

Composite Cathodes for Intermediate Temperature Solid Oxide Fuel Cells

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Introduction:

Solid oxide fuel cells (SOFCs) are electrochemical devices capable of achieving high thermodynamic efficiency with low environmental impact. Conventional SOFCs operate above 800°C, limiting their applications, requiring special construction materials and large start-up energy inputs. These limitations have led to the exploration of SOFCs that operate at intermediate temperatures (IT, 400-700°C).

These efforts have been focused on using protonic conductors as the electrolyte material. Protonic conductors have the advantage of lower activation energies compared to oxygen-ion conductors, as well as the formation of water vapor on the cathode side which prevents fuel dilution [1]. However, the use of proton conductors as electrolytes has been limited by the unavailability of compatible and optimal materials for the cathode. This project focused on exploring the chemical and electrical properties of different compositions of $\text{BaZr}_{1-x-y}\text{Pr}_x\text{Y}_y\text{O}_{3-\delta}$ (BZPYxy), for its implementation as a composite cathode for IT-SOFCs.

Experimental:

BZPYxy ($x = 10-40$, $y = 20$) was synthesized through the combustion method. Metal nitrates were dissolved in water by stoichiometric ratio. Citric acid was added in a 2:1 ratio to the metal nitrates, and 5 mL of nitric acid was added; pH was adjusted to 3, using ammonium solution. Solution was heated until all water was removed and solution was combusted.

The resulting powder was calcinated at 1100°C for six hours. X-ray diffraction (XRD) analysis was used to confirm that samples were single phase. Powder was mixed with 5% poly(vinyl butynal)1000. Dense pellets were obtained by uniaxially pressing

powders at 200 MPa and sintering at 1600°C for 10 hrs.

Conductivity measurements were performed by electrochemical impedance spectroscopy (EIS) analysis in the range of 50 mHz to 500 kHz between 350-750°C. BZPY pellets were painted with silver, placed in a current collector with gold wires in a ceramic screw-and-bolt assembly. Gold wires were connected to an alumina reactor, which was placed in a tube furnace. Different oxygen partial pressures were obtained by mixing air with argon gas. Wet atmosphere conditions were obtained by flowing gas through water at ambient temperature. The conductivity values for each measurement were obtained by analyzing the IES spectra at the transition between medium and high frequencies.

Composite cathodes inks were prepared by mixing PBCO with respective BZPY powder along with α -terpineol and ethyl cellulose. Symmetric cells were prepared by paint brushing the cathode ink on each side of a BZPY2020 pellet and sintering at 1000°C for 3 hrs. Pellets were then analyzed with the same setup as previously described. The area specific resistivity was calculated by looking at the low frequency range for the EIS spectra.

Complete fuel cells were fabricated by co-pressing the anode (BZY+Ni) with a thin layer of BZPY1020 for the electrolyte and sintering at 1400°C for 10 hrs. The cathode was paint-brushed on the electrolyte through a 5 mm mask and sintered at 1000°C for 3 hrs. The cathode was repainted

with Pt ink and dried for 10 min at 1000°C to aid the current collectors. Fuel cells were sealed around the anode using silver paint and silver current collectors were connected to the cathode. Cells were tested at 700°C flowing wet- H_2 at anode side and using ambient air at the cathode.

| Composition | Temperature (°C) | Dry Air | | Wet Air | |
|-------------|------------------|-----------------|----------------------|-----------------|----------------------|
| | | Transport Ionic | Transport Electronic | Transport Ionic | Transport Electronic |
| BZPY2020 | 500 | 0.14 | 0.86 | 0.52 | 0.48 |
| | 600 | 0.09 | 0.91 | 0.33 | 0.67 |
| | 700 | 0.07 | 0.93 | 0.28 | 0.72 |
| BZPY3020 | 500 | 0.04 | 0.96 | 0.30 | 0.70 |
| | 600 | 0.03 | 0.97 | 0.20 | 0.80 |
| | 700 | 0.02 | 0.98 | 0.13 | 0.87 |
| BZPY4020 | 500 | 0.19 | 0.81 | 0.33 | 0.67 |
| | 600 | 0.21 | 0.79 | 0.26 | 0.74 |
| | 700 | 0.20 | 0.80 | 0.20 | 0.80 |

Table 1: Transport number results for different temperatures, atmospheres and compositions.

Results and Discussions:

XRD results proved that the four BZPY compositions were obtained in single phase. Figure 1 shows an Arrhenius plot of conductivity vs. temperature measured in wet air. All the BZPY composition had similar conductivities throughout the temperature range examined.

Table 1 displays the different transport numbers for the compositions obtained by varying the oxygen partial pressure and modeling the results using the “defect model” [2]. Under dry conditions the electronic contribution to the conductivity dominates, while in wet atmosphere there is a closer ratio between the ionic and electronic contributions.

The results also indicate that with increasing Pr content the electronic contribution increases. This suggests that BZPY4020 is a better candidate for the composite cathode, since the electrodes need to have high electron mobility for higher current density to be achieved.

Figure 2 summarizes the ASR results for BZPY1020 and BZPY4020, with the latter having lower resistance overall. Figure 3 shows a scanning electron microscope (SEM) picture of the symmetrical cell at the cathode and electrolyte interface. The image suggests that lower ASR values can be obtained by reducing the cathode thickness to 20 μm and by optimizing the sintering temperature to increase cathode porosity and adhesion to electrolyte.

The performance of the composite BZPY4020+PBCO cathode was tested in an anode supported dual chamber fuel cell. The maximum open circuit voltage (OCV) for the cell was 0.91V; however, due to poor manufacturing, the maximum power density was only 1.26 mW/cm^2 .

Conclusions:

Single phase powders for BZPY_{xy} were synthesized and stable pellets were pressed from them. The conductivity of the different compositions were tested and found to not differ largely under wet atmosphere. The electronic conductivity contribution to the overall conductivity was found to increase with Pr content. The symmetrical cell results showed BZPY4020 had overall lower resistance with a minimum ASR value of 0.45 Ωcm^2 . The fuel test did not yield successful power density measurements with problems in cell sealing and cathode attachment limiting performance to only 1.26 mW/cm^2 . However, an OCV of 0.91V was obtained establishing a proof of concept model.

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References:

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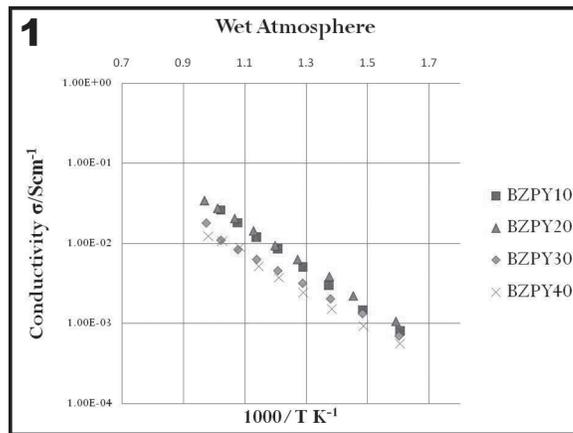


Figure 1: Conductivities for all four BZPY compositions examined under wet air.

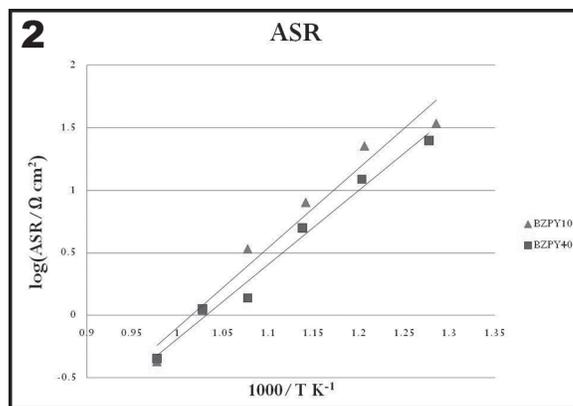


Figure 2: ASR results for BZPY1020 and BZPY4020.

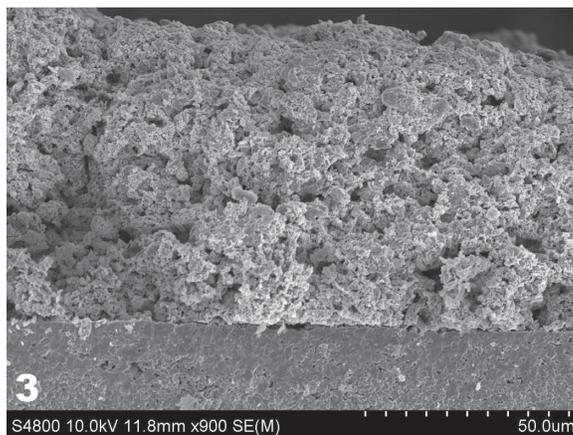


Figure 3: SEM of the cathode (top) and electrolyte (bottom) interface.