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Microstructural evolution of cobalt-doped barium cerate–zirconate at elevated temperatures under moist reducing conditions

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Abstract

Barium cerates doped with rare earth and transition metal ions are attractive candidate materials for clean-energy applications owing to their catalytic activity combined with mixed ionic–electronic conductivity for electrochemical hydrogen separation. However, the stability of these materials at elevated temperatures in the presence of moisture and CO_2 is not completely understood. In the present work, Co-doped barium cerate–zirconate pellets ($BaCe_{0.25}Zr_{0.47}Co_{0.13}O_{3-\delta}$) were exposed to a moist reducing environment at 600 °C and 927 °C for 24 h. The as-sintered and reduced pellets were sectioned using FIB and characterized using conventional TEM, STEM and XEDS. The evolution of the microstructure of the material at each step has been reported. The as-sintered material showed a tendency toward Co ex-solution resulting in the formation of a BaO–CoO phase at the grain boundaries. At elevated temperatures, reduction appeared to play a role in the transformation of the material chemistry and microstructure.

Keywords: Fuel cells; Membranes; Perovskites; Electron microscopy; Microstructure-final

1. Introduction

Diminishing fossil-fuel resources, increasing energy demands and environmental concerns have accelerated the search for alternative energy technologies capable of integration with both existing and emerging infrastructures. Polymer electrolyte membrane fuel cells (PEMFCs) operating using high-purity hydrogen are considered one of the most viable of such technologies, as hydrogen fuel may be produced from solar, wind and nuclear power via water electrolysis with a net-zero carbon footprint, or from existing fossil and emerging biomass-derived fuels. High-purity hydrogen is harvested from hydrocarbon fuels (e.g., coal, ethanol) via a combination of catalytic reforming (e.g., endothermic steam reforming and exothermic partial oxidation) and subsequent purification.[1,2] Product purification is critical, as CO and other reforming by-products (e.g., H_2S, CO_2) have deleterious effects on fuel cell performance and lifetime.[3,4]

Dense Pd films are currently the leading technology for achieving high (>1000:1) perm-selectivity toward hydrogen purification; however high material cost combined with the inability to drive hydrogen permeation rates via external electric fields (i.e., galvanic mode) limit their economic viability.[5] Electro-ceramics may provide a promising alternative to Pd for hydrogen purification, if the materials are suitably stable at elevated temperatures (400–800 °C) in reducing environments.

Solid-oxide fuel cells (SOFCs) operating at temperatures in excess of 600 °C allow for the internal reforming of hydrocarbon fuels while avoiding the deleterious effects of CO and CO_2 experienced by PEMFCs, thus removing the need for hydrogen purification. Current SOFC materials are based upon yttria-stabilized zirconia (YSZ) which requires operating temperatures of 1000 °C or more, owing to limited ionic conductivity. The development of new electro-ceramics for SOFCs has been driven by the need to reduce operating temperatures by 100 °C or more in order to mitigate material degradation and sealing challenges.[6,7] Emerging materials must be suit-

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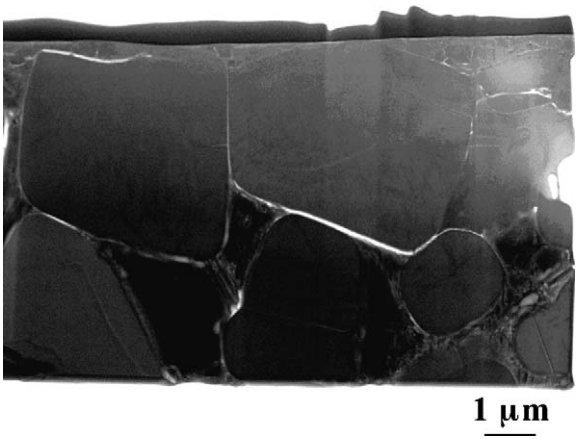

Fig. 1. FIB section of the Co-doped barium cerate–zirconate pellet after sintering at 1550 °C for 12 h.

ably stable under reducing conditions at elevated temperatures (600–900 °C).

The ABO_3 family of perovskites ($SrCeO_3$, $BaCeO_3$, $CaZrO_3$, $SrZrO_3$) has emerged as a promising alternative for addressing both hydrogen purification and SOFC challenges, with potential applications as electrolytes and in hydrogen sensors, steam concentrators, steam electrolysis, hydrogenation and dehydrogenation of organic compounds.[8–11] Doped barium cerates display combinations of protonic and oxygen-ion conductivities between 400 and 800 °C, with certain dopants introducing additional electronic conductivity.[12] Recently, our research team demonstrated that promising catalytic activity may be imparted through catalytically active transition metal dopants.[13] This combination of electrochemical and catalytic properties at intermediate temperatures makes barium cerates applicable in both SOFCs and hydrogen purification systems.

Different synthesis methods for pure and doped barium cerates and ceria have been reported in the literature as have their electrical properties.[14–18] It has been reported that barium cerates exhibit limited chemical stability under CO_2 and H_2O environments, decomposing into $BaCO_3/CeO_2$ and $Ba(OH)_2/CeO_2$ respectively.[19,20] Other studies have reported adequate practical stability of Gd-doped barium cerates under SOFC operating environments.[21–23] This indicates that the temperature, CO_2/H_2O partial pressures in the environment and the type of dopant all play a role in determining the stability of barium cerate. Doping with Zr, for example, has been reported to be a viable solution to provide a compromise between chemical stability and electrical conductivity of the cerate.[18]

In order to reduce the maintenance cost of SOFCs and in turn reduce the cost of energy, it is important to understand the stability and the course of degradation of the applied materials. A mechanistic understanding of the microstructural changes that occur during the process of degradation may generate useful insight for better design of the materials. The present work aims at understanding the microstructural and the chemical changes of Co doped barium cerate–zirconate under moist reducing conditions at 600 °C and 927 °C.

2. Experimental procedure

Cobalt-doped barium cerate–zirconate powder with a target composition of $BaCe_{0.25}Zr_{0.60}Co_{0.15}O_{3-\delta}$ was synthesized by oxalate co-precipitation. The precipitate, initially amorphous, was heat-treated at 1550 °C for 4 h. Based on XRD (X-ray diffraction) and STEM–XEDS studies, the heat-treated powder was observed to be chemically homogeneous with a single-phase cubic structure. The details of the synthesis and the structural and functional characterization have been reported elsewhere.[13] Subsequent to the initial study,[13] elemental analysis was performed on the dried precipitate obtained after the oxalate co-precipitation synthesis. The technique of inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to determine the Ba/Ce, Ba/Zr and Ba/Co mole ratios in the material.

The heat-treated powder was compacted at room temperature at ∼100 MPa and the green compact was sintered at 1550 °C for 12 h with heating and cooling rates of 5 °C/min. The sintered pellets were reduced in a 10% wet hydrogen environment

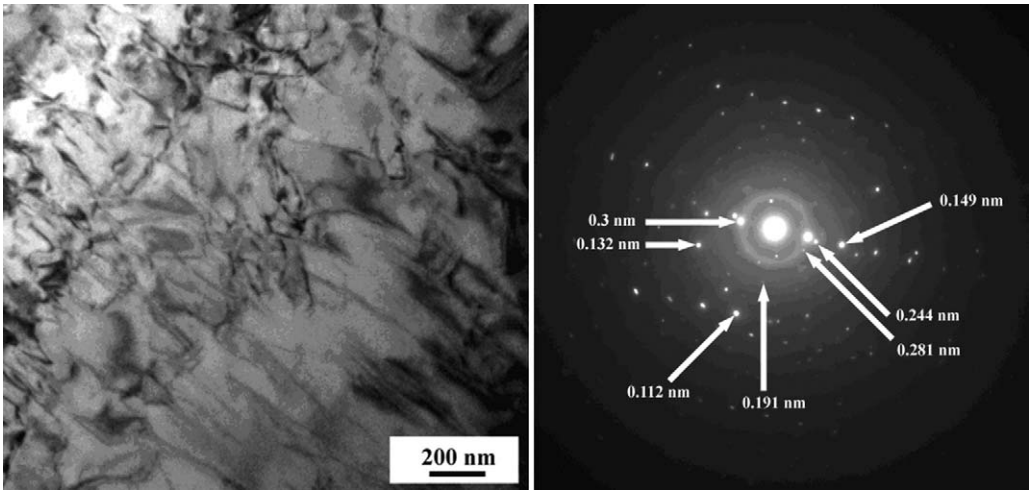

Fig. 2. TEM image of the Co-doped barium cerate–zirconate sintered sample and the diffraction pattern. Array of dislocation and defects proves the crystalline nature of the Co doped barium cerate–zirconate phase.