

Exploring electronic conduction through $\text{BaCe}_x\text{Zr}_{0.9-x}\text{Y}_{0.1}\text{O}_{3-d}$ proton-conducting ceramics

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ARTICLE INFO

Article history:

Received 3 September 2015

Received in revised form 8 January 2016

Accepted 10 January 2016

Available online 26 January 2016

Keywords:

Solid-solution barium cerate and

barium zirconate

Thin membrane

Electrolysis

Cerium reduction

Electronic leakage

Ceramic proton conductor

ABSTRACT

This work explores the formation of undesirable electronic leakage in $\text{BaCe}_x\text{Zr}_{0.9-x}\text{Y}_{0.1}\text{O}_{3-d}$ (BCZY) proton-conducting ceramic thin membranes used in H_2O -electrolysis and hydrogen-pumping applications. Very low hydrogen fluxes (hydrogen transport number below 0.4) through thin BCZY membranes during electrolysis operation were recently reported. These poor performances were explained by the presence of an undesirable electronic leakage that forms due to reduction of cerium in the BCZY material. In this paper, we investigate the influence of the cerium content in the BCZY membranes on the magnitude of this electronic leakage. Three compositions were fabricated with $x = 0, 0.1, \text{ and } 0.2$ (BZY10, BCZY18, and BCZY27, respectively). Unique gas conditions were chosen to isolate specific charge carriers present in the thin membranes, and decouple the electronic-conduction effects. While significant electronic leakage was observed in the BCZY27 material under these well-defined conditions, minimal leakage was detected in BCZY18 and BZY10. These results confirm that the presence of the electronic leakage is linked to the cerium content and is most probably due to the reduction of cerium ions under bias. Additionally, BCZY18 is the preferred composition for electrolysis applications due to its relative lack of electronic conductivity, reasonable protonic conductivity, and affinity for high-density sintering.

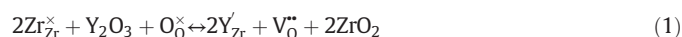
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1. Introduction

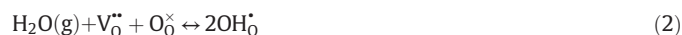
High-temperature proton-conducting ceramics are being developed for use in a broad range of applications, including fuel cells [1,2], electrolyzers [3,4] and hydrogen purification [5,6]. These materials are promising hydrogen-separation membranes as they demonstrate low activation energy for proton conduction [7–10]. The most-studied materials are the rare earth-doped perovskite oxides based on barium zirconates and cerates [11–18]. While barium cerate exhibits the highest protonic conductivity, its chemical stability in CO_2 - and H_2O -containing atmospheres is inadequate for practical use [11–12]. In contrast, barium zirconate has demonstrated excellent stability in those environments, though it suffers from lower ionic conductivity [1,2,12,15]. These properties have generated interest in solid solutions of doped barium cerate and barium zirconate; co-doping has been found to yield both the required material stability and reasonable protonic conductivity [12,14–21]. While a wide range of solid-solutions can be synthesized, $\text{BaCe}_{0.2}\text{Zr}_{0.7}\text{Y}_{0.1}\text{O}_{3-d}$ (BCZY27) has generated the most interest [21–25].

The BCZY materials are not pure ionic conductors, and can have up to four charge carriers, including protonic defects OH_0^\bullet , oxygen vacancies $\text{V}_\text{O}^\bullet$, electrons e^- and electron holes h^\bullet . The relative role of each charge carrier changes with gas composition and temperature.

Reaction 1 illustrates the creation of the oxygen vacancies resulting from the substitution of Zr^{4+} with Y^{3+} [26].



In moist conditions, the ceramic membrane is “hydrated” as protons are incorporated into the lattice through the Stotz–Wagner mechanism [27].



This hydrogen transport through such a protonic defect is generally the desired result in most applications. However, in oxidizing atmosphere, electronic defects of holes are formed as oxygen is incorporated into the lattice [28–31]:

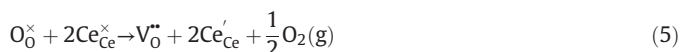


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Recently, it was proposed that these electronic defects are localized on the sites of lattice oxygen, as described in Reaction 4 [32–35]:



In addition, significant electronic conduction through high cerium-containing BCZY when subjected to reducing atmospheres was reported [36]. Cerium ions can be reduced to the lower oxidation state of 3+ to generate electrons by Reaction 5:



Such conductivity can significantly impact device performance. Under fuel-cell or electrolysis operation, electronic leakage through the electrolyte leads to reduced electrical and hydrogen-production efficiencies. Understanding the conditions at which electronic leakage becomes significant is important for harnessing the unique properties displayed by these emerging proton-conducting ceramic materials.

Our recent work showed significant undesirable electronic conduction in BCZY27 during electrolysis and hydrogen-pumping operation [25]. In electrolysis applications, an external bias is applied to reduce H₂O and drive hydrogen across the membrane against the chemical-potential gradient. Under such conditions, the theoretical flux of hydrogen $N_{\text{theoretical}}$ through a pure proton conductor is:

$$N_{\text{theoretical}} = i/n * F \text{ [moles/s]} \quad (6)$$

where i is the ionic current through the device at the applied external bias, and n and F are the number of electrons generated and Faraday's constant, respectively. Mixed ionic-electronic conductors like BCZY transport less hydrogen than the theoretical maximum, as some of the current can be carried by holes, oxygen ions, or electrons as a function of thermodynamic conditions (temperatures/gas compositions). The Faradaic efficiency is the ratio of the observed to the theoretical hydrogen flux. While pure ionic conductors like yttria-stabilized zirconia have demonstrated Faradaic efficiencies near unity [37], the proton-conducting ceramic showed very low hydrogen fluxes and low hydrogen transport numbers [25,38–40]. Additionally, this Faradaic efficiency decreased with increasing current density and applied bias. This effect is especially prevalent when transporting hydrogen against the chemical-potential gradient.

In this work, we investigate the effects of cerium content on the formation of leakage current in the BCZY materials. This is accomplished through fabrication and testing of three different barium cerate-zirconate compositions: BaCe_xZr_{0.9-x}Y_{0.1}O_{3-d} with $x = 0, 0.1, \text{ and } 0.2$ (BZY10, BCZY18, and BCZY27, respectively). As will be shown, the high electronic conductivity under DC bias was only observed in the BCZY27 material; BZY10 and BCZY18 did not display such properties.

2. Experimental

2.1. Sample preparation and characterizations

Thin, dense BaCe_xZr_{0.9-x}Y_{0.1}O_{3-d} membranes were co-sintered with thick NiO-BCZY27 electrode supports. The NiO-BCZY27 electrode support and BCZY electrolyte assemblies were fabricated by solid-state reactive sintering method as described by Babiniec, et al. [25]. Due to challenges encountered in synthesizing thin, uniform, dense electrolytes, all membranes were co-sintered with NiO-BCZY27 electrode supports. Use of NiO-BZY10 and NiO-BCZY18 supports did not result in gas-tight membranes.

Briefly, the electrode supports were fabricated by mixing NiO and the BCZY27 precursor powders (BaSO₄, CeO₂, ZrO₂, and Y₂O₃) in a 65:35 wt.% ratio. Polyethylene glycol (20,000 MW) was added at 10 wt.% as a binder. Pellets were uniaxially pressed at 35 MPa to a

diameter of 28 mm and subsequently dip-coated in ethanol-based slurry of the desired BaCe_xZr_{0.9-x}Y_{0.1}O_{3-d} electrolyte composition. In order to obtain a uniform thickness across the different membrane samples, and to balance the dynamic-shrinkage stresses that develop during high-temperature sintering, each pellet was completely submerged within the dip-slip solution, coating the entire electrode support with the thin electrolyte film. This dip-coating procedure was repeated five times. The electrode/electrolyte assemblies were then co-sintered at 1600 °C for 20 h in air. Following sintering, one surface of each disk was then polished to remove the “extra” electrolyte layer and expose the anode support. Finally, thin layers of gold and nickel oxide paste were painted on the electrolyte and the NiO-BCZY27 support respectively and were fired in-situ during testing.

Crystallographic phase identification of the thin membranes was completed using a PANalytical X'pert X-ray diffractometer (XRD) equipped with an X'Celerator detector. Following electrochemical-performance testing, the microstructure of each cell was observed using field-emission scanning electron microscopy (FESEM, JEOL JSM-7000).

The amount of cerium in the thin membranes was determined using a spectro-arcos inductively coupled plasma-optical emission spectrometer (ICP-OES). Briefly, the laser was scanned across the surface of the BaCe_xZr_{0.9-x}Y_{0.1}O_{3-d} electrolyte; surface atoms ablated during laser scanning diffuse into argon gas flowing over the sample surface. The ablated atoms are detected in an optical emission spectrometer, providing a qualitative measure of membrane composition.

2.2. Electrochemical performance testing

The cells were packaged within alumina manifolding as described in [25]. Silver wires were attached onto the gold and nickel electrodes in a four-point configuration. Electrochemical performance was measured using a Gamry Reference 600 potentiostat/galvanostat. The Gamry unit also served as a current source to drive the devices under electrolytic operation. A parallel combination of an Agilent Micro-GC gas chromatograph (GC) and an MKS Cirrus 2 mass spectrometer (MS) was used to measure the resulting changes in gas composition due to any flux of ions across the membrane.

In an effort to focus on the electronic conduction in the BaCe_xZr_{0.9-x}Y_{0.1}O_{3-d} membranes, perhaps-unusual gas compositions were designed for the experiments in an effort to isolate the charge carriers introduced into the membrane. As depicted in Fig. 1, the Ni-BCZY electrode was exposed to dry 10% H₂/90% Ar while the Au electrode was fed with dry 10% He/90% Ar. Helium was used as a leak-tracer. The temperature range was limited to 600–750 °C. Ultra-high purity gases were used in all cases. Some trace water-vapor is likely in these gas streams as no additional gas drying was used. Through our previous work, we expect water vapor partial pressure in both feed streams to be less than 100 ppm. Yet-lower water content could be realized through use of gas dryers.

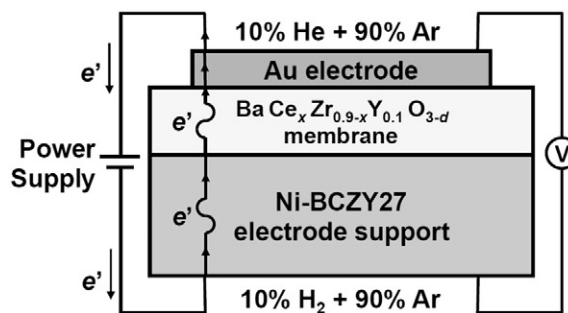


Fig. 1. Cell architecture (not to scale) and gas compositions for characterizing electronic conductivity in the BZY10, BCZY18, and BCZY27 membranes. Electrolysis operation is shown.

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