The technology is being used to deliver electricity with high efficiency at residences and office buildings worldwide.

Ceramics improve operating conditions of solid-oxide fuel cells

By **Melissae Fellet**
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Solid-oxide fuel cells (SOFCs) convert chemical energy into electricity, at higher efficiencies and with less emissions than conventional generators. The chemical energy comes from the reaction of fuel, which can be natural gas, gasoline, diesel, biofuel or hydrogen, with oxygen ions produced from air. SOFC generators are used to power homes, office buildings, and shopping centers worldwide. The units also produce heat, and when that heat is captured and reused, these fuel cells can be up to 85% efficient. In contrast, plant scale efficiency of electricity produced from coal and natural gas in the United States is about 30%.

SOFCs are most efficient when they operate at high temperatures, originally around 800 to 1000°C. This is because the electrochemical processes inside the cell are thermally driven. The higher the temperature, the faster the reactions and transport rates, and the more current produced. But high operating temperatures also enhance intrinsic mechanical and structural degradation of the materials inside the cell, thus decreasing the SOFC lifetime. According to the September 2014 issue of the *MRS Bulletin*, the challenge of current SOFC research is to create a cell that can operate at lower temperatures (below 650°C), without sacrificing performance or reliability.

Lowering the operating temperature of a SOFC also means some ceramic and expensive high chromium steel components could be replaced with ferritic stainless steel that would oxidize at higher temperatures. This replacement would reduce the cost of a cell, because metal is cheaper and easier to manufacture than ceramic.

A SOFC contains a solid electrolyte sandwiched between two electrodes, the air electrode and the fuel electrode. At the air electrode, or the cathode, oxygen gas is reduced to oxygen ions, O^{2-}. Those ions migrate through the ceramic electrolyte to the fuel electrode, the anode. At this electrode, the oxygen ions react with hydrogen and carbon monoxide, produced from reformed fuel. The oxidation reactions form steam and small amounts of carbon dioxide, about one-third less CO_2 per kilowatt-hour than internal combustion engines. This step also generates electricity.

Yttria-stabilized zirconia was used in the late 1930s as the electrolyte in the first SOFC, and it is still the most common electrolyte today. This material conducts oxygen ions very well at elevated temperatures, without transporting electrons that would short circuit the cell and decrease cell efficiency. It also has good stability toward the reducing environment of the anode on one side and the oxidizing environment of the cathode on the other.

However, its conductivity drops as the temperature is lowered. The first way researchers addressed this problem was to shrink the thickness of the electrolyte layer from a ~150 μm self-supported layer to a ~10 μm thin film attached to one of the electrodes. This strategy reduces the cell resistance by shortening the distance that oxide ions travel to reach the anode. Some researchers have continued to reduce that distance by fabricating electrolyte membranes less than 100 nm thick.

Researchers are also developing new materials for the electrolyte that have increased conductivity at lower temperatures. Ceria and bismuth oxide-based materials are fluorites, like zirconia. Doping ceria either of these with cations of lower valence creates oxygen vacancies in the crystal lattice that enable the anions to flow more freely through the material. Ceria is commonly doped with gadolinium, samarium, or yttrium. Zirconia is commonly doped with calcium, magnesium, yttrium, or scandium.

However, the strong reducing conditions at the anode surface eventually alter the properties of these doped materials. Bismuth materials decompose into pure metal, and ceria-based materials start to conduct electrons, as well as ions.

One way to accommodate this decomposition is to place a thin layer of zirconia between a ceria-based electrolyte and the anode, said Turgut M. Gür, at Stanford University. Eric D. Wachsman, at the University of Maryland, and colleagues took another approach. They designed a bilayer electrolyte with varying amounts of Er_2O_3 stabilized Bi_2O_3 on the cathode side and Gd_2O_3-doped CeO_2 on the anode side. The bismuth material blocked electron conduction from the cerium, and the resulting cell had a power density of about 2W/cm^2 at 650°C.

Perovskites, including a family based on $LaGaO_3$, have also been explored as potential SOFC electrolytes, but these materials, and others, have limitations too, Gür said. For example, the lanthanum-gallium materials react with perovskites used in the cathodes to form secondary phases.

The composition of the cathode offers another opportunity for improving cell performance at lower temperatures. The oxygen reduction reactions at the cathode, or air electrode, lag more at lower temperatures than the oxidation reactions at the anode. To counter this effect, researchers are working to improve the catalytic efficiency of oxygen ion production in potential cathode materials.

The most popular material for a high-temperature SOFC cathode is a perovskite oxide of lanthanum, strontium, and manganese. This material is compatible with the common zirconia electrolyte, and it also conducts electrons well. To improve the ionic and

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electronic conductivity at lower temperatures, researchers replace manganese with cobalt and iron to make $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$.

Beyond this family of oxides, the range of chemical compositions for cathodes, and the impacts of those changes on cell performance, becomes immense, said Sossina Haile, of Northwestern University. She hopes to develop a method to systematically evaluate cathode materials in a well-defined geometry so that reaction pathways and properties like conductivity and diffusion coefficients can be compared among the different compositions.

For the anode, reduced activity at low temperatures is due to contamination. Typical SOFC anodes are cermets, ceramic-metal composites. A common combination involves nickel metal mixed with particles of zirconia electrolyte. At lower operating temperatures, the nickel portions of this electrode become more susceptible to contaminants from the fuel, like sulfur from natural gas or carbon deposition from hydrocarbons. These deposits block catalytic sites on the anode, and reduce the electrode's ability to oxidize fuel.

Some researchers are investigating alternative, nickel-free materials for the anode in low-temperature SOFCs. All-ceramic anodes are under development, and Haile is developing anodes using a mixed electron-ionic conductor based on ceria. "In a way, there's a similarity to the materials used for the cathode," she said. "However, mixed conducting anode materials are still rare compared to their widespread use in cathodes."

More information about the materials used in SOFCs, including phase stability and tolerance for contaminants, can be found in a series of articles in the September 2014 issue of the *MRS Bulletin*. "We do not have the magic materials yet," said Gür. "All materials have their own set of advantages and desirable properties, as well as disadvantages and undesirable properties. There has been a lot of progress in the last several decades, but there is also much work to be done ahead."

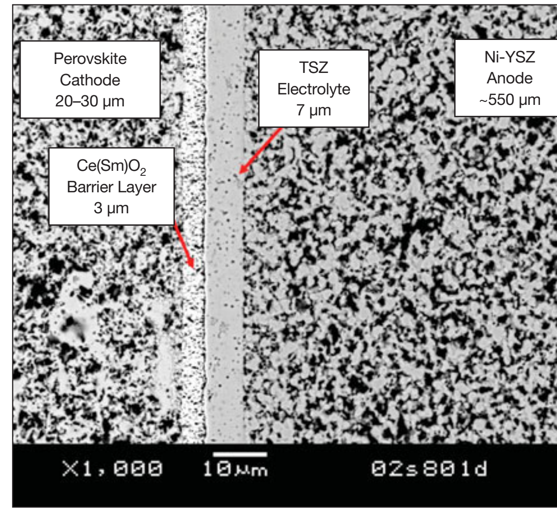
Other aspects of the current research on SOFCs involve minimizing how the materials impact each other in the harsh environment in the cell. Sometimes degradation processes in one material generate deposits that block the flow of electrons or ions in another.

The interconnect provides a good example of how the cell environment and the system interact. This component connects individual cells together to form stacks. In high temperature cells, it is made of ceramic; lower temperature cells, however, can use interconnects made from ferritic stainless steel. But chromium evaporates from this steel, poisoning the cathode and stopping the required oxide ion formation.

Some research on cathode materials involves finding formulas that are more tolerant of chrome, said Vincent Sprenkle, of Pacific Northwest National Laboratory. Other approaches involve developing coatings for the steel to prevent chromium evaporation.

In the United States, programs run by the Department of Energy and Advanced Research Projects Agency-Energy (ARPA-E) are funding academic and corporate research to advance commercialization of low-temperature SOFCs.

Bloom Energy, based in Sunnyvale, Calif., already produces 200 kW SOFC servers, which the company says is enough power to handle the base load consumption of about 200 homes. These servers have been installed at office buildings, shopping malls, a university, and a sports area in the United States. They have also been installed in Japan, a region with a market for proton-conducting fuel cells for residential power.



A cross-section micrograph, taken using scanning electron microscopy, of an anode-supported SOFC prepared using PNNL's cell fabrication protocol. Note: YSZ, yttria-stabilized zirconia. Credit: PNNL.

Other companies in the United States, Australia, and England are developing SOFCs for their local and national markets, as well as testing their products in South Korea and Japan. Because the fuel cell stacks can be combined into modules, these companies are producing units that can output watts to megawatts of power, depending on the desired application.

Ceramic Fuel Cells Ltd., in Australia, has developed a roughly 1.5 kW SOFC unit. Five units have been installed in Australia to power an office building, and a server is used to power an electric vehicle charging station in Adelaide. Besides providing electricity, the company says heat from the fuel cells can be used to warm 200 liters of water a day.

Redox Power Systems, a startup based in Maryland, is using the previously mentioned bismuth oxide-ceria bilayer electrolyte to build 25 kW boxes that run at 650°C. That's 66% more energy than the average American household uses in a month. FuelCell Energy, in Connecticut, is developing SOFC technology for a sub-megawatt power plant.

Lowering the operating temperatures for SOFCs also increases the range of potential applications. High-temperature cells need to be constantly running to avoid lengthy startup or shutdown times needed to reach internal temperatures. Lower-temperature cells could be more easily cycled up and down to follow power demands.

There are many incentives to develop and commercialize SOFCs, Gür said. There are no moving parts, the units make no noise, they are environmentally friendly, and they have high efficiency compared to all the mechanical, thermal, and chemical conversion processes we have to obtain electrical energy. As with many energy technologies, materials science and engineering is needed to help create a device that balances performance, cost, reliability, and lifetime. □