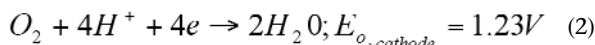
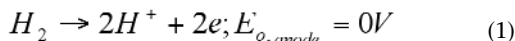


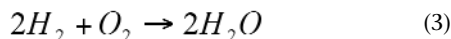
The Polymer Electrolyte Fuel Cell

by Vijay Ramani, H. Russell Kunz, and James M. Fenton

Fuel cells are electrochemical devices that convert the chemical energy of a fuel directly to electrical energy. They typically consist of an electrolyte medium sandwiched between two electrodes called the anode and cathode. For a reversible fuel cell running on hydrogen and air, the following electrode reactions occur at the anode and cathode, respectively



The protons generated during electrochemical oxidation are transported from the anode to the cathode through the ionically conducting (but electronically insulating) electrolyte. The electrons generated during oxidation pass through the external circuit to the cathode, where they complete the electrochemical reduction of oxygen to produce water. The overall cell reaction is



Ideally, the reversible cell emf ($E_{o, cell}$), defined as the difference between the standard reduction potentials of the cathode and anode reactions ($E_{o, cathode}$ and $E_{o, anode}$), should be 1.23 V. The standard free energy change (ΔG_o) of the overall reaction of the fuel cell (Eq. 3) is given by

$$\Delta G_o = -nF E_{o, cell} \quad (4)$$

where n is the number of electrons transferred and F is Faraday's constant (96,475 C/equiv). Since n , F , and $E_{o, cell}$ are positive numbers, the standard free energy change of the overall reaction is negative, indicating a spontaneous reaction. This is the thermodynamic rationale behind fuel cell operation.

Faraday's law provides a relationship between the quantity of current passed through a system and the quantity of

(electro)chemical change that occurs as a consequence. The law may be written as

$$m = M I t / n F \quad (5)$$

where m is the mass and M is the molecular weight of the substance undergoing change, I is the current passed in amperes, and t is the time for which the current is passed in seconds. Thus, the current drawn from a fuel cell is directly related to the rate at which hydrogen and oxygen react at their respective electrodes. In an ideal (reversible) fuel cell, the cell voltage is independent of the current drawn, and would remain at 1.23 V. Practically, the ideal cell voltage of 1.23 V is not realized even at open circuit (zero current) due to the myriad irreversibilities that arise during fuel cell operation.

Fuel cells are primarily classified (Table I) according to the electrolyte material. The choice of electrolyte material also governs the operating temperature of the fuel cell. This article focuses primarily on the polymer electrolyte fuel cell.

Polymer Electrolyte Fuel Cells (PEFCs)

A PEFC (Fig. 1) is unique in that it is the only kind of low temperature fuel cell that uses a solid electrolyte. The most common polymer electrolytes used in PEFCs are perfluoro-sulfonic acid (PFSA) ionomers such as Nafion, which are available in films of thicknesses varying from 25 to 175 μm . These materials have a fluorocarbon backbone, akin to polytetrafluoroethylene (PTFE), with side chains ending in pendant sulfonic acid moieties. The presence of sulfonic acid promotes water uptake and enhances the proton conductivity of the membrane. The electrodes are typically made from platinum or platinum alloy supported on carbon with an appropriate amount of ionomer added to bind each electrode and to promote protonic conductivity. Humidified H_2 and air enter the system through flow fields machined into graphite plates, flow through porous carbon backings with a bimodal pore distribution, and are distributed uniformly throughout the active area of the respective electrodes, where the electrochemical oxidation and reduction reactions discussed in the previous section occur.

Table I. Fuel cell classification.

Fuel cell type	Electrolyte	Operating temperature ($^{\circ}\text{C}$)
Polymer electrolyte	Polymer membrane.....	60-80
Alkaline	Potassium hydroxide	70-120
Phosphoric acid	Phosphoric acid	160-200
Molten carbonate	Lithium / potassium carbonate	650
Solid oxide	Ytria-stabilized zirconia	1000

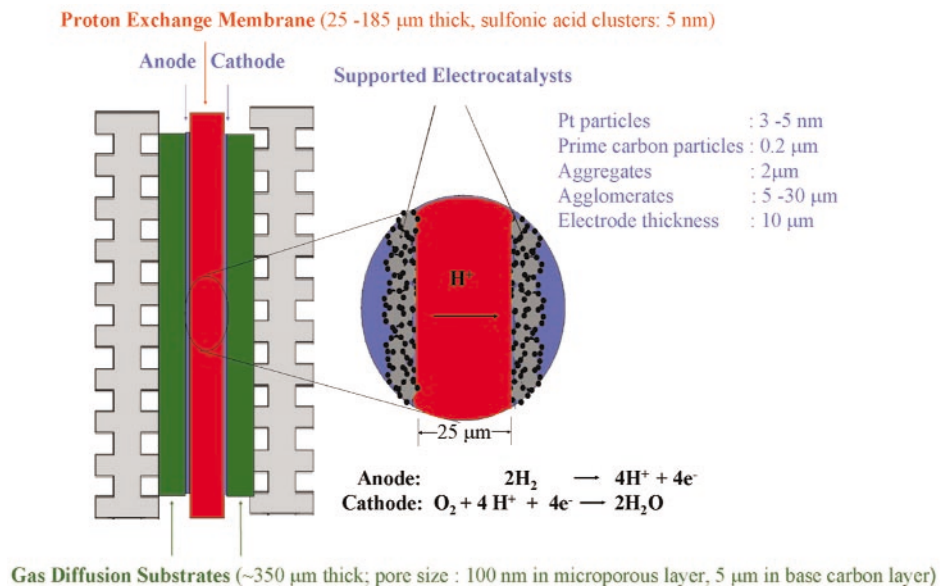


Fig. 1. Schematic of a PEFC listing key dimensions.

PEFC Operating Characteristics

The difference between actual cell voltage at a given current density (current per unit active electrode area) and the reversible cell voltage for the reaction is termed overvoltage (overpotential when referring to a single electrode). A comprehensive discussion of irreversibility and overvoltage in fuel cells is presented in the literature.¹ Some of the more prominent sources of overvoltage in a PEFC are

- **Mixed potential** at electrodes arising due to unavoidable parasitic reactions that tend to lower the equilibrium electrode potential – one particularly important cause of mixed potential is the crossover of hydrogen gas through the membrane from anode to cathode. This is the dominant source of losses at open circuit.
- **Activation overpotential** arising predominantly due to the sluggish oxygen reduction kinetics at the cathode (assuming pure hydrogen is used at the anode). The effects of these losses are most pronounced at low current densities (~0 to 100 mA/cm²).
- **Ohmic overpotential** arising due to the resistive losses in the membrane and in the electrodes. The effects of these losses are most pronounced at intermediate current densities (~100 to 500 mA/cm²).
- **Concentration (mass transport) overpotential** arising due to non-reacting diffusion in the gas diffusion layer and to reacting diffusion in the electrode layers (especially the cathode). The effects of these losses are most pronounced at high current densities (> 500 mA/cm²).

The combined contributions of these sources of overvoltage cause the cell voltage output to decrease with increasing current density. A plot of cell voltage vs. current density is known as a polarization curve, a typical example of which is shown in Fig. 2.

Because the power output of the fuel cell (in mW/cm²) is given by the product of voltage and current density, *i.e.*, the area under the polarization curve, one primary focus of current PEFC research is to elevate and flatten the polarization curve to maximize power output. This is best accomplished by mini-

mizing the contribution of each source of overvoltage at the desired operating current density.

Critical Technological Roadblocks and Research Directions

Among the primary factors currently impeding commercialization of PEFCs is the high materials cost—Nafion and Pt-based electrocatalysts cost several dollars a gram. Efforts are currently ongoing to reduce overall fuel cell cost by maximizing individual cell performance (fewer number of cells needed for given power output) while simultaneously minimizing the amount of electrocatalyst and membrane material used per unit active area. This dual approach is possible only by carefully evaluating, understanding, and reducing the contributions of individual overvoltage sources to the overall overvoltage. Research is also ongoing to develop inexpensive alternate materials such as sulfonated hydrocarbon based membranes² and non-noble metal catalysts to replace existing materials.

Durability is another key issue hindering commercialization.³ Depending on the application, 2,000-40,000 hours of PEFC operation with minimal to no deterioration in performance is usually desired. Primary PEFC failure mechanisms include chemical attack of the electrolyte membrane, which is caused by hydrogen peroxide produced within the cell. This leads to membrane thinning, reactant crossover, internal shorting, and eventually catastrophic failure. Other failure modes include catalyst deactivation over time due to particle ripening and gradual poisoning by impurities in the feed. Research efforts in this area currently encompass accelerated materials testing (subjecting fuel cell materials to more extreme conditions for shorter time periods) followed by post-test analyses to determine key failure mechanisms.

Finally, operation at temperatures over 100°C, which is desired to promote heat rejection, improve reaction rates, improve tolerance to impurities, and improve overall efficiency, is currently precluded at atmospheric pressure due to unacceptable ohmic losses arising from poor electrolyte conductivity at low relative humidities. Ongoing efforts include investigation of new electrolyte materials such as sulfonated hydrocarbons and acid doped polymers⁴ that in addition to being cheap, conduct protons at high temperatures without

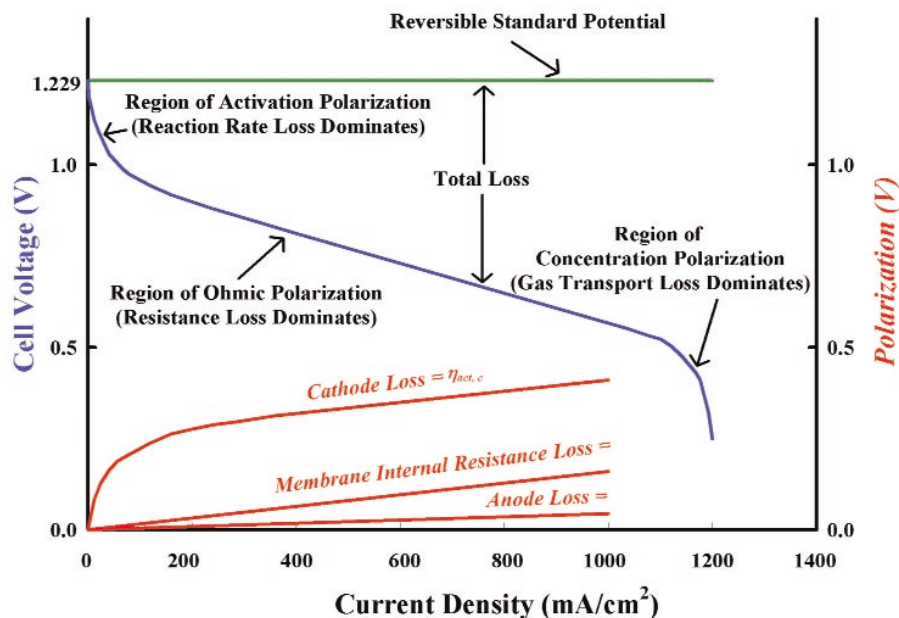


Fig. 2. Typical PEFC polarization curve indicating different overvoltage sources.

the need for water. Another approach being studied is the identification of low vapor pressure compounds such as imidazoles to replace water as the primary vehicle for proton conduction. This approach and several other strategies have been recently reviewed.^{5,6}

Conclusion

PEFCs represent an environmentally friendly technology involving electrochemical oxidation of fuels using air to produce water and electricity. Unlike traditional fossil fuel com-

bustion technologies, fuel cells are not limited by the Carnot cycle and therefore offer potentially greater efficiencies. Their ability to operate continuously obviates the need for recharging, which represents a significant advantage over batteries. These unique features make PEFC technology an attractive future proposition, with disparate applications in the transportation, stationary power, portable electronics, and military sectors. While substantial progress has been made in PEFC technology over the past few decades,^{7,8} several key challenges

(continued on page 45)

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remain. To this end, considerable research efforts are ongoing in academia and industry to help alleviate critical issues such as cost, durability, and operating range to permit rapid PEFC commercialization. ■

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