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Raymond J. Gorte

University of Pennsylvania, gorte@seas.upenn.edu

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Abstract

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Comments

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Recent Developments Towards Commercialization of Solid Oxide Fuel Cells

Raymond J. Gorte
University of Pennsylvania
Department of Chemical & Biomolecular Engineering
311 Towne Building, 220 S. 33rd St.
Philadelphia, PA 19104 USA

Solid oxide fuel cells (SOFC) are receiving an increasing level of attention for both small- and large-scale applications due their high fuel flexibility compared to other types of fuel cells. This article reviews recent work in SOFC materials research, with an emphasis on anodes that can directly utilize hydrocarbon fuels.

Introduction:

The promise of direct and efficient conversion of chemical to electrical energy makes fuel cell development an area of great technological interest. In principle, fuel cells can be much more efficient than heat engines and can provide that high efficiency at low loads. Fuel cells are also environmentally friendly, producing no NO_x or SO_x. Compared to normal batteries, fuel cells can have much higher energy densities and can be "recharged" more quickly and easily.

Among the types of fuel cells that are currently under development, solid-oxide fuel cells (SOFC) are gaining increased attention. SOFC are based on ceramic electrolytes that are oxygen-ion conductors but electronic insulators. They are intrinsically high-temperature devices because available ceramics only achieve high ionic conductances at temperatures above 773 K. Primarily because of this high-temperature requirement, SOFC are often viewed as having applications only in large-scale power plants.

However, a number of groups are now targeting applications for smaller devices, including even portable power supplies with loads as small as 20 W.¹ These applications are possible because of developments that have decreased operating temperatures and improved power densities. The primary reason for the renewed interest in SOFC is their high fuel flexibility compared to other types of fuel cells that can only operate on H₂ and are sensitive to traces of CO and other impurities. Furthermore, it has been demonstrated that SOFC can operate directly on hydrocarbon fuels under some conditions, without reforming those fuels.²

This paper will provide a brief overview of present research in SOFC. The discussion will begin with a review of SOFC operating principles; but emphasis will be placed on materials research, especially for fuel electrodes that can use hydrocarbons directly. More information on various aspects of SOFC can be found in a recent collection of reviews.³

Basic Operating Principles

Like all fuel cells, SOFC consist of three main components: a cathode (or air electrode), an anode (or fuel electrode), and an electrolyte, as shown in Fig. 1. The distinguishing feature of an SOFC is that the electrolyte is an ion-conducting ceramic that is also an electronic insulator. The electrolyte must be dense in order to separate the fuel and air compartments of the fuel cell, and it must retain its high ion conductivity and low electronic conductivity over a very wide range of oxygen fugacities, from values close to 1 atm on the cathode side to values that could be below 10⁻²⁰ atm at the anode. The material most often used as the electrolyte is yttria-stabilized zirconia (YSZ).⁴

Oxygen ions are delivered to the electrolyte by the cathode where molecular oxygen is reduced to oxygen anions using electrons supplied from an external circuit according Eqn 1):



In order to deliver both electrons and O²⁻ ions to the cathode-electrolyte interface, the cathode must be electronically conductive and must be able to dissociate O₂. Ionic conductivity is desirable to allow a larger fraction of the cathode to activate O₂. Because most metals would be oxidized in the presence of air at high temperatures, the required cathode properties are achieved with electronically conductive oxides, such as the perovskite, Sr-doped LaMnO₃ (LSM). Finally, the cathode material must have a Coefficient of Thermal Expansion (CTE) that is a reasonable match with that of the electrolyte.

At the anode, the oxygen ions are consumed by fuel at the electrolyte interface, producing combustion products and electrons. When the fuel is H₂, the anode half-cell reaction is given by Eqn 2):



The anode must again be an electronic conductor, be able to catalyze the oxidation of the fuel, preferably be an ionic conductor, and have a similar CTE to that of the electrolyte. The most commonly used material for the anode is a ceramic-metallic (cermet) composite of Ni and the electrolyte oxide, in which Ni provides electronic conductivity and catalytic activity, while the oxide provides ionic conductivity and a CTE match with the electrolyte.

It is important to recognize that the electrochemical reactions in both electrodes occur only at the Three-Phase Boundary (TPB), that line of contact between the gas phase, the ionic conductor, and the electronic conductor. To establish a good TPB, the electrode must be sintered to the electrolyte at high temperatures, since poor contact between the electrolyte and the electrode would prevent O²⁻ ions from freely moving between the two components of the cell. Ionic conductivity within the electrode greatly lengthens the TPB. Furthermore, effective electrodes must have a relatively low surface area, since high-surface-area materials will be poorly connected for ions from the electrolyte and for electrons from the external circuit.

In an ideal fuel cell, electrons are produced at a potential given by the Nernst Equation; for H₂, this is Equation 3):

$$E = E^\circ + (RT/2F) \cdot \ln \{P(\text{H}_2 \text{ anode})P(\text{O}_2 \text{ cathode})^{1/2}/P(\text{H}_2\text{O}_{\text{anode}})\} \quad 3)$$

The Nernst Equation is nothing more than a restatement in electrical units of how $\Delta G (= 2F \cdot E)$ changes with the oxygen fugacity across the electrolyte membrane. The oxygen fugacity at the anode is established by equilibrium with H₂ and H₂O, with E° being analogous to ΔG° for oxidation of H₂. Because the electrical power per unit area that is produced in the cell is the product of the current density, *i*, and the cell potential, *E*, the theoretical efficiency is very high, $\Delta G/\Delta H$.⁵

In reality, energy losses are unavoidable. First, it is not possible to produce electrons when the fuel has been completely consumed, particularly in an SOFC where the combustion products remain together with the fuel. A "fuel utilization" of 90% is a typical goal, implying that 10% of the fuel is simply lost. More important, the operating potential, given by Equation 4), is usually much lower than the Nernst potential:

$$E = E_{\text{Nernst}} - i \cdot R_{\text{electrolyte}} - \eta_{\text{cathode}} - \eta_{\text{anode}} \quad 4)$$

In this equation, $R_{\text{electrolyte}}$ is the resistance of the electrolyte, η_{cathode} is the potential loss in the cathode, and η_{anode} is the potential loss in the anode. The losses in the electrodes are the most difficult to control and usually dominate the cell performance. The source of these losses can be gas-phase diffusion but is most often best described as simply electrochemical activity. Because η_{cathode} and η_{anode} frequently increase linearly with current density in SOFC, it is common to characterize the electrode losses by their impedance, R_{cathode} and R_{anode} , which can be compared more readily to $R_{\text{electrolyte}}$.

Notice that the high operating temperatures of an SOFC are not a source of inefficiency. All of the energy from the fuel that does not become electrical energy becomes heat. This heat is usually more than sufficient to maintain the operating temperature of the cells. Indeed, because the waste heat produced at high temperatures is more useful, the overall system efficiency can be much higher with high-temperature fuel cells.

Materials Issues:

Electrolytes

The high operating temperatures of SOFC are required in part for high ionic conductivity (low $R_{\text{electrolyte}}$ in Equation 4) in the electrolyte. However, because conductivity is a property of the material, this can be calculated and controlled by using thin electrolytes. For example, if the total cell impedance ($R_{\text{cathode}} + R_{\text{anode}} + R_{\text{electrolyte}}$) is targeted to be $0.5 \Omega\text{cm}^2$, a value sufficient to achieve a power density of 0.5 W/cm^2 , and $R_{\text{electrolyte}}$ is assumed to be $0.15 \Omega\text{cm}^2$, the requirement is achieved at 973 K using a YSZ electrolyte with a thickness of $15 \mu\text{m}$.⁶ Since claims of leak-tight electrolytes with YSZ thickness of $5 \mu\text{m}$ are common, 973 K is a reasonable operating temperature for YSZ-based cells. If the fuel is syngas, there may be disadvantages to working at lower temperatures because of CH_4 formation.

There are alternative electrolytes that can lower the theoretical operating temperature significantly for use with H_2 . Ceria, doped with either Gd_2O_3 or Sm_2O_3 , has received the most attention, with some recent reports demonstrating power densities approaching 0.4 W/cm^2 at temperatures as low as 773 K.⁷ While it has been known for many years that ceria has an ionic conductivity roughly ten times that of YSZ, ceria is reducible, particularly at higher temperatures. When reduced, ceria becomes electronically conductive. Its reducibility also makes it brittle and more difficult to work with, although recent work with supported ceria films on porous stainless steel may solve this problem.⁷

Other promising electrolytes that are receiving attention are Sc-doped zirconia (SDZ) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM). SDZ has a conductivity that is roughly three times that of YSZ and it has better mechanical properties than YSZ. Unfortunately, scandium is rare and expensive. LSGM was discovered more recently and has an ionic conductivity similar to that of doped ceria. While it is not reducible like ceria, the fact that it is a stoichiometric compound implies that the composition must be precise.

Cathodes

Since cathode losses dominate the performance of many SOFC designs, the development of better SOFC cathodes remains a very active research topic.⁸ The standard material with YSZ-based cells, a composite of YSZ and Sr-doped LaMnO_3 (LSM), is a compromise between performance, stability, and ease of fabrication. LSM is a reasonably good electronic conductor and has a good CTE match for YSZ, but it has a very low ionic conductivity. The YSZ within the composite electrode provides connectivity with the electrolyte and allows conduction of ions from the electrolyte into the electrode. As pointed out in the discussion of the TPB, it is necessary to calcine the electrode composite to the electrolyte at temperatures sufficient to sinter the YSZ in the electrode to the electrolyte. One can increase the performance of LSM-based cathodes significantly by engineering the cathode-electrolyte interface to increase the length of the TPB.⁹

The factors that limit the performance of LSM-based cathodes continue to be debated, but it is certain that much better electrode performance can be achieved with other conductive oxides such as Sr-doped LaFeO_3 (LSF), Sr-doped LaCoO_3 (LSCo), and related materials.¹⁰ In addition to having somewhat better electronic conductivity, these oxides tend to be good ionic conductors, a factor that has a large impact on the electrode impedance. With materials like LSM that are only electron conductors, the width of the TPB may be on the order of 1 nm.¹⁰ Ionic conductivity greatly increases the active region of the electrode.¹¹

Unfortunately, there is a problem with CTE matching with these alternative cathode materials (The CTE of LSCo is more than double that of LSM and YSZ.). More important, the

temperatures required for sintering the electrodes to the electrolyte are high enough to cause solid-state reactions between YSZ and both LSF and LSCo. A product of the reactions with YSZ is the insulating phase, $\text{La}_2\text{Zr}_2\text{O}_7$.⁴ Solid-state reactions occur also between LSM and YSZ above approximately 1500 K, but this temperature is just sufficient to adequately sinter the cathode to the electrolyte.

Significant effort has gone into trying to take advantage of the excellent cathode properties of LSF and LSCo. One method for doing this is to insert a barrier layer, such as doped ceria, between the YSZ and the cathode.^{12,13} The ceria layer is essentially part of the electrolyte and prevents contact between the YSZ and the cathode material. The approach has been shown to provide excellent cathode performance; however, it requires an additional processing step and the mechanical properties of these electrodes tend to be poor. An alternative approach to using LSF and LSCo, pioneered at Penn, involves producing a porous YSZ layer in contact with the YSZ electrolyte, then impregnating the porous layer with salt solutions to fabricate the perovskites inside the porous YSZ layer.^{14,15} This procedure decouples the calcination of the YSZ in the electrode to the YSZ electrolyte from the calcination of the perovskite within the electrode, so that high sintering temperatures can be used without causing solid-state reactions. More work is needed to determine whether this approach is practical but initial results appear promising.

Anodes

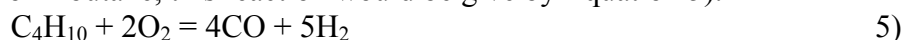
As mentioned earlier, most SOFC designs use a Ni cermet as the anode. The anode must be reasonably porous to allow gas to diffuse to the TPB sites at the electrolyte interface; the Ni content must be ~30 vol% in order to achieve good electronic conductivity.⁴ Often, the composition and porosity are "graded" in order to optimize the length of the TPB in the vicinity of the electrolyte and diffusion of gases farther from the electrolyte. Because Ni cermets can be mechanically strong, many cell designs use it as the support for thin electrolytes. Ni cermets can also provide some catalytic activity for steam reforming of hydrocarbons, although an external catalyst bed is usually required because of the low surface areas of the anodes.

While the electrochemical performance of Ni cermets in H_2 can be excellent, the material has limitations. First, oxidation of Ni must be avoided; this can happen during shut-down procedures and at low temperatures with high fuel utilization (high $\text{H}_2\text{O}:\text{H}_2$ ratio). Second, the Ni cermets are affected by H_2S at ppm concentrations.¹⁶ Third, Ni catalyzes the formation of carbon fibers in CO at low temperatures and in hydrocarbons at higher temperatures.¹⁷ This carbon formation can result in the loss of Ni from the anode through a corrosion process sometimes referred to as "dusting".¹⁸

Regarding carbon formation, it is commonly assumed that thermodynamic calculations can be used to determine operating conditions for which carbon will or will not form.¹⁹ This is not a good assumption; reaction kinetics, not thermodynamics, usually dictate whether or not carbon will form. For example, thermodynamic calculations suggest that it is possible to operate a Ni-based anode in the presence of n-octane at 973 K so long as the $\text{H}_2\text{O}:\text{C}$ ratio is greater than 1.5. However, the rate of carbon-fiber formation on Ni is so much faster than the oxidation of carbon by steam that these conditions will not be stable. Likewise, if the rate of formation of carbon is slow, carbon formation can be avoided, even under conditions where carbon would be thermodynamically predicted.

Direct oxidation of hydrocarbons, without first reforming them to syngas, is theoretically possible in an SOFC; and this would have significant advantages if carbon formation could be

avoided. With large systems, it is possible to recover some of the energy losses in the cell, given in Equation 4), by driving the endothermic, steam-reforming reactions, at least when CH₄ is the fuel. However, for smaller systems and with other fuels, at least some of the syngas is produced by partial oxidation. For n-butane, this reaction would be given by Equation 5).



While the enthalpy change for oxidation of 4CO + 5H₂ at 973 K is only 11% lower than that for C₄H₁₀, the loss in available Gibbs free energy (ΔG) is 37%. Because the maximum electrical energy that can be generated in a fuel cell is given by the change in ΔG , reforming results in a significant loss of efficiency.

The possibility of oxidizing hydrocarbons directly has led to a search for new anode materials that will not catalyze carbon formation. Electronically conductive ceramics are particularly attractive because they tend to be resistant to sintering and could be stable to oxidation-reduction cycling. Some success has been achieved with these materials but performance tends to be modest due to poor electronic conductivity. In one case, excellent performance was obtained using a very thin anode made from Gd-doped ceria,²⁰ even though the conductivity of this material is only 0.08 $\Omega^{-1}\text{cm}^{-1}$ at 1073 K. In this case, however, the conductivity problem was simply shifted onto the current collector, which was Au. Higher electronic conductivities can be achieved in mixed oxides having the doped-perovskite structure. Unfortunately, few of these show good conductivity under highly reducing conditions; ones that do, such as doped SrTiO₃,²¹ exhibit conductivity over too narrow a range of oxygen fugacities.²² Still, there has been progress in the development of new oxides in the past few years and this remains an area of active research.^{23,24}

Another solution to avoiding the coking problems associated with Ni-based anodes is to replace the Ni with a metal that is not a catalyst for carbon formation. At Penn, we have focused on Cu-based cermets, since Cu does not catalyze carbon formation and remains metallic in the range of P(O₂) experienced in the anode.² Because Cu is not a good oxidation catalyst, we add a separate material, ceria, to achieve this function. Preparation of Cu-based anodes required the development of new fabrication procedures.^{25,26} The biggest problem with Cu anodes is the fact that Cu tends to sinter at temperatures above 1073 K, limiting its use to lower operating temperatures. Recent results with Cu-Co bimetallic anodes suggest that thermally stable materials are possible by using mixed-metal composites.²⁷

Stack Issues:

The above discussion has focused on materials development for SOFC but the reader should know that major advances are being made in the development of stacks. A range of stack designs has been devised, including tubular and planar configurations, some of which require minimal or no seals. Unfortunately, space does not allow a complete discussion of this topic and the interested reader is referred elsewhere.^{4,28}

Summary:

While stable SOFC have been successfully demonstrated in large-scale systems,²⁸ the present focus on smaller systems, operating at lower operating temperatures (873 to 1073 K) and with hydrocarbon fuels, requires a re-examination of the materials to be used in SOFC, especially for the cathodes and anodes. Because electrode performance depends strongly on both composition and structure and is not understood in detail on a fundamental level, opportunities

remain for finding novel materials that exhibit better electrochemical activity with good mechanical properties and thermal stabilities.

Acknowledgements

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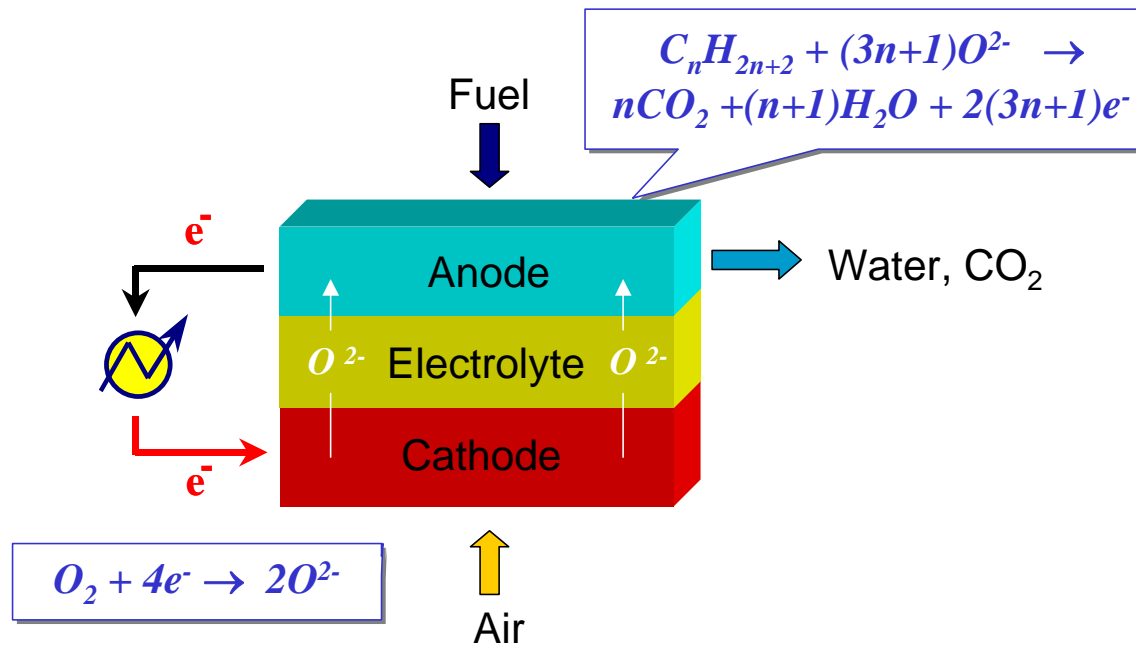


Fig. 1. Schematic diagram, demonstrating the working principles behind an SOFC