Fuel Cells: The Next Evolution

Robert W. Lashway, Guest Editor

Abstract

The articles in this issue of *MRS Bulletin* highlight the enormous potential of fuel cells for generating electricity using multiple fuels and crossing a wide range of applications. Fuel cells convert chemical energy directly into electrical energy, and as a power-generation module, they can be viewed as a continuously operating battery. They take in air (or pure oxygen, for aerospace or undersea applications) and hydrocarbon or hydrogen fuel to produce direct current at various outputs. The electrical output can be converted and then connected to motors to generate much cleaner and more fuel-efficient power than is possible from internal combustion engines, even when combined with electrical generators in today's hybrid engines. The commercialization of these fuel cell technologies is contingent upon additional advances in materials science that will suit the aggressive electrochemical environment of fuel cells (i.e., both reducing and oxidizing) and provide ionic and electrical conductance for thousands of hours of operation.

Keywords: *ceramics, electrochemistry, fuel cells, molten carbonates, polymer electrolyte membranes, solid-oxide membranes.*

Introduction

The invention of the solid-state transistor in the late 1940s led to a new age. The technological evolution of microprocessing, from simple watches and calculators to personal computing and wireless communications, has also been responsible for the progress in micro-manufacturing (e.g., microelectromechanical systems, cleanroom technology, and other advances in materials science). The solid-state fuel cell has the potential to generate another new age, in the areas of distributed energy, a cleaner environment, and more efficient use of the earth's natural resources. The need for cleaner energy-producing equipment is becoming a commercial necessity and will continue to grow in importance as the demand for oil outpaces production capacity in the next decade.[1] Advancements in materials science as well as in microprocessing will be needed to ensure the chemical and mechanical long-term reliability of the thin electrolyte membranes used in most fuel cell technologies.

What Is a Fuel Cell?

A fuel cell is an electrochemical device, like a battery, that is continuously fueled (e.g., by fuel plus oxygen from the air). Each cell consists of an electrolyte (a conducting ionic membrane) with an integrated porous anode and cathode. Hydrogen and/or hydrocarbon fuels react at the anode side, while oxygen (from air) reacts at the cathode side. The output is electrical energy in the form of direct current. When hydrogen is used as the fuel, the final exhaust product is simple water (i.e., zero oxides of sulfur and nitrogen, zero hydrocarbon soot, and zero carbon dioxide or monoxide).

A fuel cell assembly is composed of multiple cells that are generally placed in stacks and electrically connected in series. The electrolyte conducts the ions, but must also retain a hermetic seal in order to separate the fuel flow at the anode side from the air/oxygen flow at the cathode side. Both electrodes are integrated onto the electrolyte membrane and must contain open porosity for fuel and air-flow reactions with the input gases, ions, and output electrons.

The fuel cell assembly depends upon the type of electrolyte medium used, but generally is composed of the following:

- Electrolyte membrane (with high ionic conductivity and retained hermetic seal),
- Anode (fuel side of the electrode with a porous composite structure containing ion-conducting media, high surface areas for reaction, and catalysts lodged at the triple points where the reaction occurs among the gases, ions, and electrons),
- Cathode (air side of the electrode, with the same properties as the anode but in an oxidizing environment), and
- Separator and gas-flow structures (supplying air and fuel flow to the electrodes and also separating each cell hermetically while conducting electrons).

Each of these components will be described for the fuel cell types discussed in the following articles. The common denominator for the commercial success of fuel cells depends upon future research, especially in materials science, because the applications require long operational lifetimes in aggressive environments (e.g., >5 years in a reducing plus oxidizing environment).

Nanotechnology will play a great role in advancing the life and efficiency of fuel cell systems. Polymer electrolyte membrane (PEM) fuel cells, also referred to as proton-electrolyte membrane or proton-exchange membrane fuel cells, currently use platinum catalysts, and the amount of Pt must be minimized (i.e., <0.2 mg/W). Nanotechnology and advances in surface chemistry will lower production costs and improve reactivity rates (vital for higher power output over longer operating times) by increasing the surface areas at the triple points of the electrode. Each fuel cell technology is undergoing a scientific evolution, especially in the electrolyte, cathode, and anode chemistries. The rate of progress in solid-oxide fuel cell (SOFC) technology is demonstrated in the fact that there have already been at least three generations as of 2004.[2]

Fuel Cell Types and Technologies

Today, there are many types of fuel cell technologies, but polymer electrolyte membrane fuel cells (PEMFCs) and solid-oxide fuel cells (SOFCs) are considered the primary candidates, based on the billions of dollars per year spent in worldwide research and development (R&D). These two technologies have the lowest manufacturing costs, as shown by Department of Energy (DOE) studies and by large energy equipment manufacturers (i.e., General Electric, Siemens Westinghouse, Toyota, Ballard, and others). Table I illustrates the major features, operating conditions, fuels, and other key parameters for several fuel cell technologies.

Each fuel cell type represents different technologies requiring unique materials solutions. The differences range from the electrolyte chemistry and operating temperatures (i.e., from 80°C for PEMFCs to 800°C for zirconium oxide SOFCs), to the chemistry and microstructure of the elec-

Table I: Comparison of Fuel Cell Types.

Parameters	Primary Fuel Cell Types			
	Polymer Electrolyte Membrane Fuel Cell (PEMFC)	Solid-Oxide Fuel Cell (SOFC)	Molten Carbonate Fuel Cel (MCFC)	Phosphoric Acid Fuel Cell (PAFC)
Electrolyte	polymer	ceramic	molten carbonate	phosphoric acid
Conducting Ion	H^+	O^{2-}	CO_3^{2-}	H^+
Operating Temperature	90°C	800°C	650°C	100°C
Fuel	pure H_2	CH_4, CO (both or separate)	CH_4, CO	pure H_2
Cycling Ability	high	low	very low	medium
Lifetime (h)	>5,000	>40,000	>40,000	>30,000
Efficiency	35%	45%	50%	40%
Power Range	up to 150 kW	5–250 kW	megawatt	5–250 kW
Applications	transportation, mobile/small devices (PCs, laptops), telecommunications	distributed generation, marine	biomass, marine, water utilities	distributed generation, backup generation

trode integrated onto the electrolyte surfaces (front and back). Likewise, the gas-flow and separator structures and chemistries also must match the electrolyte temperature and environment (both chemically and mechanically, including such parameters as thermal expansion). The eventual scientific solutions for each of the different fuel cell components, electrolytes, electrodes, and separation/gas-flow structures are critical for current and future R&D. Each fuel cell technology encounters a very aggressive environment, and long-term reliability significantly affects the economics and commercialization of the technology (all of which are tied to the materials' life in its hostile environment.).

Fuel Cell Research and Development: Solutions for the Future

This issue of *MRS Bulletin* will focus on three fuel cell types:

- Polymer electrolyte membrane fuel cells,
- Solid-oxide membrane fuel cells and SOFC interconnects, and
- Molten carbonate fuel cell (MCFC) technology.

Other technologies not covered here include phosphoric acid and zinc-air fuel cells.

This collection of articles presents a tutorial approach for the general technical audience. In addition to discussions of the key electrolytes, aspects of the cell and system engineering are treated (primarily in the case of SOFC interconnects and molten carbonate fuel cells). These include important design features as well as manufacturing and economic data that are vital to the long-term commercial success of the technology. Many of these engineering examples illustrate the need for advanced materials science (i.e., somewhere in the SOFC cell structure, there will be a point that will have to accommodate both reduction and oxidation as the partial pressure of oxygen changes). Since fuel cells must perform reliably over thousands of hours, the materials must function continuously under the differing operating conditions.

PEMFCs are one of the largest research areas in fuel cell development. The U.S. automotive industry is advancing fuel cell research using hydrogen, as part of DOE's promotion of a hydrogen economy. Other major industrial nations have similar government-sponsored programs in place. The key drivers in the U.S. are the environment (i.e., concern over the carbon dioxide greenhouse effect) and reducing the country's reliance on imported oil. In addition, restrictions on emissions of nitrogen oxides and sulfur oxides (especially starting in 2007, when new federal standards take effect), as well as on particulates from carbon sources, will make fuel cells an attractive alternative, due to their lower operating temperatures and lower emissions as compared with internal combustion engines.

The current interest in hybrid engines (gas/diesel engines plus generators with electric motors for automotive power) is a forerunner to all-solid-state power in the form of fuel cells. Fuel cell technology is cleaner, quieter, and more fuel-efficient than internal combustion engines, even hybrids. PEMFC technology is also attracting heavy investment in research for lower-power applications as a replacement for batteries. Methanol is the fuel used, and tests are under way with laptop PCs using direct methanol fuel cells. The key benefits of fuel cells over batteries are longer life and lighter weight, which are especially important in mobile applications. Fuel cells offer energy densities that are much higher than those of batteries, which is a notable advantage when hydrogen is used as the fuel.

Both the SOFC and the MCFC are directed at stationary, distributed power generation for buildings and industry. These applications require long lifetimes; the DOE has set 40,000 h as a minimum operating-life goal for stationary fuel cells under their SECA (Solid-State Energy Conversion Alliance) program.[3]

The most important challenge in fuel cell research is providing sustainable high power density at a reasonable cost. Power density is generally measured by the power output of the fuel cell membrane area (e.g., watts per square centimeter) and power loss, also referred to as power degradation over time, given as the loss in percent per 1000 h of operation. Cost is generally discussed as the price per kilowatt of power for the fuel cell system. The articles in this issue will refer to these criteria and others to describe many of the R&D efforts in this technology area.

Overview by Article

The first article, by Rajendran, discusses polymer electrolyte technology. Rajendran's focus is on hydrogen applications, but this discussion is also relevant to membranes for direct methanol use. One of the major R&D areas for PEM fuel cells is the management of water throughout the fuel cell operation; this is particularly important in cold temperatures (the system must be designed to prevent freezing) and when the system is idle. This article will touch on the development of new technologies to alleviate water management problems. The discussion will also touch on polymer chemistry and microstructures to attain sustainable high power densities. Sulfonated fluoropolymers have been the workhorse of PEM fuel cells; however, new compositions, such as sulfonating poly(ether ether ketone) (PEEK),[4] are in the testing stage. In addition, research is under way to develop reinforced membranes to strengthen and increase fuel cell tolerance to hydration. These membranes could include composites of PEM in a SOFC matrix.

The article by Yokokawa and colleagues covers solid-oxide electrolytes for SOFCs. The most common materials in current use are zirconia-based membranes doped with yttria or scandia in thin structures (i.e., electrode-supported, to keep the thickness of the membranes under 25 μm so as to reduce cell resistance). The dopant chemistry and concentration dictate the operating temperature and ionic conductance (based on optimum ionic conductance of oxide ions). Another approach under investigation for solid-oxide ion conduction is lanthanum gallate doped with strontium, magnesium, and other elements, which operate at lower temperatures than zirconia-based electrolytes (650°C versus 800°C, respectively). The goal is to maintain a higher ionic conductance at lower operating temperature; however, the tensile strength of lanthanum gallate is less than half that of zirconia. Therefore, lanthanum gallate research includes a search for reinforcements to increase strength. The article also discusses some of the electrode chemistries and barrier layers such as gadolinia ceria.

Japan, Europe, and the United States are investing heavily in SOFC technology for distributed power generation and auxiliary power units (APUs). Because of the higher operating temperatures of SOFCs, they are more difficult to employ in transient applications with numerous on–off cycles than PEM technology. As an example, PEMFCs are expected to be the primary power source for transportation applications, while SOFCs are being developed for stationary applications. There are some APU applications within vehicles where SOFCs might be applicable, such as in trucks for quiet, overnight "hotel" power usage with the main engine off.

Although the articles in this issue cannot cover all the assembly technologies within each fuel cell type, one unique SOFC assembly technology will be discussed. SOFCs require materials that can endure an oxidizing/reducing environment at a much higher operating temperature than PEMFCs. In addition, the separator and gas-flow materials must continually conduct electrons, not ions, while providing matched coefficients of thermal expansion with the electrolyte.

There are three current approaches to SOFC interconnection being developed:

- Metal interconnect structures that oxidize on the surface to provide electrical conductivity with the addition of dopants or deposited coatings;
- Electrically conducting ceramic perovskite-type materials; and
- Nonconducting ceramic structures with electrically conducting holes, or vias, as they are commonly referred to in the electronics packaging industry.

The last approach is unique in that the fuel cells can contain conductive interconnects "embedded" in the ceramic interconnect structure, thereby extending the corrosion resistance of the conducting media in the vias and planar lines. This approach is seeing renewed interest because the metals in current use employ chromium. In contrast to other alloys and dopants, chromium forms an electrically conductive layer (germane to the cathode/oxidizing side of the cell). The problem is that chromium migrates to the electrode/electrolyte interfaces and causes irreversible increases in resistance that degrade the power density of the system.[5]

The third article in this issue, by Morris et al., discusses nonconducting ceramic via interconnect technology. This approach allows the cell to be constructed with the optimum thermal expansion match to the electrolyte. The authors will describe the chemistry and structures of this technology as well as the ability to manufacture these fuel cells at a lower cost through multilayer cosintering technology (as is currently in use for high-volume manufacturing of electronics and ceramic multilayer capacitors).

The final article, by Farooque et al., will discuss the molten carbonate fuel cell. The MCFC is in the commercialization phase and is particularly attractive for use with biomass or utility plant effluents. The article will describe design/structures, application technologies, cell chemistries, and the basic materials science needs for a sustainable system. The discussion will include design and manufacturing, which are important to achieving the reliability required.

Conclusion

Fuel cells offer the advantages of cleaner, quieter power generation while decreasing the use of natural resources. It is envisioned that all fuel cell types listed in Table I will find multiple applications, and their use will vary by application. The internal combustion engine combined with electrical generation cannot compare with the fuel cell for electrical conversion efficiency. In addition, fuel cells offer much higher specific energy densities than batteries. The key to the future success of the fuel cell is achieving higher sustainable energy densities at a competitive cost relative to the internal combustion engine, taking into consideration environmental impacts and the increasing cost of oil.

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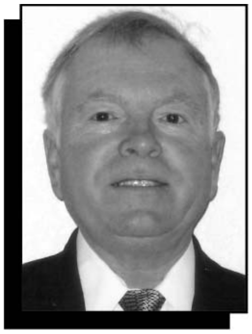

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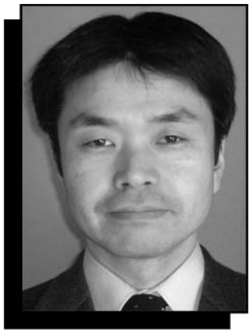

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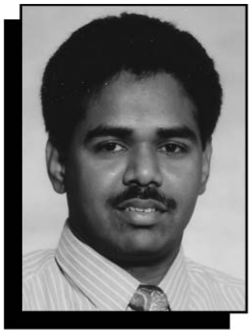

Raj G. Rajendran

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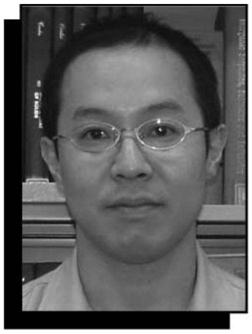

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