

## Innovative Approach of Improving ORR Kinetics using Non-Noble Metal based additives in Cathode Catalyst for PEM Fuel Cell Applications

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### Introduction

Proton exchange membrane (PEM) fuel cells can operate at high power densities and have several other advantages (over other higher temperature fuel cell systems) such as faster start up and wider choice of materials due to its lower operating temperature. While a significant reduction in the size and cost of the PEM fuel cell system could be attained by operating the fuel cell at high current densities, the fuel cell would still have to be operated at a voltage as high as 0.8V to attain a reasonable energy conversion efficiency. The current state-of-the-art PEMFC operating at ambient pressure (anode and cathode gas stoichiometries of 1.2 and 2) has a power density of 100mW/cm<sup>2</sup> at 0.8V. However, power density enhancements of about 100-200% would be required to meet the cost and performance targets for automobile and stationary application.

Most fuel cell systems today would be required to operate on hydrogen produced by reforming hydrocarbon fossil fuels, the primary source of energy today and in the foreseeable future. This could result in a loss of performance due to the poisoning of PEM fuel cell anodes by the CO present in the fuel stream (if not removed by a complicated CO cleanup system). Bleeding air into the fuel stream is the most common approach to address this, but could have system complexity, safety and endurance implications. Operating PEM fuel cells at temperatures greater than 120°C would mitigate the effect of CO on the fuel cell performance by weakening the CO chemisorption.

Increasing the operating temperature also offers other advantages such as enhancements in the anode and cathode reaction kinetics, availability of higher quality waste heat, less expensive cooling system, system startup and shutdown without liquid water, and other system integration advantages. However, operation at temperatures higher than 100°C at ambient pressure in PEM fuel cells would lead to dehydration of the Nafion<sup>®</sup> based ionomers that are widely used as the membrane and in the catalyst layers. The ionomer proton conductivity drops drastically as the ionomer dries. This leads to increased resistive ohmic voltage loss in the membrane as well as catalytic activity loss in the electrodes. Mass transfer also becomes impaired at these conditions due to the dehydration, resulting in further performance loss. Increasing the operating pressure for raising the humidity level is not attractive since a compressor would be required, leading to cost and energy penalties for the system. Therefore, both a high temperature membrane and a modified nano-electrode structure would be needed to improve the performance of PEM fuel cells at temperatures greater than 120°C. New high performance nano-cathode structures will be developed at FCE (from a deep understanding of the issues affecting the high-temperature performance of the PEM fuel cells) will be presented.

### Results and Discussion

Significant research efforts in the cathode structure development have been directed towards optimizing the composition of Nafion in the catalyst layer<sup>1</sup> and improving the water removal properties of the gas diffusion electrode<sup>2,3,4</sup>. Little effort has been focused on reducing the mass transfer and ionic losses in the catalyst layer. Even fewer studies have been carried out to improve high temperature MEA cathode structures. Among the various factors that affect the cathode performance, those of significant importance in high temperature operation are

1. Proton activity and conductivity in the cathode
2. Mass transfer of oxygen
3. Water management in the cathode
4. Catalytic area and activity

Detailed analysis of the microscopic structure of the cathode (Figure 1) revealed additional necessity of an intimate contact between the nano-Pt catalyst particles, protonic species and the oxygen reactant, for a high cathode performance. Without such a microscopic intimate contact, even sufficient bulk and macroscopic proton conductivity of the ionomer phase cannot be transformed into a high cathode performance. This could be illustrated by the possible absence of the protonic species right next to the Pt particles. This requirement of a microscopic intimate contact with Pt is not as essential for the electrolyte membrane, which requires only sufficient bulk macroscopic proton conductivity. Therefore, membrane improvement alone is not sufficient for guaranteeing high cell performance. Enhancing the intimate contact in the cathode is also important.

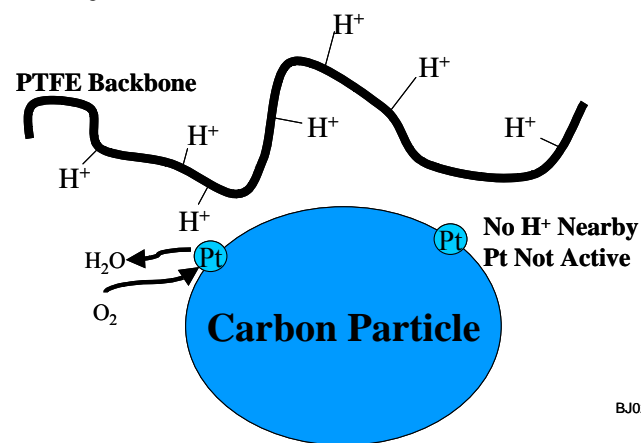


Figure 1. Schematics of Microscopic Structure of PEMFC Cathode:

There have been extensive studies of compounds that demonstrate proton conductivity at PEMFC operation temperatures such as hydrous ruthenium oxide<sup>v</sup>, tungsten trioxide<sup>v</sup>, iron oxide, manganese oxide<sup>vi</sup> and phosphates of zirconium<sup>vii</sup>. However not all of these are

applicable for use on the cathode. While some of these compounds have been added to the membrane or painted on the electrodes to improve proton conduction<sup>viii</sup>, they have not been incorporated near the catalyst site to act as a source of protons.

Improvements of about 15% in performance were observed in prior studies at Fuel Cell Energy using ruthenium oxide as a proton flux agent<sup>ix</sup>. The studies conclude that the proton flux agents enhance the ORR kinetics. Newer materials with mixed proton and electron conductivity are being considered in this project to develop cathode structures that would yield larger performance enhancements. Manganese oxide based nano-octahedral molecular sieves (OMS-2) developed by the University of Connecticut have been shown to possess good proton and electronic conductivity at the temperature of interest in PEM fuel cells<sup>xa-d</sup>. OMS-2 nanomaterials found to have free oxygen that will provide improvements in oxygen flux for cathodic reaction. The free oxygen in OMS-2 was available due to unique structural properties wherein Mn has different oxidations states<sup>18a-d</sup>.

Recent studies have indicated 3 to 14 fold oxygen flux enhancements<sup>xi</sup> and large improvements in performance<sup>xii</sup> when polystyrene beads and magnetic materials were incorporated to PEM fuel cell cathodes operating at well-humidified conditions. The ionic conductivity of Nafion<sup>®</sup> was also reported to be increased by the presence of these materials and was attributed to the restructuring of the ionomer<sup>xiii</sup>. These results indicate the possibility of enhancing performance of PEM fuel cell by reducing the mass transfer and ohmic losses in the catalyst layer. Since oxygen solubility in Nafion is reduced at high temperature when the ionic phase dries out<sup>xiv</sup>, lowering the ORR kinetics, the mass transfer in the catalyst layer needs to be supplemented.

Manganese oxide based nano-octahedral molecular sieves (OMS-2) were also found to have good oxygen storage and transfer capabilities<sup>18a-d</sup>. The oxygen storage capacity of OMS-2 is about 0.1 wt% and the OMS-2 oxygen enrichment is fairly rapid at 25°C and increases at high temperatures. Since OMS-2 is both electronically and ionically conductive, it could be incorporated in the catalyst layer adjacent to the Pt particles. Studies have shown that it is possible to produce extremely small particulates of nanosize porous manganese oxide materials<sup>xv</sup> that would enable uniform dispersion of the particulates in the cathode. OMS-2 [KMn<sub>8</sub>O<sub>16</sub>(nH<sub>2</sub>O)] is a hydrated oxide and retains significant amount of water in its crystalline structure, (about 18g/100g OMS-2). Thermogravimetric studies<sup>xvi</sup> have shown that  $\gamma$ -MnO<sub>2</sub> (a material similar to OMS-2 chemical composition) loses some molecular water absorbed on the microporous surfaces between 20°C and 150°C (between B and C in Figure 2). It still retains large amounts of structural water, which is gradually lost only between 200°C and 400°C (between C and D in Figure 2). Therefore, it would help retain water and proton conduction in the high temperature MEA (~150°C) (Figure 2). The structural water is either present as OH<sup>-</sup> ions in the lattice or is associated with Mn<sup>3+</sup> ions and promotes proton conduction<sup>xvii</sup>.

The PEM fuel cell cathode designs that will be evaluated in this project will comprise of supported Pt catalyst, proton conducting ionomer (Nafion<sup>®</sup>), and OMS-2. A schematic diagram that illustrates this cathode design is shown in Figure 3. Nafion acts as a proton conductor and a binder for the catalyst layer. OMS-2 would act as an additional conduit for both proton (the diffusion coefficient for protons in MnO<sub>2</sub> is reported<sup>27</sup> to be  $6 \times 10^{-10}$  cm<sup>2</sup>/s) and oxygen

transport, while also help retain some product water in the catalyst layer. Since OMS-2 is also electronically conductive, large amounts of OMS-2 could be incorporated in the cathode.

Another modification to the cathode structure that will be studied in this project is the introduction of a new oxygen permeable water barrier layer that would inhibit the loss of water on the cathode while permitting sufficient amounts of oxygen transport into the cathode for the ORR. The approach will begin with the introduction of oxygen transporting additives into the pores of the cathode electrode. This will form an oxygen permeable water barrier layer on the cathode electrode. The purpose of the barrier layer is to prevent the water in the cathode electrode layer from experiencing the drying conditions of atmospheric dry air at 120°C. This will ensure that the ionomer component of the electrode and membrane are well hydrated. However, the barrier layer must be able to pass oxygen and electrons to the cathode catalyst site with little losses. Initial results on using water barrier Krytox additive MEA has shown significant improvement in performance over baseline design. These results are presented in Figure 4 and MEA was prepared by Ion Power, FCE's subcontractor in the proposed project. If all of this can be achieved, the cathode will experience a total pressure higher than that of the reactant air in the cathode flow channels. This is termed the "oxygen permeable water barrier layer". An illustration of this cathode structure is shown in Figure 5.

Materials do exist that have enough oxygen permeability to sustain a current density of 1 A/cm<sup>2</sup> at one atmosphere of air. For example Teflon AF, which has been considered as a material for oxygen enrichment membranes, has a permeability of  $990 \times 10^{-10}$  Barriers (cm<sup>3</sup>-cm/s/cm<sup>2</sup>/cm-Hg)<sup>xviii</sup>. In addition there are fluids with a very high ability to absorb and transport oxygen. They have been used as blood substitutes or even to completely fill the lungs of laboratory animals with the fluid and allow the animal to "breathe" from the oxygen in the fluid<sup>xix</sup>. Some of these perfluorocarbon fluids, for example Krytox<sup>™</sup>, have an extremely low vapor pressure ( $<4 \times 10^{-15}$  Torr)<sup>xx</sup>. The low vapor pressure is required so that over the lifetime of the cell (40,000hours for stationary applications and 5,000h for transport applications) an insignificant amount of the material would be lost due to vaporization. Water is not soluble in these fluids so the product water would move via diffusion through the thin PEM membrane and exit the cell through the anode exhaust stream. These results will be presented in the presentation.

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