Proton Exchange Membrane Fuel Cells for Transportation Applications

by Johna Leddy and James Fenton

A fuel cell is an electrochemical power source with advantages of both the combustion engine and the battery. Like a combustion engine, a fuel cell will run as long as it is provided fuel; and like a battery, fuel cells convert chemical energy directly to electrical energy. As an electrochemical power source, fuel cells are not subject to the Carnot limitations of combustion (heat) engines. An electrochemical power source can be, in theory, 100% efficient; practical efficiencies are approximately 50% with >90% efficiencies in some demonstration projects. Automotive combustion engines have a 40% maximum theoretical efficiency and a practical efficiency of about 25%.

The construction of a fuel cell is conceptually simple. Electrodes are placed on either side of the separator. The fuel fed to the anode and the oxidant fed to the cathode are discharged electrochemically to generate current and voltage. The high efficiency of the fuel cell arises because the discharge is electrochemical as opposed to thermal.

Sir William Grove demonstrated the first fuel cell in 1839. The system used hydrogen and oxygen as fuel and oxidant, platinum strip electrodes, and a dilute sulfuric acid electrolyte. Since that time, fuel cells have been developed in various environments. The broad classes of fuel cells are named by their separators or electrolytes. Currently, the major classes of fuel cells are phosphoric acid; solid oxide; molten carbonate; and the subject of this special issue: proton exchange membrane (PEM) fuel cells. PEM fuel cells use an ion exchange membrane as the separator. Typically, it is the properties of this membrane along with the catalyst that set the operating limit of the fuel cell. For PEMs, this is usually in the range of 80 to 100 °C. The fundamentals of a PEM fuel cell were elaborated in a tutorial in these magazine pages (Vol. 13, No. 3, p. 17, Fall 2004).

Consider the diagram of a simple hydrogen-fed fuel cell in Fig. 1. The ion exchange membrane serves as the separator between the anode where hydrogen is oxidized and the cathode were oxygen is reduced. In this system, oxygen may be either pure oxygen or oxygen from the air. Each electrode consists of a heterogeneous, porous layer that serves as electron conductor, ion conductor, and gas transport region. The catalytic reaction occurs at the three-phase contact with the catalyst. Here, the catalyst is shown as a platinum site, but any variety of catalysts, usually noble metals, may be employed under different conditions. As the gases react, protons generated at the anode cross the membrane to the cathode as electrons flow through the external circuit to drive reduction. The membrane provides ionic conduction and prohibits direct reaction of the hydrogen and oxygen at the platinum catalyst. Typically, a single fuel cell is constructed by making two electrodes of catalyst layers

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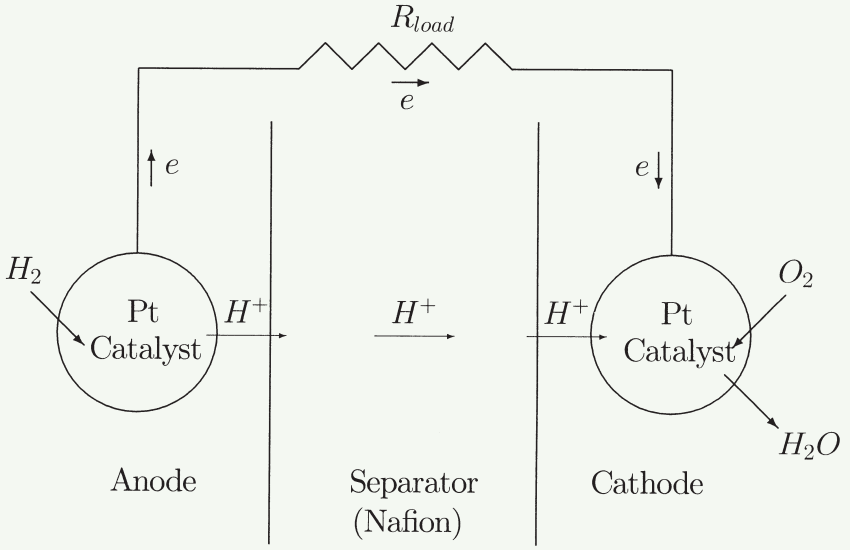

FIG. 1. *Schematic of a PEM fuel cell for H_2/O_2 and H_2/air.*

applied to porous carbon substrates (such as carbon paper and cloth); placing a Nafion membrane between the two electrodes; and heat pressing to form the membrane electrode assembly (MEA). The resulting structure resembles a piece of overhead transparency with small felt squares centered on each side. Often, to generate appropriate voltage, MEAs must be used in a stack. Current is increased by using larger electrodes.

In a system, several events must be effective for the fuel cell to generate appropriate power. The catalyst for the anode and cathode must be efficient. The membrane must be ionically conducting and yet provide separation of the potentially explosive fuel and oxidant. The catalyst layers must allow for effective and balanced transport of gases, electrons, and protons.

Thermodynamically, the reactions of hydrogen and oxygen should yield 1.23 V under standard conditions through a four electron/four proton process. Fuel cells do not yield the thermodynamically anticipated voltage. Several important factors contribute to the less than ideal performance of PEM fuel cells. The kinetics of the anode and cathode are not necessarily ideal. In particular, the oxygen reduction kinetics are a limiting factor, even with noble metal catalysts. Under high flux conditions, the membrane may be carrying currents on the order of amperes per centimeter squared. Under these conditions large quantities of protons are crossing the membrane, and each of these protons may be heavily hydrated. At the same time, hydrated protons are being delivered from the anode to the cathode, where additional water is generated as a consequence of the oxygen reduction. This crossover of solvent leads to dehydration of the anode and flooding of the cathode. The kinetics for hydrogen are largely not rate limiting, but questions remain as to whether or not hydrogen is the optimum fuel for a variety of fuel cell applications. These questions arise for reasons of safety, cost effective generation of hydrogen, and efficient storage of hydrogen. Thus, the principle difficulties with hydrogen fuel cells are issues of oxygen reduction catalysis, crossover of solvent, and appropriateness of hydrogen as a fuel. Often improvements for one of these challenges lead to further degradation in another. For example, an increase in the temperature of the fuel cell improves the oxygen reduction kinetics, but tends to dehydrate the membrane.

Fuel cells are also specified by their fuel and oxidant as fuel/oxidant. Technologically viable PEM systems are available for H_2/O_2 and H_2/air. Hydrogen-rich organic fuels such as alcohols can be produced from biomass and natural gas and could serve as useful fuels for transportation and off-grid applications because of their high energy density. There are, however, significant remaining challenges to using organic fuels in fuel cells. A direct reformation fuel cell uses a mixture containing organic fuels that is fed directly to the anode. For a direct methanol fuel cell (DMFC), the fuel cell would be fed CH_3OH + H_2O/air. The oxidation of methanol to CO_2 proceeds by a 6 electron/6 proton process, progressing through many intermediates that bind to the catalyst surface. Generally, catalyst technologies have yet to mature sufficiently to do this conversion with high efficiency. For some applications, such as automobiles, indirect reformation has been used. A mixture of fuel (*e.g.*, alcohol and water) is converted thermally to H_2 + CO_2 that is fed to the anode. The difficulty with PEM fuel cells is that under operating conditions, CO_2 is slightly reduced to CO. The CO typically poisons the noble metal catalysts. Currently, in fuel cell research, the majority of work on hydrogen systems is directed at optimizing the existing technology, whereas for organic fuels, the need for better catalysts and membranes drives more fundamental research.

Fuel cells have found applications in many sectors, including transportation; portable electronics; back-up power supplies (UPS); off-grid power generation; distributed power; and load leveling. The technology, especially for hydrogen systems, has advanced tremendously in recent years with fuel cell powered systems now approaching technical and cost viability. Many advances have been made to improve the performance with organic fuels. PEM fuel cells offer advantages of reduced greenhouse emissions, reduced reliance on oil reserves, and generation of distributed power from renewable resources. Tremendous opportunities remain for improving PEM fuel cells.

In this special issue of *Interface*, PEM fuel cells are featured within the context of transportation applications. In the first article, Mathias *et al.* discuss the key issues associated with polymer electrolyte fuel cells (or PEFCs, an alternative abbreviation for PEMFCs) for automotive applications. This overview immediately identifies the key fuel cell system components as the membrane and the catalyst. Thus the second article by Dunwoody and Leddy reviews proton exchange membranes with particular reference to Nafion. The last article by He *et al.* focuses on the catalyst itself and specifically, the cost, performance, and durability issues. Readers may recall that PEMFCs have been featured before in these magazine pages: "Is a Fuel Cell in Your Future?" by Tom Fuller (Vol. 6, No. 3, p. 26, Fall 1997); "Fuel Cells: An Electrochemical Solution to Global Climate Change

in the 21st Century" by Wilkinson (Vol. 10, No. 1, p. 22, Spring 2001); "Engineering a Membrane Electrode Assembly" by Weidner *et al.* (Vol. 12, No. 4, p. 40, Winter 2003); and most recently, a tutorial entitled "The Polymer Electrolyte Fuel Cell, " by Ramani *et al.* (Vol. 13, No. 3, p. 17, Fall 2004).

Thus, the present crop of articles builds upon this body of information and further updates the progress made in the intervening months. This progress has been so remarkable that it may not be too far-fetched to think of having a fuel cell car (or perhaps two!) in every garage. Yet the challenges associated with developing a hydrogen infrastructure (a topic of a recent issue of *Interface*, Vol. 13, No. 3, Fall 2004) are certainly formidable and are not addressed in this volume per se. It is our hope that the feature articles and this special issue will contribute in a small measure to inspire future R&D advances needed to make fuel cell powered cars an everyday reality, and thus ensure an environment for our future generations that is free from fossil fuels and pollution. ■

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