respective alloying component. The *in situ* measurements were made at various potentials in the range from 0 to 1.0 V/RHE. The EXAFS investigation on the Pt-Ni alloy rules out any evidence for a redox mechanism and was confirmed by the lack of potential dependence in the XANES studies. However, an increase of the Pt L<sub>3</sub> XANES reveals an emptying of the d states. The results on Pt-Co indicate a similar behavior. The XANES for Pt-Cr does not show any effect on the Pt-d states indicating a different electrocatalytic pathway from that of Pt-Ni. The lack of dependence of the Ni XANES and EXAFS with respect to potential suggest the possibility of the outer alloy surface being Pt. A correlation of the electronic and geometric factors for Pt and the alloys, as ascertained from the XANES and EXAFS studies, during oxygen reduction at two potentials is presented in Table 1. Optimum values for the d-orbital vacancy and bond distance are necessary to obtain the highest electrochemical performance. The best values correspond to those for Pt-Cr.

#### NOVEL METHOD FOR DETERMINATION OF TRANSPORT PARAMETERS OF H<sub>2</sub> AND O<sub>2</sub> IN PEMFCs

The permeation method used for the determinations of diffusion coefficients and solubilities of hydrogen in thin metallic membranes was extended for the determinations of these mass transport parameters for the fuel cell reactants in Nafion® and in Aciplex®-S membranes. In these experiments the transient and steady state currents were recorded as functions of the time for the oxidation of hydrogen or reduction of oxygen transported through the membranes, when the pressures of these gases were either increased or decreased instantaneously. An analysis of these measurements yields the diffusion coefficients and solubilities (Table 2). The values of the D are higher for the Nafion® than for the Aciplex®-S membranes. The reverse is the case for the C. However, the value of the product DC, the essential parameter governing mass transport rate, is higher for the Aciplex®-S than for Nafion®.

#### EXPERIMENTAL AND MODELING ANALYSIS OF MASS TRANSPORT PHENOMENA IN PEMFCs

One of the major challenging problems in PEMFCs is to minimize overpotential losses due to mass transport phenomena at the oxygen electrode when using air as the cathodic reactant. Experimental studies were conducted in PEMFCs to determine the effect of the type of inert gas (He, Ar, N<sub>2</sub>) and the oxygen content in the gas mixture on the PEMFC performance. A theoretical analysis led to the following conclusions: (i) mass transport overpotentials are less when using O<sub>2</sub>/He rather than O<sub>2</sub>/N<sub>2</sub> or O<sub>2</sub>/Ar gas mixtures; (ii) above 40% O<sub>2</sub> in the gas mixtures, departure from linearity of the cell potential (E) vs current density (i) plot occurs at higher current densities; (iii) the higher slope of the linear region in the E-i plot is due to mass transport in the

electrocatalytic layer, and (iv) the departure from linearity of the E-i plot is due to mass transport in the substrate-diffusion layer.

A second type of mass transport analysis is underway in our laboratories from experimental measurements of performance of PEMFCs at different flow rates of the cathodic reactant ( $O_2$  or air). The preliminary results show that (i) even at high current densities, there is hardly any dependence of performance on flow rate; and (ii) with air, there is a significant flow rate dependence at current densities of  $300 \text{ m A/cm}^2$  and higher. The problem with air at 1 atm is that when one takes into consideration the vapor pressure of water at about  $70^\circ\text{C}$ , the partial pressure of oxygen at 1 atm total pressure is only about 0.12 atm. Thus in order to satisfy the oxygen requirement at the higher current densities, extremely high flow rates of air are necessary.

#### ACKNOWLEDGEMENTS

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**Table 1. Comparison of Electronic and Geometric Parameters in the Electrocatalysis on some Binary Alloys of Pt: In-situ XANES and EXAFS results at 0.3 V and 0.6 V vs SCE**

Electrocatalyst	Double Layer Region (0.3 V vs SCE)			Oxygen Reduction Region (0.6 V vs SCE)		
	(Du)s	Pt-Pt (R) (Å°)	Pt-Pt (N)	(Du)s	Pt-Pt (R) (Å°)	Pt-Pt (N)
Pt/C	0.329	2.77	8.7	0.370	2.77	6.8
Pt/Mn	0.331	2.76	7.5	0.344	2.76	8.3
Pt/Cr	0.360	2.71	6.1	0.358	2.71	6.1
Pt/Fe	0.368	2.70	5.7	0.370	2.71	5.5
Pt/Co	0.401	2.68	6.9	0.390	2.68	7.6
Pt/Ni	0.409	2.68	9.1	0.404	2.68	9.5

(Du)s : Pt *d* orbital vacancy per atom

R : Interatomic distance

N : Co-ordination number around the first co-ordination shell

Table2. Dependence of Temperature on Transport Parameters in PEMFCs with Aciplex®-S and Nafion®-117 Membranes. Values of Activation Energy for the Diffusion Coefficient are also presented.

(1) H<sub>2</sub>

Parameter T or ΔE <sup>‡</sup>	Aciplex-S			Nafion-117		
	D×10 <sup>6</sup> cm <sup>2</sup> /s	C <sub>o</sub> mM	DC <sub>o</sub> ×10 <sup>6</sup> mM·cm <sup>2</sup> /s	D×10 <sup>6</sup> cm <sup>2</sup> /s	C <sub>o</sub> mM	DC <sub>o</sub> ×10 <sup>6</sup> mM·cm <sup>2</sup> /s
50°C	0.78	89.4	69.73	2.44	10.86	26.50
70°C	1.33	78.3	104.14	3.91	12.13	47.43
95°C	1.87	100.4	187.75	5.88	12.28	72.21
85°C*						
ΔE <sup>‡</sup> kcal/mol	4.68			5.75		

\* Nafion-117

(2) O<sub>2</sub>

Parameter T or ΔE <sup>‡</sup>	Aciplex-S			Nafion-117		
	D×10 <sup>6</sup> cm <sup>2</sup> /s	C <sub>o</sub> mM	DC <sub>o</sub> ×10 <sup>6</sup> mM·cm <sup>2</sup> /s	D×10 <sup>6</sup> cm <sup>2</sup> /s	C <sub>o</sub> mM	DC <sub>o</sub> ×10 <sup>6</sup> mM·cm <sup>2</sup> /s
50°C	2.88	4.13	11.89	6.94	1.19	8.26
70°C	3.11	6.68	20.77	8.54	1.81	15.46
95°C	5.04	8.61	43.39	11.50	1.99	22.89
85°C*						
ΔE <sup>‡</sup> kcal/mol	3.41			3.39		

\* Nafion-117

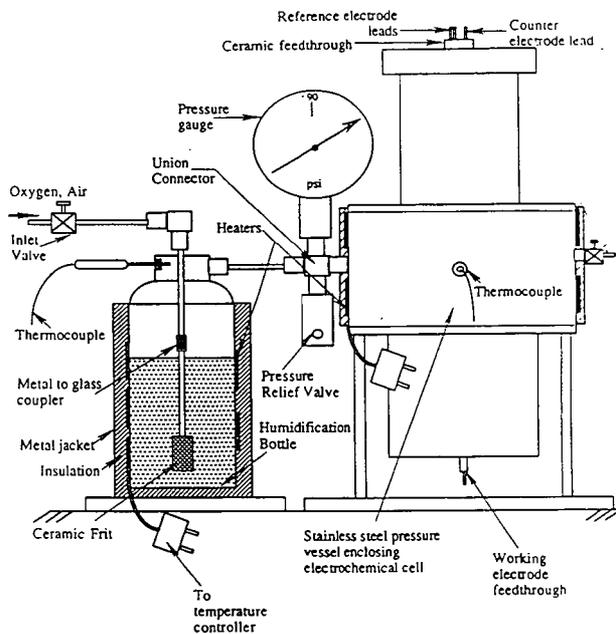


Fig 1 Schematic of the pressure vessel housing the electrochemical cell and the humidification set-up.

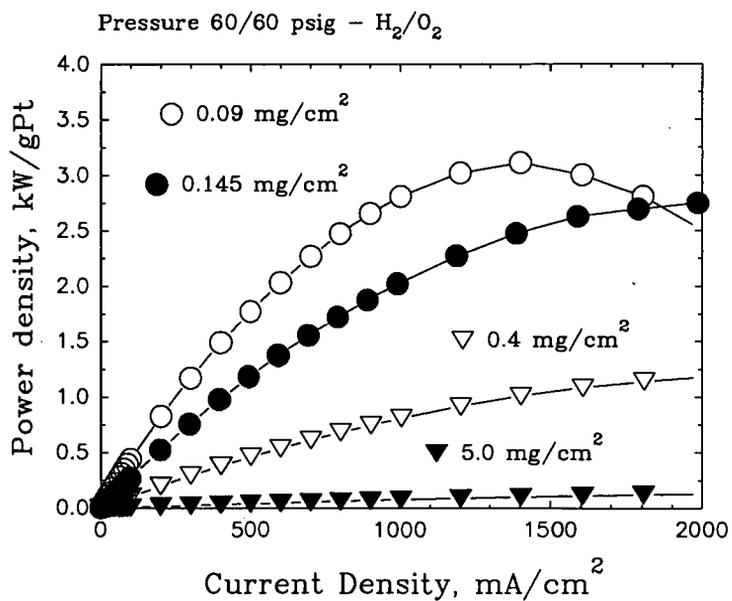


Fig 2. Effect of Pt loading in the electrode on power vs current density in PEMFC (●) 0.090 and (O) 0.145 mg Pt/cm<sup>2</sup>-CESHR; (▽) 0.4 mg Pt/cm<sup>2</sup> ETEK, Inc.; 5 mg Pt/cm<sup>2</sup>-Johnson & Mathey at 95°C and 5 atm.