

Fuel Cells

by Vijay Ramani

Fuel cells are electrochemical devices that directly convert chemical energy to electrical energy. They consist of an electrolyte medium sandwiched between two electrodes (Fig. 1). One electrode (called the anode) facilitates electrochemical oxidation of fuel, while the other (called the cathode) promotes electrochemical reduction of oxidant. Ions generated during oxidation or reduction are transported from one electrode to the other through the ionically conductive but electronically insulating electrolyte. The electrolyte also serves as a barrier between the fuel and oxidant. Electrons generated at the anode during oxidation pass through the external circuit (hence generating electricity) on their way to the cathode, where they complete the reduction reaction. The fuel and oxidant do not mix at any point, and no actual combustion occurs. The fuel cell therefore is not limited by the Carnot efficiency and, theoretically (although not practically), can yield 100% efficiency. Fuel cells are primarily classified according to the electrolyte material. The choice of electrolyte material also governs the operating temperature of the fuel cell. Table I lists the various types of fuel cells along with electrolyte used, operating temperature, and electrode reactions.

Operating Principles

The reversible cell electromotive force (emf; $E_{o,cell}$) is defined as the difference between the standard reduction potentials of the cathode and anode reactions ($E_{o,cathode}$ and $E_{o,anode}$). The actual number may vary depending on the reactions that occur at these electrodes, but is always positive. For example, in a hydrogen/oxygen polymer electrolyte fuel cell operated at standard conditions, the reversible cell emf is 1.23 V. The standard free energy change (ΔG_o) of the overall reaction of the fuel cell is given by

$$\Delta G_o = -nFE_{o,cell} \quad [1]$$

where n is the number of electrons

transferred and F is Faraday's constant (96,475 C/equiv). Because 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.

In an ideal (reversible) fuel cell, the cell voltage is independent of the current drawn. Practically, the reversible cell voltage is not realized even under open-circuit (zero current) conditions due to the myriad irreversibilities that arise during fuel cell operation. 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). Prominent sources of overvoltage in a fuel cell are

1. **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 fuel through the electrolyte from anode to cathode or vice versa. This is the dominant source of losses at open circuit, especially in direct methanol fuel cells where fuel crossover through the electrolyte membrane is high.
2. **Activation losses** arising predominantly due to the kinetics at the electrodes. The effects of these losses are most pronounced at low current densities (~1 to 100 mA/cm²). Examples include sluggish oxygen reduction kinetics at the cathodes of polymer electrolyte and phosphoric acid fuel cells and sluggish methanol oxidation kinetics at the anode of a direct methanol fuel cell
3. **Ohmic losses** arising due to the resistive losses in the electrolyte and in the electrodes. The effects of these losses are perhaps most pronounced at intermediate current densities (~100 to 500 mA/cm²).
4. **Mass transport losses** arising due to nonreacting diffusion in the gas-diffusion layer and to reacting diffusion in the electrode layers. 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 polarization curve for a hydrogen fueled polymer electrolyte fuel cell is shown in Fig. 2. The power output of the fuel cell (in mW/cm²) is given by the product of voltage and current density. A comprehensive discussion of irreversibility and overvoltage in fuel cells is presented in the literature.¹

Challenges

Each type of fuel cell has its own advantages and disadvantages. For example, alkaline fuel cells allow the use of nonprecious metal catalysts because of facile oxygen reduction kinetics at high pH conditions, but suffer from the problem of liquid electrolyte management and electrolyte degradation. Similarly, molten carbonate fuel cells can tolerate high concentrations of carbon monoxide

(continued on next page)

Table I. Classification of fuel cells

Fuel Cell Type	Electrolyte Used	Operating Temperature	Electrode Reactions
Polymer Electrolyte	Polymer Membrane	60-140°C	Anode: $H_2 = 2H^+ + 2e^-$ Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$
Direct Methanol	Polymer Membrane	30-80°C	Anode: $CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$ Cathode: $\frac{3}{2} O_2 + 6H^+ + 6e^- = 3H_2O$
Alkaline	Potassium Hydroxide	150-200°C	Anode: $H_2 + 2 OH^- = H_2O + 2e^-$ Cathode: $\frac{1}{2} O_2 + H_2O + 2e^- = 2 OH^-$
Phosphoric Acid	Phosphoric Acid	180-200°C	Anode: $H_2 = 2H^+ + 2e^-$ Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$
Molten Carbonate	Lithium/Potassium Carbonate	650°C	Anode: $H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$ Cathode: $\frac{1}{2} O_2 + CO_2 + 2e^- = CO_3^{2-}$
Solid Oxide	Yttria Stabilized Zirconia	1000°C	Anode: $H_2 + O^{2-} = H_2O + 2e^-$ Cathode: $\frac{1}{2} O_2 + 2e^- = O^{2-}$

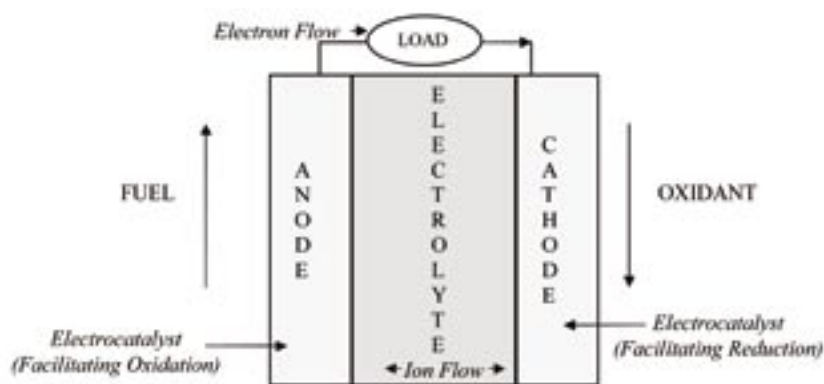


Fig. 1.

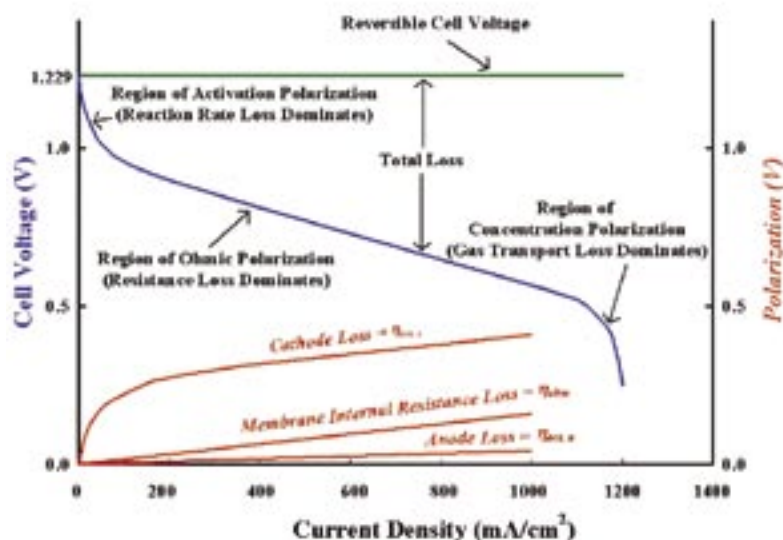


Fig. 2.

in the fuel stream (CO is a fuel for such fuel cells!), but their high operating temperature precludes rapid start-up and sealing remains an issue. Solid oxide fuel cells offer high performance, but issues such as slow start-up and interfacial thermal conductivity mismatches must be addressed. High cost is an issue that affects each type of fuel cell. It is difficult to enumerate the merits and demerits of each type of fuel cell given the limited scope of this article. Hence, the discussion below is restricted to polymer electrolyte fuel cells (PEFCs) and outlines a few of the challenges that currently impede PEFC commercialization.

A PEFC is unique in that it is the only kind of low temperature fuel cell that uses a solid electrolyte, usually a polymer electrolyte membrane (PEM). Perhaps the most common PEM in use today is Nafion® a well-researched² perfluorosulfonic acid (PFSA) ionomer which is commercially available in films varying from 25 to 175 μm thick. PEFCs presently operate at relatively low temperatures (60-120°C; more toward the lower end of the range). The operating environment is kept well hydrated to maximize membrane conductivity. Hydration is typically achieved by humidifying inlet reactant gases by bubbling them through saturators containing water at a fixed temperature. By varying the saturator temperature relative to the cell operating temperature, the desired inlet relative humidity can be maintained.

There has been enhanced interest in recent times to operate PEFCs at temperatures >100°C for a multitude of reasons: (i) to minimize the poisoning effect of carbon monoxide impurities in the reformat hydrogen feed stream; (ii) to enable rapid heat rejection

with a reasonably sized radiator (for transportation applications); and (iii) to enhance reaction rates and simplify water management issues. It is difficult to operate much above 100°C and maintain 100% relative humidity without incurring parasitic power losses due to pressurization. Hence, PEMs that have high conductivities at elevated temperatures and low relative humidities are sought.³ Unfortunately, the conductivity of Nafion® drops with decreasing relative humidity (RH), leading to unacceptable ohmic losses and precluding elevated temperature operation sans pressurization. This is one important challenge facing the PEFC community today. In response to this challenge, extensive efforts have been made to improve the properties of Nafion® and to identify alternate replacement materials. These efforts can be divided into three broad categories: (i) modification of Nafion® and similar perfluorinated membranes by inclusion of inorganic additives;⁴⁻¹⁰ (ii) membranes based on sulfonated hydrocarbon backbones;¹¹⁻¹⁷ and (iii) acid impregnated polymer matrices.¹⁸⁻²⁰

A second important issue is the poor kinetics of the oxygen reduction reaction (ORR) in acidic media. Even with the use of high loadings of expensive noble metal catalysts such as platinum in the electrode, the activation overpotential for the ORR is on the order of 500 mV at acceptable current densities. Using such high platinum loadings (0.4 mg/cm²) lead to fuel cell costs that are too high by at least an order of magnitude (two orders of magnitude for transportation applications) to permit commercialization. Three approaches are being pursued to resolve this issue: (i) efforts are ongoing to enhance the activity of the noble metal catalyst through alloying. By enhancing activity, it is anticipated that the amount of catalyst required can be lowered; (ii) a variety of less expensive, non-noble metal catalysts such as metal porphyrins are being investigated in acidic media; and (iii) in a more indirect approach, attempts are being made to engineer the electrode in a manner designed to ensure that ohmic and mass transport losses are kept to an absolute minimum and that the reaction is activation controlled. Gasteiger *et al.*²¹ provide an excellent review of these approaches and suggest that Pt-alloy catalysts seem to offer the best chance of achieving sufficient enhancement in mass activity over pure platinum.

The third challenge relates to durability. Typically, lifetimes of 40,000 h of continuous operation (for stationary applications) and 5,000-10,000 h of cyclic operation (for transportation applications) are targeted as a precursor to

(continued on next page)

The Hydrogen Rush: Boom or Bust?

by Krishnan Rajeshwar

Energy has been listed as humanity's number one problem for the next 50 years by several agencies. That it surpasses other issues such as water, food, environment, poverty, terrorism, war, disease, education, democracy, and population, underscores the criticality of energy in almost everything that a society does. The U.S. Department of Energy projects (<http://www.eia.doe.gov/oiaf/ieo>) that the world's total energy consumption will rise by 54% between 2001 and 2025. This projected increase may be an underestimation due to the rapid economic development in heavily populated countries like India and China. This worldwide competition for energy sources is likely to create tensions among countries unless they can develop new energy sources. To meet our future energy needs, we must develop alternative energy sources because (i) the fossil fuel reserve will not be sufficient to meet the demand beyond 2050; and (ii) an over-reliance on fossil fuels (many of them are located in politically unstable regions in the Middle East, Central Asia, Africa, and Latin America) has both environmental and political implications.

The U.S. and much of the world currently rely heavily on coal, oil, and natural gas for energy. These fossil fuels are nonrenewable, finite resources that will eventually dwindle, becoming too expensive or too environmentally damaging to retrieve. To achieve a sustainable energy future, we must develop fuel diversity. By contrast, hydrogen can be mined from diverse sources, in particular water, using nonfossil fuel energy such as solar, wind, and nuclear and later used for the world's energy needs with minimal environmental impact. The element is abundant and can be found not only in water but also in many organic compounds. Once separated from other elements, hydrogen can be burned as a fuel or converted into electricity through fuel cells (see the accompanying article on fuel cells). Developing this marvelous clean energy carrier as a solution to the world's energy appetite requires electrochemists working together with other scientists, engineers, venture capitalists, business leaders, and government leaders to research, develop, and deploy hydrogen technologies that will not only be cost effective but will generate long-term technological and economic benefits for the countries first to mine this particular element successfully.

The development of hydrogen and fuel cell technologies has been accelerated by the \$1.2 billion in research funding proposed by President Bush in his 2002 State-of-the-Union Address (Freedom Fuel initiative). The call for energy independence was reiterated in his 2006 address where he specifically emphasized we had to overcome our "addiction to oil." Furthermore, the Energy Policy Act

of 2005 includes \$3.7 billion for hydrogen and fuel cell research and development. The bill also includes a fuel cell tax credit up to \$1,000 per kilowatt on the purchase of fuel cells used in residential or commercial applications. President Bush's just-announced budget for fiscal year 2007 includes increases in both solar and hydrogen funding. Gold, copper, and other metals spurred much of the economy in this country during the 1800s and communities sprouted up and became ghost towns as the metal deposit veins were mined and depleted in turn. Before the 1800s, wood was the dominant energy source, later replaced by more energy-dense fossil fuels. The mining of hydrogen and other alternatives to fossil fuels (*e.g.*, ethanol and methanol) will ignite a new rush with hydrogen becoming the dominant energy force in the 21st century.

The Energy Technology Division (ETD) within ECS has responded to this tremendous challenge by sponsoring or co-sponsoring several symposia related to energy conversion and storage. Examples include "Energy for Cleaner Transportation" (208th Meeting, Los Angeles, CA); "Photovoltaics for the 21st Century III"—sequel to I and II in earlier meetings (208th Meeting, Los Angeles, CA); "Proton Exchange Membrane Fuel Cells V" (208th Meeting, Los Angeles, CA); "Energy Systems for the Twenty-First Century: Opportunities for Applications of Solar and Conversion Technologies" (209th Meeting, Denver, CO); "Electrode Materials and Processes for Energy Conversion and Storage" (209th Meeting, Denver, CO); "Portable Energy Sources" (209th Meeting, Denver, CO); "Biological Fuel Cells" (209th Meeting, Denver, CO); "Hydrogen Production, Transport, and Storage" (209th Meeting, Denver, CO); "Direct Methanol Fuel Cells" (209th Meeting, Denver, CO); "Organic Photovoltaics" (210th Meeting, Cancun, Mexico).

A fuller account of the renewable hydrogen story may be found in the special issue of this magazine titled "Hydrogen: Production and Storage" which came out in fall 2004 (Vol. 13, No. 3). ■

Acknowledgment

Dr. Robert McConnell (National Renewable Laboratory, Golden, CO) provided many helpful comments.

About the Author

KRISHNAN RAJESHWAR is a Distinguished University Professor of Chemistry and Biochemistry and Associate Dean (College of Science) in the University of Texas at Arlington. His research interests are in photoelectrochemistry, photocatalysis, and solar energy conversion. He may be reached at rajeshwar@uta.edu.

Fuel Cells

(continued from previous page)

commercialization. By inference, the 25-50 μm thick membrane and the 10-15 μm thick electrodes should be able to survive for this time frame. From a membrane standpoint, with the possible exception of Nafion[®], few (if any) membrane materials can claim to meet these requirements, largely because of the degradation mechanisms in play during fuel cell operation. PEM degradation mechanisms can be classified as mechanical (pinhole and crack formation), thermal (dry-out, solvolysis, and desulfonation), and chemical (peroxide initiated free radical degradation).²² Mechanical and thermal degradation can be minimized by proper choice of materials, careful fuel cell fabrication, and by maintaining reasonable operating temperatures and humidities. However, chemical degradation of the membrane can be difficult to mitigate. One reason for this difficulty is the generation of hydrogen peroxide at the oxygen reduction electrode (a four electron reduction at the cathode produces water, but a two electron reduction yields hydrogen peroxide). Such generation has been demonstrated by Schmidt *et al.*²³

Metal ion impurities in the carbon based electrocatalyst support used in fuel cells serve to combine with the generated peroxide to yield reactive oxygen species (such as free radicals) which initiate and accelerate membrane degradation.²² Two approaches that have been employed to minimize reactive oxygen species include (i) the use of free radical scavengers, and (ii) the use of dispersed peroxide decomposition catalysts within a composite membrane.²² The former approach can only delay the onset of degradation for a definite period due to steady consumption of the scavenger molecules. A third approach that suggests itself is the design of electrocatalysts with enhanced selectivity toward four electron reduction, thereby minimizing the generation of hydrogen peroxide through the two electron pathway. In addition to minimizing the concentration of reactive oxygen species, attempts are also ongoing to render the ionomer more resistant to degradation by improving the synthesis methodology.

Membrane durability alone is not sufficient. The electrocatalyst also must retain its activity over the entire span of operation. Unfortunately, this is a difficult task, especially at the oxygen reduction electrode, where high potentials are attained at low loads. Under high potential conditions, given the low pH of the acidic electrolyte, conditions are tailor-made for platinum dissolution. This is evidenced by a glance at the Pourbaix diagram for platinum. Such

dissolution followed by redeposition leads to an increase in catalyst particle size. Precipitation in the membrane phase also occurs if the dissolved platinum migrates significantly. Both these processes lead to reduced surface area and mass activity and result in lowered performance. These effects tend to be exacerbated under load cycling conditions, as would be common in automotive applications. Further details about these processes, as well as factors such as catalyst support degradation and membrane degradation are presented in an excellent overview by Mathias *et al.*²⁴ The interrelationships between operating temperature, operating humidity, and degradation rates are also discussed at length in the above overview.

Concluding Remarks

Should the above challenges be overcome, PEFC technology promises to be an attractive future proposition, with applications in the transportation, stationary power, portable electronics, and military sectors. Typical applications that have been proposed include replacing internal combustion engines with 75-80 kW PEFC stacks; using 1-5 kW stacks to power individual homes; using 250 kW and larger stacks to provide highly reliable power to installations such as credit card clearing centers and hospitals; developing 1-100 W methanol fueled stacks to power consumer electronics such as cellular phones and laptops (replacing rechargeable batteries); and developing methanol fueled portable power for military applications. Other fuel cell technologies also have their own niche applications (*e.g.*, solid oxide fuel cell based auxiliary power units for large vehicles, molten carbonate fuel cell based combined cycle power plants, etc.). Considerable research efforts are ongoing in academia and industry to help alleviate existing bottlenecks to permit rapid fuel cell commercialization.

The Electrochemical Society, particularly the Energy Technology Division, has taken a leadership role in PEFC technology by sponsoring a series of symposia on many of the topics addressed above. A Fuel Cells Subcommittee has also been constituted [see *Electrochem. Soc. Interface*, **14**(3), 11 (2005)] for coordinating fuel cell symposia within ECS and to promote ECS as the leading professional organization for the development of fuel cells. ■

References

1. H. A. Liebhafsky and E. J. Cairns, *Fuel Cells and Fuel Batteries: A Guide to Their Research and Development*, John Wiley & Sons, New York (1969).
2. K. A. Mauritz and R. B. Moore, *Chem. Rev.*, **104**, 4535 (2004).
3. R. K. A. M. Mallant, *J. Power Sources*, **118**, 424 (2003).

4. P. Antonucci, A. Aricò, P. Creti, E. Ramunni, and V. Antonucci, *Solid State Ionics*, **125**, 431 (1999).
5. K. Adjemian, S. Lee, S. Srinivasan, J. Benziger, and A. Bocarsly, *J. Electrochem. Soc.*, **149**, A256 (2002).
6. S. Malhotra and R. Datta, *J. Electrochem. Soc.*, **144**, L23 (1997).
7. B. Tazi and O. Savadogo, *Electrochim. Acta*, **45**, 4329 (2000).
8. V. Ramani, H. R. Kunz, and J. M. Fenton, *J. Membr. Sci.*, **266**, 110 (2005).
9. G. Alberti and M. Casciola, *Solid State Ionics*, **97**, 177 (1997).
10. K. A. Mauritz, *Mater. Sci. Eng., C*, **6**, 121 (1998).
11. D. J. Jones and J. Rozière, *J. Membr. Sci.*, **185**, 41 (2001).
12. K. D. Kreuer, *J. Membr. Sci.*, **185**, 29 (2001).
13. J. A. Keres, *J. Membr. Sci.*, **185**, 3 (2001).
14. G. Alberti, M. Casciola, L. Massinelli, and B. Bauer, *J. Membr. Sci.*, **185**, 73 (2001).
15. P. Jannasch, *Curr. Opin. Colloid Interface Sci.*, **8**, 96 (2003).
16. G. Alberti and M. Casciola, *Annu. Rev. Mater. Res.*, **33**, 129 (2003).
17. D. J. Jones and J. Rozière, *Annu. Rev. Mater. Res.*, **33**, (2003).
18. R. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt, and C. Rogers, *J. Electrochem. Soc.*, **141**, L46 (1994).
19. Q. Li, R. He, R. Berg, H. A. Hjuler, and N. J. Bjerrum, *Solid State Ionics*, **168**, 177 (2004).
20. L. Xiao, H. Zhang, E. Scanlon, L. S. Ramanathan, E.-W. Choe, D. Rogers, T. Apple, and B. C. Benicewicz, *Chem. Mater.*, **17**, 5328 (2005).
21. H. A. Gasteiger, S. S. Kocha, B. Sompalli, and E. T. Wagner, *Appl. Catal., B*, **56**, 9 (2005).
22. A. B. LaConti, M. Hamdan, and R. C. McDonald, *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 3, W. Vielstich, H. A. Gasteiger, and A. Lamm, Editors, p. 647, John Wiley & Sons (2003).
23. T. J. Schmidt, U. A. Paulus, H. A. Gasteiger, and R. J. Behm, *J. Electroanal. Chem.*, **508**, 41 (2001).
24. M. F. Mathias, R. Makharia, H. A. Gasteiger, J. J. Conley, T. J. Fuller, C. J. Gittleman, S. S. Kocha, D. P. Miller, C. K. Mittelsteadt, T. Xie, S. G. Yan, and P. T. Yu, *Electrochem. Soc. Interface*, **14**(3) 24 (2005).

About the Author

VIJAY RAMANI is an assistant professor of chemical engineering in the Department of Chemical and Environmental Engineering at the Illinois Institute of Technology, Chicago. His interests include developing novel materials for polymer electrolyte fuel cells and organic photovoltaics, fuel cell membrane and electrode durability, and fuel cell education and outreach. He may be reached at ramani@iit.edu.