Fuel Cells: Current Status and Future Challenges.

Stuart B. Adler, University of Washington.

Fuel cells convert chemical energy sources directly to electricity, offering improved efficiency over current means of energy conversion. But what role do they potentially play in the broad spectrum of energy choices, and a hydrogen-based economy? After briefly reviewing and comparing polymer electrolyte and solid oxide fuel cells, this paper will focus on several significant scientific challenges remaining before these technologies can become a commercial reality.

Why Fuel Cells?

Fuel cells are not a new idea. Sir William Grove first demonstrated the conversion of hydrogen to electricity using an acid-electrolyte fuel cell in 1839. Turning this idea into a practical means for energy conversion, however, has proved elusive during the 20th century. One of the major technical and cost barriers has been implementation of liquid electrolytes, on which most commercial fuel cells have been based (e.g. alkaline fuel cells, molten carbonate fuel cells). In contrast, the fuel cells of greatest commercial interest today are based on solid electrolytes, which have benefited recently from advances in materials and manufacturing.

For the purposes of discussion, we can divide solid electrolyte fuel cells into two types: a) Polymer Electrolyte Fuel Cells (PEFCs), often referred to as Proton Exchange Membrane (or PEM) fuel cells, and 2) Solid Oxide Fuel Cells (SOFCs). Fig. 1 illustrates how these types of fuel cells function.

A commonly heard justification for fuel cells has been environmental protection - the idea that fuel cells only produce water as a combustion byproduct, and thus are "zero emission". However, it is difficult to make the case for fuel cells on this argument alone. Most notably, even if fuel cells themselves only produce water, the production of hydrogen from hydrocarbons, such as oil or coal, involves production of CO_2 and requires suppression of SOx, and thus merely transfers the problem elsewhere. In

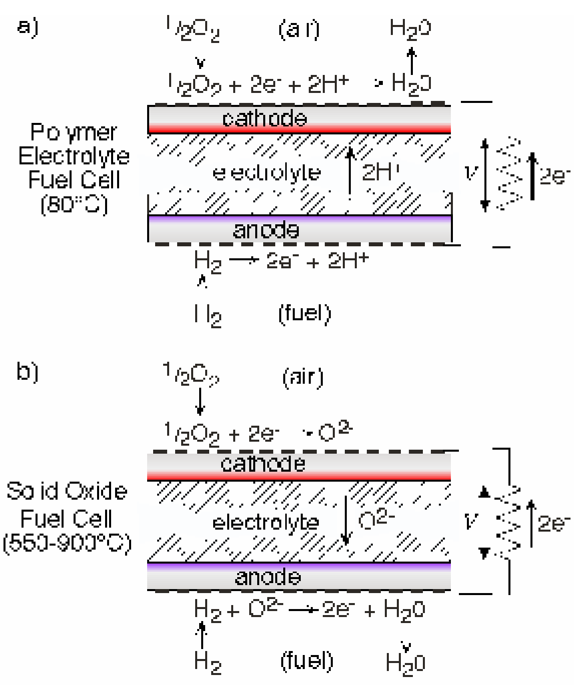

Fig. 1. Two types of solid electrolyte fuel cells. a) In a PEFC, a proton-conducting polymer membrane is exposed on one side to fuel (hydrogen), and on the other to air. On the hydrogen side (anode), H_2 gas is oxidized, and the protons thus created migrate to the other side of the membrane (cathode), where O_2 gas in the air is reduced to water. Some portion of the reversible work of the net reaction is recovered as a voltage difference between cathode and anode, delivered to an external circuit by the flow of electrons. PEFCs Typically operate at 80~100°C. b) In a SOFC, a ceramic oxygen ion conductor at elevated temperatures (500~1000°C) serves as the electrolyte membrane. In this case, the fuel (which can be a mixture of H_2, CO, and/or hydrocarbons) is oxidized to H_2O and CO_2 at the anode, while O_2 is reduced to O^{2-} at the cathode. In both types of fuel cells, cells are normally assembled into multi-cell stacks, which serve to increase system voltage, and provide means of distributing gases (fuel and air) over each cell evenly.

addition, numerous technologies already exist today that can be used to eliminate SOx and NOx from combustion. The reason these technologies have not been implemented universally today is mostly a matter of cost, and political will. One can imagine an energy economy based entirely of combustion of hydrogen or other generic (multi-source) fuels, which does not involve fuel cells.

To understand the potential role of fuel cells we must instead turn toward the primary advantage fuel cells offer as an enabling (rather than displacing) technology: *efficiency*. Fuel cells recover work normally lost by the irreversible process of combustion. Thus fuel cells potentially offer a path toward reduced overall fuel usage that combustion simply cannot provide, even after many years of incremental improvement. Increased efficiency may in turn offer environmental benefits by reducing the overall amount of CO_2 produced per kW of useable power. In addition, the required retooling of the fuel infrastructure toward more generic small-molecule fuels (H_2, CO, CH_4) might have other benefits, such as centralization of CO_2 production for purposes of sequestration, or reduced sensitivity of a particular energy sector to the availability of a particular fuel source (e.g. the dependence of gasoline prices on the availability of mid-east oil).

Comparative Roles of PEFCs and SOFCs in Energy Conversion

A primary factor influencing the trade-off of capital vs. efficiency in fuel cells is operating temperature. SOFC stacks, which operate at temperatures ranging from 550 to 900°C, produce high quality waste heat that can be captured for increased efficiency, combined heat and power, or reformation of hydrocarbons (HC). SOFC stacks tend to be operated adiabatically, where excess air is used as the primary coolant, and the heat recovered from the SOFC exhaust. This feature has made SOFCs very attractive for stationary power, where efficiency and ability to operate on HC reformate holds greatest weight, and allowable capital costs are about 10 times higher ($400/kW)[1]. than for PEFCs in automotive applications. Meanwhile, by using thin film ceramics supported on low-cost metal alloys, SOFC developers have reduced material and manufacturing costs, lowered operating temperatures, and significantly mitigating cell degradation problems. Figure 2 shows an example of a metal-supported cell based on a thin ceria electrolyte, capable of stable power densities of ~500 mW/cm^2 at 570°C[2]. Systems based on this type of cell are nearing efficiency and cost targets for use in homes (combined heat and power), or auxiliary power units (APUs) for trucks or aircraft.

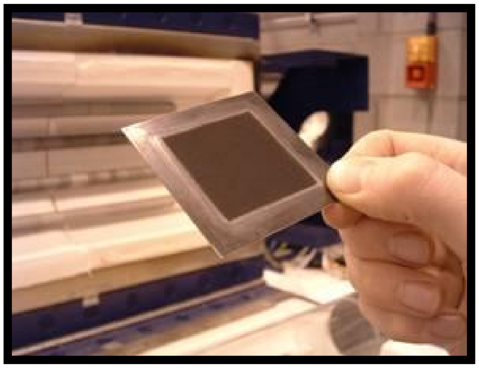

Fig. 2. Example of a metal-supported thin-film solid oxide fuel cell, capable of operation below 600°C. Photo courtesy of Ceres Power, Ltd., reproduced with permission.

In contrast, PEFC's have historically been designed to operate isothermally, at or below 80°C. The ability to operate at such low temperatures has generally made them more suitable for small or mobile applications, where capital cost requirements are much more stringent, pure H_2 is assumed available, and the efficiencies of heat integration hold less of a premium. By far the most challenging market from a capital cost perspective is motive power (cars), for which allowable capital costs are estimated to be on the order of $35/kW[3]. PEFCs are also generally thought to best match the size, weight, and startup constraints for primary power in automobiles. Substantial progress has been made in increasing power density (>1 kW/kg)[4], as well as reducing the amount of Pt catalyst to a

Fig. 3. Sandy Spallino, first individual customer to purchase a PEFC-powered car, fills up her Honda FCX at one of many H_2 refueling stations planned for California (June 2005 Honda press release).

level that is reasonable to recycle[4,5] (< 15g/vehicle, 3-4 times that in a catalytic converter). As illustrated in Figure 3, these successes have led several of the world's largest automakers to build demonstration and cars, including General Motors, Ford, Daimler, and Honda.

Despite such visible advances, solid electrolyte fuel cells have not yet achieved widespread penetration into the energy market for many reasons. A primary reason is cost: fuel cells systems remain too costly to be competitive with existing technology at current energy prices. This situation may change somewhat as fuel prices rise, and capital costs come down with manufacturing improvements and economies of scale. However, fundamental technological barriers remain that must be overcome before such cost reductions are possible. Many of these technological hurdles are outlined in detail elsewhere[6]. Here we highlight a few of the most major general hurdles, which if overcome, would have a major enabling impact on commercial fuel cell development.

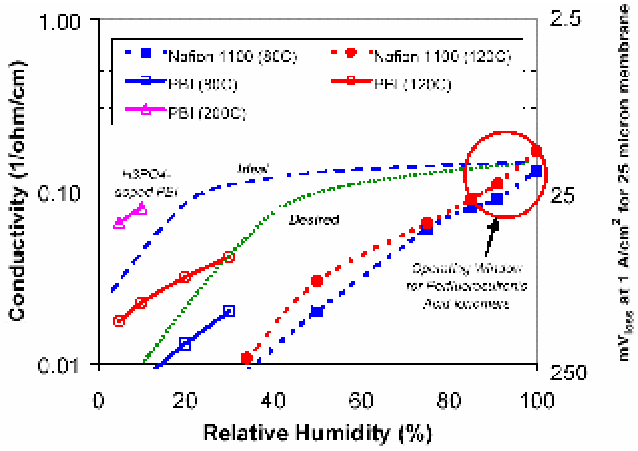

Fig. 4. Relationship between proton conductivity and relative humidity in the adjoining gas at various temperatures for PFSA and phosphoric-acid-doped polybenzimidazole (PBI). Curves are also shown for materials that would enable and be ideal for system simplification. Reprinted from Reference 8.

.

Advanced Materials Design

Many of the materials used in SOFCs and PEFCs are similar to the ones used 25 years ago. Examples include the Ni-cermet anode used in most SOFCs, or the perfluorosulfonic acid (PFSA) membrane used as the electrolyte in most PEFCs (Dupont Nafion®). Despite numerous difficulties with these materials, they remain state-of-the art because workers have so far been unable to match their unique combination of properties. However, fundamental problems loom on the horizon. In particular, Ni-cermet has very poor sulfur tolerance, especially below 800°C, making it unsuitable as a long-term SOFC anode[6]. Likewise, as illustrated in Figure 4, PEFC developers have concluded that to be successful in cars, the system must operate at 110~120°C, which introduces severe performance and degradation problems for PFSA[7]. To date, the approach to finding new materials has generally been one of trial and error. Further advances are likely to require a more directed design approach[8], or adopting combinatorial methods[9].

Probing and Controlling Microstructure

Despite the many technological advances made in SOFC and PEFC technology in the last ten years, our ability to understand and design them has mostly been at a macroscopic/empirical level. The microstructure of a PEFC electrode, for example, is still only understood in a very general sense; understanding exactly how the catalyst, ionomer, and gas come together and effect performance is generally not well understood or amenable to intelligent design. For example, one proposed strategy for improving catalyst utilization in PEFC cathodes is to concentrate Pt particles near the opening of aqueous flow channels in the PFSA ionomer, rather than being distributed randomly throughout the electrode matrix. This type of nanostructural analysis, let alone control, is not possible today. As shown in Figure 5, one possible technique on the horizon for SOFCs is focused-ion beam (FIB) milling coupled to electron microscopy or other surface analytical techniques (AFM, SIMS)[10]. Such techniques may make it possible to analyze and direct electrode microstructures in new ways. For example, workers have demonstrated recent success

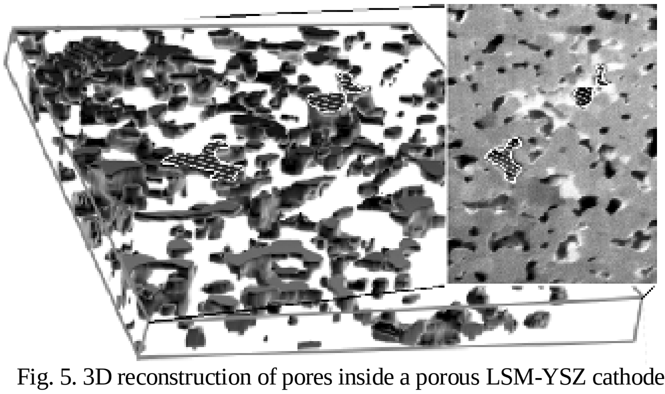

Fig. 5. 3D reconstruction of pores inside a porous LSM-YSZ cathode, based on 2D FIB-SEM image slices. Inset: cross-sectional image slice corresponding to the top plane of the reconstruction. Black contrast is porosity, grey and white are YSZ and LSM, respectively.

using of solution impregnation of materials into an electrolyte host matrix to obtain SOFC electrodes with improved hydrocarbon activity or O_2 reduction performance[11, 12].

Understanding Electrode and Other Degradation Processes

The vast majority of work in the last ten years has focused on improved fuel cell *performance*. However, as the technology has begun to reach performance targets, and more cells and stacks have been tested for longer periods of time, long-term durability has risen to the top of the list in terms of a performance barrier. As an example, Figure 6 shows the degradation of various SOFC cathode materials when exposed to chromia poisoning. Although electrode degradation has been positively tied to Cr contamination from metal interconnects, it is not clear why some electrode materials are more sensitive than others, or why seemingly similar electrodes tested by different groups degrade at different rates. The answers to these questions require a much deeper mechanistic and scientific understanding of electrode processes than we currently possess. Recent advances in microfabrication and diagnostics may significantly enhance workers' ability to control and analyze electrode reactions[14,15]. Hopefully this work will have future benefits in diagnosing how and why electrodes degrade, and in guiding new material and fabrication choices that mitigate degradation.

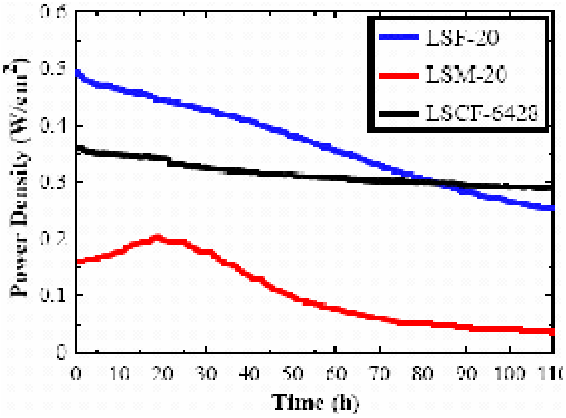

Fig. 6. Impact of chromia poisoning on various perovskite SOFC cathodes (as measured by total cell power output). From reference 13.

Outlook

As discussed above, fuel cells continue to face major technological hurdles that may require many years of research and development to overcome. In addition, the widespread adoption of fuel cells is unlikely to occur in isolation, but rather as part of a larger shift in fuel infrastructure and efficiency standards, requiring sustained pressure and time to occur. Finally, like any technology, economy of scale involves a natural maturation process over many years or decades[16]. Taken together, these considerations suggest that widespread adoption of fuel cell technology is not likely to occur in the short term. To be successful, our approach to advancing fuel cell technology will likely require a sustained, long-term commitment to fundamental research, commercial development, and incremental market entry.

References

1. U.S. Department of Energy, Office of Fossil Energy, *Fuel Cell Program Annual Report*, National Energy Technology Laboratory, Morgantown (2004).

2. N.P. Brandon, "Metal Supported Solid Oxide Fuel Cells for Operation at 500-600°C," *presented at the 15th Annual Meeting on Solid State Ionics*, Baden-Baden, July, 2005.

3. "The Path to a Hydrogen Economy," Hearing Before the Committee on Science, 108th Congress, Serial Number 108-4, March, 2004.

4. H.A. Gasteiger, S.S. Kocha, B. Sompalli, and F.T. Wagner, "Activity Benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs," *Applied Catalysis B: Environmental* **56**, p. 9-35 (2005).

5. J.S. Cooper, "Recyclability of Fuel Cell Power Trains," *SAE International* 2004-01-1136 (2004).

6. U.S. Department of Energy, Office of Fossil Energy, *Fuel Cell Handbook (7th Ed.),* National Energy Technology Laboratory, Morgantown (2004).

7. H.A. Gasteiger and M.F. Mathias, "Fundamental Research and Development Challenges in Polymer Electrolyte Fuel Cell Technology", Presented at the Workshop on High Temperature PEM Fuel Cells, The Pennsylvania State University, December, 2003.

8. M.A.Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, and J.E. McGrath, " Alternative Polymer Systems for Proton Exchange Membranes (PEMs)", *Chemical Reviews* **104**(10), 4637-4678 (2004).

9. J. A. Kilner, J. C. H. Rossiny and S. Fearn, "Combinatorial Searching for Novel Mixed Conductors", presented at the 15th Annual Meeting on Solid State Ionics, Baden-Baden, July, 2005.

10. J. Wilson, W. Kobsiriphat, R. Mendoza, J. Hiller, D. Miller, K. Thornton, P. Voorhees, S. Adler, and S. Barnett, "Three Dimensional Reconstruction of Solid Oxide Fuel Cell Electrodes," *submitted* (2005).

11. S. McIntosh and R.J. Gorte, "Direct Hydrocarbon Solid Oxide Fuel Cells," *Chemical Reviews* **104**(10), 4845-4865 (2004).

12. Y.Y. Huang, J.M. Vohs, and R.J. Gorte, "Characterization of LSM-YSZ composites prepared by impregnation methods", *J. Electrochem. Soc*. **152**(7): A1347-A1353 (2005).

13. S.P. Simner, and J.W. Stevenson. "Cathode - Chromia Interactions," presented as part of the *SECA 2004 Annual Meeting and Core Program Review*, Boston, 2004.

14. S.B. Adler, "Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes", *Chemical Reviews* **104**(10), 4791-4844 (2004).

15. J.R. Wilson, D.T. Schwartz, and S. B. Adler, “Nonlinear Electrochemical Impedance Spectroscopy for Mixed-Conducting SOFC Cathodes, ***Electrochemica Acta***, (*in press*) (2005).

16. J. DeCicco, "Fuel Cell Commercialization Perspectives: Market Context and Competing Technologies", presented at the 2001 Gordon Conference on Fuel Cells, Bristol, R.I., July 29-August 3, 2001.