

A Novel Composite Cathode for Low-Temperature SOFCs Based on Oxide Proton Conductors**

By Lei Yang, Chendong Zuo, Shizhong Wang, Zhe Cheng, and Meilin Liu*

The demand for clean, secure, and renewable energy has stimulated great interest in fuel cells. Among all types of fuel cells, solid oxide fuel cells (SOFCs) have attracted much attention because of its high energy efficiency, modularity, and excellent fuel flexibility; in fact, they are the only fuel cell system that has the potential for direct utilization (or through internal reforming) of readily available fuels, gasified coal gas, and renewable fuels.^[1] Unfortunately, the current SOFC systems are still too expensive for broad commercialization. To be economically competitive, the operating temperature has to be sufficiently low so that much less expensive materials may be used.^[2] Compared with low-temperature SOFCs based on oxygen ion conductors (e.g., Gd-doped ceria or Y-stabilized zirconia), SOFCs based on oxide proton conductors offer several advantages.^[3–7] First, lower activation energy for proton than for oxygen ion transport implies that the ionic conductivities of proton conductors have less temperature dependence, potentially exhibiting higher ionic conductivities at intermediate or low temperatures. Second, the fuel will not be diluted during fuel cell operation since water is produced in the cathode compartment, not in the fuel side as does for an oxygen ion conductor-based SOFC.

However, the development of low-temperature SOFCs based on oxide proton conductors is still in its infancy.^[8] While BaCeO₃-based composition exhibits high ionic conductivity, they are not suitable for SOFC applications due to the instability in H₂O- and CO₂-containing atmospheres.^[9,10] Secondly, electrolyte supported configuration was commonly adopted due to the requisite conditions for fabrication of these materials in the required form (e.g., the high sintering temperature).^[8] Recently, we have developed a new composition of oxide proton conductor, Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3–δ} (BZCY7), in the Barium–Zirconium–Cerium–Yttrium family^[11,12] which exhibits not only adequate proton conductivity but also sufficient chemical and thermal stability over a wide range of conditions relevant to SOFC operation.^[3] A modified co-pressing and co-firing method was successfully developed to fabricate

anode supported crack-free electrolyte membranes of ~65 μm thick at a relatively low co-firing temperature (1350 °C for 6 h). The performance of low-temperature SOFCs, however, depends sensitively on the cathode materials used. To date, only a few studies have been reported on oxide cathode compatible with proton conductors.^[13] Conventional mixed ionic (oxygen ion)-electronic conducting cathodes have been used for oxide proton-conducting electrolytes, including Sm_{0.5}Sr_{0.5}CoO₃ (SSC), Ba_{0.5}Pr_{0.5}CoO₃, La_{0.5}Sr_{0.5}CoO₃, La_{0.6}Ba_{0.4}CoO₃, and La_{0.7}Sr_{0.3}FeO₃.^[14,15] Yet, the electrode performances are inadequate for practical applications, due most likely to limited active sites for oxygen reduction at the interface between the proton-conducting electrolyte and the oxygen ion conducting cathodes. Indeed, it has been previously shown that the interface between SSC cathode and Y-doped BaCeO₃ electrolyte was quite resistive.^[14] To make better use of the new proton conductors such as BZCY, efficient cathode materials must be developed. While BZCY exhibits some oxygen ion conductivity, which would moderate the problems of charge transfer associated with oxygen reduction at the cathode, the oxygen ion conductivity is insufficient for fast charge transfer under fuel cell operating conditions. Here we report a novel composite cathode, derived from BZCY and SSC, for low-temperature SOFCs based on oxide proton conductors. This cathode material is very active for oxygen reduction because it allows the simultaneous transport of proton (H⁺), oxygen vacancy (V_O^{••}), and electronic defects (e[•] and/or h[•]), extending the “active” sites for oxygen reduction to a large extent and significantly reducing the cathodic polarization resistance. To the best of our knowledge, the demonstrated peak power densities are the highest for any SOFCs based on oxide proton conductors ever reported under the testing conditions, representing a new-class of low-temperature, cost-effective SOFCs for many applications.

The pairing of oxide proton conducting electrolytes with chemically compatible electrode materials is very important to the performance of SOFCs. To investigate the compatibility between BZCY and SSC, a mixture of BZCY and SSC powders (weight ratio of 2:3) was fired at different temperatures. Shown in Figure 1 are the X-ray diffraction (XRD) patterns of a BZCY–SSC mixture before and after calcination at 900, 1000, and 1100 °C. The XRD data suggest that there were no observable chemical reactions between SSC and BZCY when fired at 900 °C for 3 h. However, new phases other than BZCY and SSC were formed when the calcination

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

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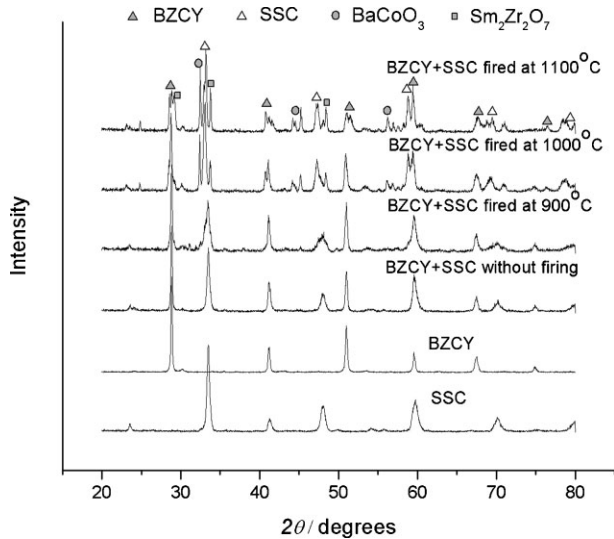


Figure 1. XRD patterns of BZCY, SSC, and BZCY–SSC mixtures before and after calcinations at 900, 1000, and 1100 °C for 3 h.

temperature was increased to 1000 and 1100 °C. Additional phases such as BaCoO₃ and Sm₂Zr₂O₇ were identified in the XRD patterns. The BaCoO₃-based phase is an excellent mixed conductor with high oxygen ion and electronic conductivity^[16,17] whereas the Sm₂Zr₂O₇ phase is a proton conductor with relatively high proton conductivity.^[18] This implies that firing of the BZCY–SSC composite cathode onto an BZCY electrolyte at proper temperatures could produce desirable phases for oxygen reduction in addition to forming strong bonding between the electrolyte and cathode. When the firing temperature was too high (at 1100 °C), however, large amounts of Sm₂Zr₂O₇ phase were formed, which has low electronic conductivity and could lead to high sheet resistance when used as a cathode. More importantly, it is evident that the peaks corresponding to BZCY were shifted to right, especially at high angles of diffraction after firing at 1000 and 1100 °C, suggesting that Co might have doped into the B-site of BZCY,^[19] since Co³⁺ ($R^{\text{III}} = 0.53 \text{ \AA}$) is smaller than Ce⁴⁺ ($R^{\text{IV}} = 0.87 \text{ \AA}$) and Zr⁴⁺ ($R^{\text{IV}} = 0.72 \text{ \AA}$). Further, conductivity measurements under various conditions indicate that the Co-doped BZCY is an excellent mixed proton-electronic conductor, transporting both proton (H⁺) and electronic defects (e^- and/or h^+), and thus is an active phase for oxygen reduction.^[19] Thus, when properly fired, the entire surface of the BZCY–SSC cathode could become active for oxygen reduction since each of the major phases is in fact a mixed conductor, dramatically reducing the cathodic polarization resistance due to oxygen reduction.

Figure 2 shows the morphologies of BZCY–SSC surfaces and the interfaces between electrolyte and cathode fired at 900, 1000, and 1100 °C. For the samples fired at 900 °C, the adhesion of the electrode to the electrolyte is relatively poor. The connectivity between particles within the cathode is insufficient for the transport of ions and electrons required for cathode

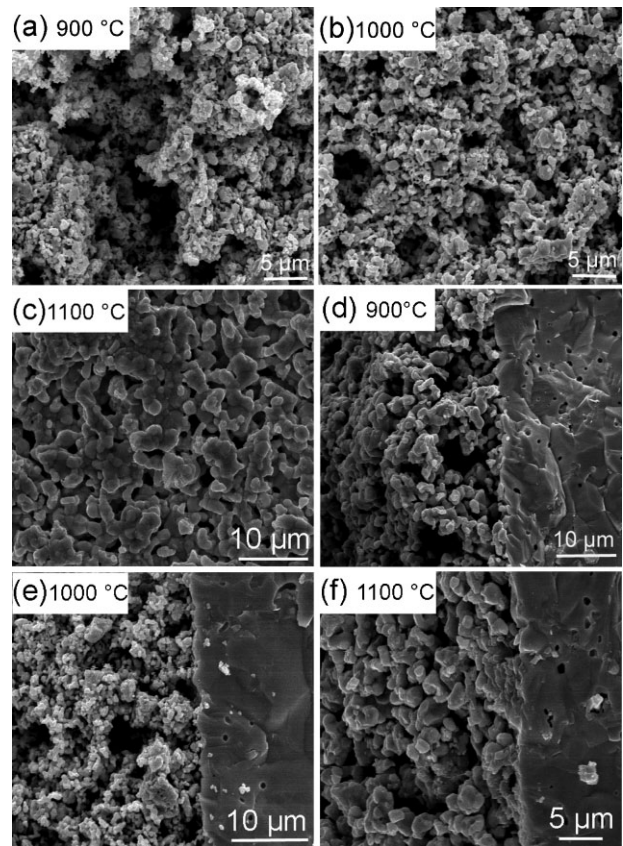


Figure 2. Surface and cross-sectional views (SEM images) of BZCY–SSC cathode and the interface between BZCY electrolyte and the composite cathode fired at (a,d) 900, (b,e) 1000, and (c,f) 1100 °C.

reactions. For the BZCY–SSC cathode fired at 1000 °C, in contrast, the adhesion of the electrode to the electrolyte is significantly improved. The interparticle connectivity is also much better, producing a uniform and porous structure. Further, because of the chemical interactions between BZCY and SSC at 1000 °C, the cathode was then composed of two major phases, Co-doped BZCY and SSC (each being a mixed ionic-electronic conductor), and some minor phases such as BaCoO₃ (mixed conductor) and Sm₂Zr₂O₇ (proton conductor). However, when the firing temperature of BZCY–SSC was increased to 1100 °C, the cathode was overdensified, leading to a dramatic loss of porosity and an increase in concentration polarization of the cathode. Further, the formation of excessive amounts of less conductive phases (such as Sm₂Zr₂O₇) resulted in poor performance.

The electrochemical performances of the cells based on a BZCY electrolyte and BZCY–SSC cathodes fired at 900, 1000, and 1100 °C were characterized under various fuel cell operating conditions. Shown in Figure 3 are the current–voltage characteristics and the corresponding power densities at different temperatures for a fuel cell based on a BZCY electrolyte membrane of 65 μm thick and BZCY–SSC composite

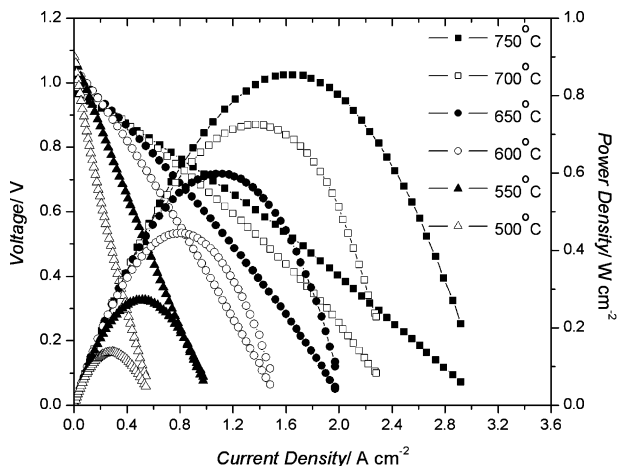


Figure 3. Cell voltages and power densities as a function of current density for fuel cells consisting of Ni-BZCY anode, 65- μm -thick BZCY electrolyte, and BZCY-SSC cathode fired at 1000 $^{\circ}\text{C}$.

cathode fired at 1000 $^{\circ}\text{C}$. The open circuit voltages (OCV) at 700, 600, and 500 $^{\circ}\text{C}$ were 1.00, 1.05, and 1.08 V, respectively, indicating that the BZCY electrolyte was sufficiently dense and exhibited negligible electronic conduction. The peak power densities are about 725, 598, 445, 272 mW cm^{-2} at 700, 650, 600, and 550 $^{\circ}\text{C}$, respectively. The observed current and power densities represent the highest performance ever reported in the literature for SOFCs based on an oxide proton conductor, even higher than the conventional oxygen ion conducting cells based on 20- μm -thick GDC and GDC-SSC cathode.^[20] The observed fuel cell performances are very encouraging, especially for operation at low temperatures to dramatically reduce the cost of SOFC systems. Shown in Figure 4 are the current

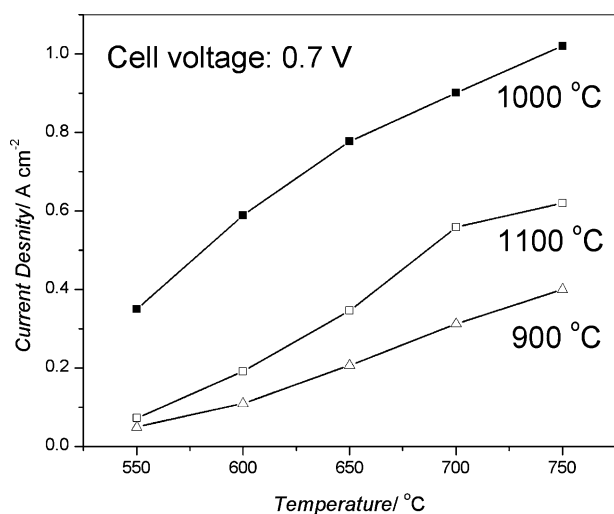


Figure 4. Current densities measured at a cell voltage of 0.7 V at different temperatures for the cells with BZCY-SSC cathode fired at 900, 1000, and 1100 $^{\circ}\text{C}$.

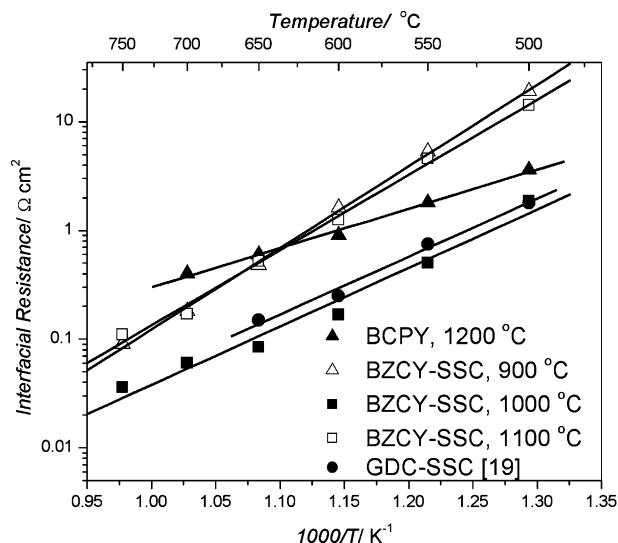


Figure 5. Polarization resistances between BZCY and different cathodes as determined from impedance spectroscopy under open circuit conditions: BZCY/BCPY, BZCY/BZCY-SSC (fired at 900 $^{\circ}\text{C}$), BZCY/BZCY-SSC (fired at 1000 $^{\circ}\text{C}$), and BZCY/BZCY-SSC (fired at 1100 $^{\circ}\text{C}$). The cathodic interfacial resistance of GDC-SSC is from ref. [20].

densities measured at a cell voltage of 700 mV at different testing temperatures for cells with BZCY-SSC cathode fired at 900, 1000, and 1100 $^{\circ}\text{C}$. The cathode fired at 1000 $^{\circ}\text{C}$ displayed the best performance. For the cell with BZCY-SSC cathode fired at 900 $^{\circ}\text{C}$, the peak power density of the cell reduced to about 248, 151, 81, and 45 mW cm^{-2} at 700, 650, 600, and 550 $^{\circ}\text{C}$, respectively. Similarly, when the cathode was fired at 1100 $^{\circ}\text{C}$, the peak power density dropped to 423, 265, 153, and 66 mW cm^{-2} at 700, 650, 600, and 550 $^{\circ}\text{C}$, respectively.

Shown in Figure 5 are the polarization resistances of Ni-BZCY/BZCY/BZCY-SSC cells with the BZCY-SSC cathodes fired at 900, 1000, and 1100 $^{\circ}\text{C}$, as compared with a similar cell using $\text{BaCe}_{0.4}\text{Pr}_{0.4}\text{Y}_{0.2}\text{O}_3$ (BCPY) as the cathode. These polarization resistances were determined from impedance spectroscopy under open circuit conditions. As expected, the cell with BZCY-SSC cathode fired at 1000 $^{\circ}\text{C}$ showed the lowest interfacial resistances. At 600 and 550 $^{\circ}\text{C}$, the interfacial resistances are estimated to be about 0.168 and 0.501 Ωcm^{-2} , respectively, comparable to the lowest cathodic interfacial resistance of the GDC-SSC composite cathode on an GDC electrolyte.^[20]

The present study demonstrated that high power densities can be achieved in SOFCs based on oxide proton conductors using properly designed proton-oxygen ion-electron conducting cathode derived from BZCY and SSC. The composite fired at 1000 $^{\circ}\text{C}$ offers unique transport properties and greatly increase the number of active sites, facilitating the electrochemical reactions involving H^+ , O^{2-} , and e' or h' on the entire cathode surfaces. Additional improvement is possible by optimization of cathode composition and microstructure.

Furthermore, reduction of the thickness of BZCY electrolyte could yield further increase in power density.

Experimental

Preparation of BZCY Powders: BZCY powders were synthesized by a conventional solid state reaction method. Stoichiometric amount of high-purity barium carbonate, zirconium oxide, cerium oxide, and yttrium oxide powders (all from Aldrich Chemicals) were mixed by ball milling in ethanol for 48 h, followed by drying in an oven and calcinations at 1100 °C in air for 10 h. The calcinated powder was ball milled again, followed by another calcination at 1150 °C in air for 10 h to produce single phase BZCY, as confirmed by XRD analysis (PW-1800 system, $2\theta = 20\text{--}80^\circ$).

Fabrication of Anode-Supported SOFCs: NiO-BZCY supported BZCY bilayers were fabricated by a modified co-pressing and co-firing (at 1350 °C for 6 h) method [3]. The weight ratio of NiO to BZCY was 1:1.92. Proper amount of rice starch was used as the pore former in the anode. Subsequently, a cathode slurry, consisting of BZCY and SSC powder (weight ratio of 3:7), V006 thinner (from Heraeus), and acetone, was brush painted on the BZCY surface of a NiO-BZCY/BZCY bilayer, followed by firing at 900, 1000, and 1100 °C for 3 h. The thickness of the anode (NiO-BZCY), electrolyte (BZCY), and cathode (BZCY-SSC) were about 500, 65, and 25 μm , respectively. Two silver wires were connected to each electrode as current leads.

Characterization of Phase Composition and Microstructure of Cell Components: The phase composition of the mixture of BZCY and SSC calcined at different temperature was determined by XRD. Powders of BZCY and SSC with a weight ration of 2–3 were well mixed, pressed into a pellet, and calcined at 900, 1000, and 1100 °C for 3 h. The microstructure and morphology of the tested cell were examined using a scanning electron microscope (SEM, Hitachi S-800).

Electrochemical Measurement: The button cells were mounted on an alumina supporting tube for fuel cell testing at 400–750 °C with humidified hydrogen (3 vol-% H₂O) as fuel and stationary air as oxidant. The Ohmic and the interfacial resistances were separated by impedance spectroscopy using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyzer

interfaced by a computer in the frequency range from 0.01 Hz to 10 MHz. The current–voltage characteristics of the cells were monitored using a Solartron 1286 interfaced with a computer.

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