

Experimental

Solution Preparation: All chemicals are reagent grade (Aldrich [17]) and were used without further purification. The concentration of the copper nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}]$ precursor solution was 0.30 mol L^{-1} . Nanopure deionized water (resistivity $\rho > 18.0 \text{ M}\Omega$) was used for all solutions. The 10 vol.-% ethanol solution was made prior to adding metal precursors to the solution. All solutions were stirred for 3 h using a magnetic stirrer.

Characterization: For the X-ray diffraction spectra, particles were collected by filtration immediately downstream of the furnace. The X-ray diffraction of the film was carried out using a Philips [17] PW 1800 diffractometer with a graphite monochromator and $\text{Cu K}\alpha$ radiation.

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Novel Cathodes for Low-Temperature Solid Oxide Fuel Cells**

By Changrong Xia and Meilin Liu*

Worldwide use of fossil energy is the largest source of greenhouse gases and atmospheric pollution, which are profoundly changing global climate and the atmosphere that sur-

rounds us. The use of solid oxide fuel cells, which represent the cleanest, most efficient, and versatile technologies for chemical-to-electrical energy conversion, may significantly reduce the production of greenhouse gases while minimizing pollutant emission. Unfortunately, the cost of the current solid oxide fuel cell (SOFC) systems is still prohibitive for broad commercialization. To be economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced. One effective approach to cost reduction is to reduce the operating temperature. If SOFCs can be operated below 600°C , for example, many components (such as the interconnect and heat exchangers) can be fabricated from much less expensive materials.^[1–3] Additional benefits of lower operating temperature include greater system reliability, longer operational life, and increased potential for mobile applications and for cost-effective fabrication. The work reported in this communication aims at radically reducing the operating temperature and, hence, the cost of SOFC systems by creating novel cathode materials of minimal resistance, a critical step toward making SOFCs affordable for a wide variety of applications.

A SOFC is a device that converts the chemical energy of fuels (such as hydrogen, natural gas, and other hydrocarbon fuels) directly to electricity through electrochemical oxidation of the fuels with an oxidant, typically oxygen from air. When an electronic conductor (such as Pt) is used as cathode, the reduction of oxygen takes place only at or near the triple phase boundaries (TPBs) between the electrode, the electrolyte, and oxygen gas (air). Further, the TPB is electrochemically active only if electrons, oxygen vacancies or ions, and oxygen gas can transport to or away from the TPB. The required simultaneous transport of oxygen ions and electrons implies that a mixed conductor, a material conductive to both oxygen ions and electrons, would make a better cathode than a pure electronic conductor. Unfortunately, for many mixed-conducting electrodes studied, single phase or composite, it is often found that the electrode interfacial resistances (polarization losses) are associated primarily with inadequate ionic transport within the electrode structures.

Cathode materials for traditional SOFCs based on yttria-stabilized zirconia (YSZ) are composites consisting of strontium-doped lanthanum manganites (LSMs) and YSZ. At reduced temperatures, it is necessary to use ionic conductors with higher conductivity than YSZ to obtain adequate performance. Gadolinia-doped ceria (GDC), which has much higher conductivities than YSZ at low temperatures, has been successfully used to replace YSZ. The interfacial polarization resistance of an LSM–GDC composite cathode is about two to three times smaller than that of an LSM–YSZ composite cathode on an YSZ electrolyte when they have similar microstructures.^[4] The smallest polarization resistance for the interface between an LSM–GDC cathode and an YSZ electrolyte was reported to be about $0.49 \Omega \text{ cm}^2$ at 750°C .^[4]

To further reduce the cathodic interfacial polarization resistances, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC), which are mixed ionic and electronic conductors

[*] Prof. M. Liu, Dr. C. Xia
Center for Innovative Fuel Cell and Battery Technologies
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245 (USA)
E-mail: meilin.liu@mse.gatech.edu

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(MIEC) with considerable ionic conductivities, are used to replace LSM, which is a poor ionic conductor.^[5] For example, the polarization resistances between an LSCF–GDC cathode and a GDC electrolyte are much smaller, $0.2 \Omega \text{ cm}^2$ around 600°C .^[6] Resistances of less than $0.18 \Omega \text{ cm}^2$ at 600°C were achieved recently for the interface between an SSC–SDC (SDC, samaria-doped ceria) cathode and an SDC electrolyte, offering much higher power densities at low temperatures.^[7]

While significant progress on development of cathode materials for intermediate-temperature SOFCs has been achieved, an immediate problem arises for low-temperature SOFCs since the activation energies for oxygen diffusion in mixed conductors (such as LSCF) are relatively high. Oxygen ion conductivities decrease rapidly as temperature is reduced, leading to high interfacial resistances at low temperatures.^[1] For example, the resistance between an LSCF–GDC cathode and a GDC electrolyte increased from about $0.2 \Omega \text{ cm}^2$ at 600°C to about $10 \Omega \text{ cm}^2$ at 500°C .^[6] Our results showed that the resistance between an SSC–SDC cathode and an SDC electrolyte increased from less than $0.18 \Omega \text{ cm}^2$ at 600°C to about $1 \Omega \text{ cm}^2$ at 500°C .^[7] Clearly, to develop cathode materials with high electro-catalytic activity for oxygen reduction at low temperatures, it is essential to use conductors with oxygen-ion conductivities much higher than doped cerias or stabilized zirconias.

A new group of low-temperature oxygen-ion conducting materials based on bismuth vanadate ($\text{Bi}_4\text{V}_2\text{O}_{11}$) emerged in the late 1980s.^[8] Among copper-substituted bismuth vanadates (BICUVOX), the one with composition $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ (BICUVOX.10) was reported to have the highest conductivity below 600°C ($10^{-2} \text{ S cm}^{-1}$ at 350°C and $10^{-1} \text{ S cm}^{-1}$ at 600°C), about 50 to 100 times higher than any other known oxygen-ion conductors in this temperature range.^[9] While it is noted that BICUVOX can not be used as electrolyte for SOFCs because it can be readily reduced under fuel cell conditions, it is an excellent oxygen-ion conductor in an oxidizing atmosphere ($P_{\text{O}_2} > 10^{-4} \text{ atm}$),^[9,10] such as the conditions to which a cathode is subject in an SOFC. The high oxygen-ion conductivities of BICUVOX suggest that this oxide could be used as the ionically conducting component in a composite cathode for low-temperature SOFCs. Since the electronic transference numbers of BICUVOX materials are relatively low (only a few percent),^[11] an electronically conducting phase has to be added to make the composite cathode a mixed conductor with rapid ambipolar transport. In this work, this hypothesis was examined by investigating the electrochemical properties of a composite consisting of BICUVOX.10 and silver as the cathode in a low-temperature SOFC.

Shown in Figure 1 are two typical impedance spectra measured at 500°C . Spectrum (a) represents the impedance of the whole cell measured under open circuit conditions using a two-electrode configuration. Thus, the intercept with the real axis at high frequencies represents the resistance of the electrolyte and lead wires, whereas the resistance between the two intercepts with the real axis (about $0.55 \Omega \text{ cm}^2$) corresponds to the impedance of the two interfaces, the cathode–

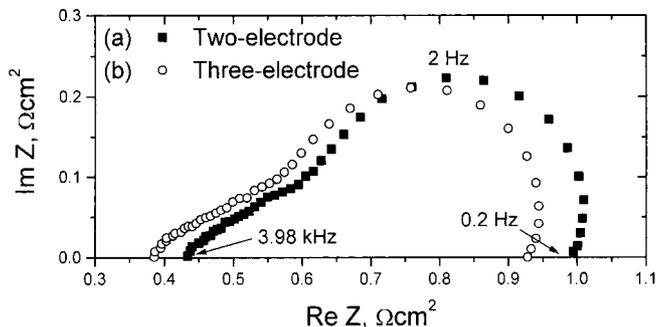


Fig. 1. Impedance spectra measured at 500°C using a) a two-electrode and b) a three-electrode configuration.

electrolyte interface and the anode–electrolyte interface. The electrolyte resistance is estimated by eliminating the lead-wire resistance. In contrast, spectrum (b) is a typical impedance spectrum of the half-cell containing the cathode–electrolyte interface under the same operating conditions as for spectrum (a). In spectrum (b), the resistance between the two intercepts with the real axis (about $0.53 \Omega \text{ cm}^2$) corresponds to the impedance of the cathode–electrolyte interface. Thus, the resistance of the anode–electrolyte interface can be estimated from the two spectra shown in Figure 1; it is about $0.02 \Omega \text{ cm}^2$, much smaller than that of the cathode–electrolyte interface ($0.53 \Omega \text{ cm}^2$). Shown in Figure 2 are the cathode–electrolyte interfacial resistances as a function of cell operating temperature, together with the total cell resistances and the electrolyte resistances. The interfacial resistance between the Ag–BICU–

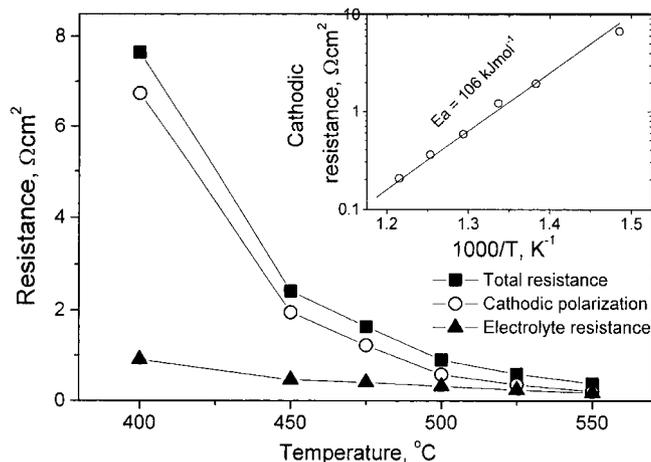


Fig. 2. Total cell resistances, cathode–electrolyte interfacial polarization resistances, and electrolyte resistances as determined from impedance spectra.

VOX cathode and the GDC electrolyte at 500°C is only about $0.53 \Omega \text{ cm}^2$, much smaller than those of the LSCF–GDC ($\approx 10 \Omega \text{ cm}^2$),^[4] SSC–SDC ($\approx 1 \Omega \text{ cm}^2$),^[7] or SSC–GDC ($\approx 1 \Omega \text{ cm}^2$)^[13] cathode. The interfacial resistance of the Ag–BICUVOX cathode may be further reduced since the electrochemical performance of a composite cathode can be significantly improved by optimizing their microstructures and composition.^[3–6]

Shown in Figure 3 are the current–voltage characteristics and the corresponding power densities for a fuel cell using the Ag-BICUVOX cathode. Each datum point was recorded about 30 min after the cell reached a steady state. Maximum power densities were 130, 231, and 443 mW cm⁻² at 450, 500,

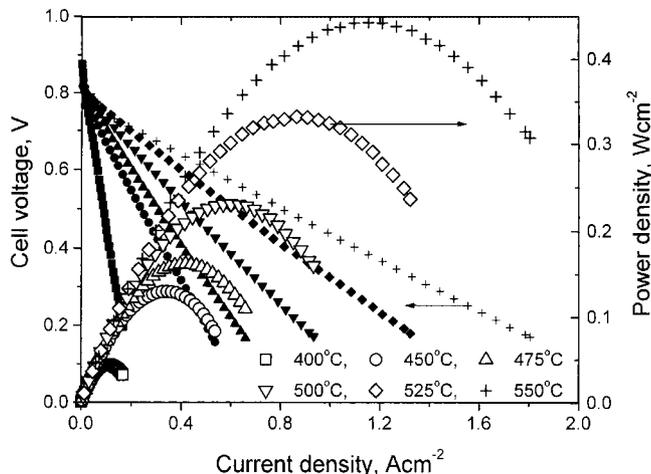


Fig. 3. Cell voltages (solid symbols) and power densities (open symbols) as a function of current density for a fuel cell consisting of a Ag-BICUVOX composite cathode, a GDC electrolyte, and a Ni-GDC composite anode.

and 550 °C, respectively. The observed current and power densities at temperatures around 500 °C represent the highest performances ever reported in the literature for SOFCs operated at these temperatures.

Composites consisting of silver and bismuth vanadates exhibit remarkable catalytic activity for oxygen reduction at 500–550 °C and greatly reduce the cathode–electrolyte (doped ceria) interfacial polarization resistances of low-temperature SOFCs, down to about 0.53 Ω cm² at 500 °C and 0.21 Ω cm² at 550 °C. The observed power densities of 231, 332, and 443 mWcm⁻² at 500, 525, and 550 °C, respectively, make it possible to operate SOFCs at temperatures about 500 °C. While the long-term stability of the cathodes is yet to be characterized, the demonstrated remarkable performances (low interfacial resistances and high power densities) at low temperatures are very encouraging, implying that a new generation of low-temperature SOFCs is hopeful. Significant reduction in operating temperature will dramatically reduce not only the cost of materials but also the cost of fabrication. It also implies greater system reliability, longer operational life, and increased potential for mobile applications. Low-temperature SOFCs have great potential to be affordable for many applications, including residential and automotive applications.

Experimental

Powders of BICUVOX.10 were prepared using a solid-state reaction method starting from Aldrich chemicals of Bi₂O₃ (99.9%), V₂O₅ (99.6%), and CuO (min. 99%). Stoichiometric amounts of oxide powders were mixed and ground

in an agate mortar. The mixed powder was then fired for 12 h in air successively at 600, 700, and 800 °C and, finally, cooled down to room temperature at a cooling rate of 20 °C per hour. The stabilized γ' phase of BICUVOX.10, as confirmed using X-ray diffraction (XRD, PW-1800 system, 2θ = 10–70°), was reground, uniaxially pressed into a disk-shaped compact, and sintered at 800 °C for 5 h. The conductivities were about 0.056 S cm⁻¹ at 500 °C and 0.11 S cm⁻¹ at 600 °C as measured by impedance spectroscopy.

The electrochemical performance of the Ag-BICUVOX.10 composite cathodes was characterized in a low-temperature SOFC based on a GDC (Gd_{0.1}Ce_{0.9}O_{1.95}) electrolyte. The cell was fabricated by a dry-pressing process and sintered at 1350 °C for 5 h [12,13], resulting in a dense GDC film (about 30 μm thick) on an GDC/NiO substrate. Slurry of BICUVOX.10 and Ag (57 wt.-%), prepared using Heraeus V006, was applied to the GDC film as cathode by brush painting, followed by drying and firing at 575 °C in air for 4 h with a heating and cooling rate of 300 °C per hour. The cathode area was about 0.5 cm² and the thickness was about 30 μm. A silver reference electrode was prepared by painting silver paste (Heraeus 8710) on to the electrolyte (about 2 mm away from the edge of cathode) and firing at 500 °C for 1 h. Upon exposure to hydrogen, the NiO in the anode was reduced to metallic Ni, resulting in a porous Ni-GDC composite anode with porosity more than 30% [14]. Shown in Figure 4 are the typical microstructures of each cell component, as revealed using a scanning electron microscope (SEM, Hitachi S-800).

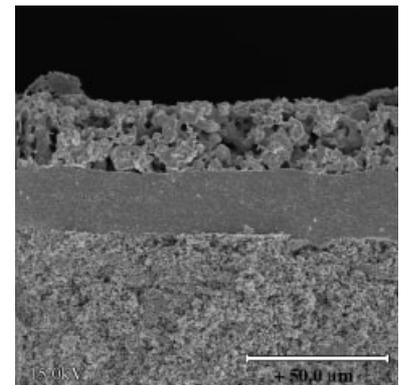


Fig. 4. A cross-sectional view (SEM image) of a single cell with an Ag-BICUVOX composite cathode (top layer), a GDC electrolyte (middle layer), and a Ni-GDC composite anode (bottom layer).

Electrochemical performances of the fuel cells and the composite cathodes were characterized at 400 to 550 °C with humidified (3 vol.-% H₂O) hydrogen as fuel and stationary air as oxidant at ambient pressure. The impedances were typically measured in the frequency range from 0.01 Hz to 1 MHz using a Solartron 1255 HF frequency response analyzer in combination with a Solartron 1286 electrochemical interface. The fuel cell performance was acquired using the Solartron 1286 interfaced with a computer.

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