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Promoting the ambient-condition stability of Zr-doped barium cerate: Toward robust solid oxide fuel cells and hydrogen separation in syngas

Ying Yang[b], Yimin Zeng[d], Babak S. Amirkhiz[d], Jing-Li Luo[c], Ning Yan[a,*]

[a] Van't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Amsterdam, 1098XH, The Netherlands
[b] Department of Mechanics and Engineering Structure, Wuhan University of Technology, No.22 Luoshi Road, 430070, Wuhan, Hubei, China
[c] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 1H9, Canada
[d] CanmetMATERIALS, Natural Resources Canada, Hamilton, Ontario, L8P 0A5, Canada

HIGHLIGHTS

- Various Zr-doped barium cerates can suffer surface degradation in ambient air.
- 10 mol% doping of Sn improves ambient-condition stability of cerates.
- Sn-doped cerate shows good performances in SOFC and H_2 permeation tests.

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ABSTRACT

Increasing the stability of perovskite proton conductor against atmospheric CO_2 and moisture attack at ambient conditions might be equally important as that at the elevated service temperatures. It can ease the transportation and storage of materials, potentially reducing the maintenance cost of the integral devices. In this work, we initially examined the surface degradation behaviors of various Zr-doped barium cerates ($BaCe_{0.7}Zr_{0.1}Y_{0.1}Me_{0.1}O_3$) using XRD, SEM, STEM and electron energy loss spectroscopy. Though that the typical lanthanide (Y, Yb and Gd) and In incorporated Zr-doped cerates well resisted CO_2-induced carbonation in air at elevated temperatures, they were unfortunately vulnerable at ambient conditions, suffering slow decompositions at the surface. Conversely, Sn doped samples (BCZYSn) were robust at both conditions yet showed high protonic conductivity. Thanks to that, the anode supported solid oxide fuel cells equipped with BCZYSn electrolyte delivered a maximum power density of 387 $mW\ cm^{-2}$ at 600 °C in simulated coal-derived syngas. In the hydrogen permeation test using BCZYSn based membrane, the H_2 flux reached 0.11 $mL\ cm^{-2}\ min^{-1}$ at 850 °C when syngas was the feedstock. Both devices demonstrated excellent stability in the presence of CO_2 in the syngas.

1. Introduction

Perovskite structured oxides have garnered tremendous attention over the past decades as a promising series of high-temperature proton conductors [1–4]. They constitute the electrolyte of proton-conducting solid oxide fuel cells (PC-SOFCs) that are advantageous, in terms of the efficiency, over the conventional ones based on the oxygen ionic conductor [5]. Thanks to the excellent protonic conductivity, PC-SOFCs work nicely at a much lower temperature. This significantly reduces the materials cost and boosts the long-term stability [6–8]. Recent work has demonstrated that PC-SOFCs maintained superior performances at temperature as low as 350 °C after hundreds of hours of operation [8]. In addition, the reactors derived from PC-SOFCs also show the capabilities for alternative applications including alkene dehydrogenation, water electrolysis and CO_2 conversions [9–11]. The hydrogen pump is another key application of the perovskite proton conductor. After compositing with a suitable electronic conductor, this hybrid membrane enables spontaneous hydrogen separation with excellent selectivity [4,12]. Because no external power supply is required, this approach offers outstanding energy efficiency compared to the conventional pressure swing adsorption and the cryogenic separation techniques [13].

A wide variety of perovskite oxides exhibit protonic conductivity at elevated temperatures [1,2]. This includes doped $BaCeO_3$, $BaZrO_3$, $SrCeO_3$, $SrZrO_3$ and $LaNbO_3$, among which Y-doped barium cerates prevail owing to their excellent ionic conductivity and sinterability. Co-doping cerates using a secondary trivalent cation, e.g., Yb and Gd [14,15], can further optimize the transport properties. Nonetheless,

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[*] Corresponding author.
E-mail address: n.yan@uva.nl (N. Yan).

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many cerates are instable at elevated temperature when exposing to acidic gases (e.g., CO_2 and H_2O) [16]. Their detrimental reactions cause the decomposition of cerates and often degrade the performances of the devices. Conversely, barium zirconate is much robust, well resisting the CO_2 attack at high temperatures [16,17]. But its conductivity is much lower than that of cerate. To enhance the chemical stability and maintain the high protonic conductivity of cerate, incorporating Zr is logically and practically the most viable solution. In particular, 10–30 mol.% Zr doped cerates are of great research interest [11,12,15,18–20]. Because of their good proton conductivity and reasonable stability in mild environment at high temperatures, they have been widely applied as the membrane materials for PC-SOFC and hydrogen pump.

Despite their excellent high temperature properties, we recently discovered that the 10 mol.% zirconium doped barium cerate suffered slow degradation at ambient conditions [21], posing a great challenge for the transportation and storage of the material and potentially increasing the maintenance cost of the integral devices. In this work, we initially investigated the ambient-condition stability of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_3$, one of the classical perovskite proton conducting materials [15], and screened a number of acceptor and isovalent dopants in order to promote the robustness of cerates. The Sn doped cerate demonstrated excellent stability at both ambient and working conditions, enabling excellent yet robust PC-SOFC and hydrogen separation performances in simulated coal-derived synthesis gas.

2. Experimental

2.1. Materials preparations

The conventional sol-gel method was used to prepare the perovskite oxide powders with varied compositions, including $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_3$ (BCZY), $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}$ (BCZYYb), $BaCe_{0.7}Zr_{0.1}Y_{0.1}Sn_{0.1}$ (BCZYSn), $BaCe_{0.7}Zr_{0.1}Y_{0.1}In_{0.1}$ (BCZYIn) and $BaCe_{0.7}Zr_{0.1}Y_{0.1}Gd_{0.1}$ (BCZYGd). Initially, stoichiometric amounts of metal (oxy)nitrates were dissolved into deionized water with vigorous stirring. Then appropriate amounts of ethylenediaminetetraacetic acid (EDTA, from Acros-organis) and citric acid (CA, from Sigma-Aldrich) were added as the chelating agents. The molar ration of total metal ions: EDTA: CA was 1.5: 1: 1. The subsequent mild heating under constant agitation induced water evaporation and the gelation of the residual. The obtained gel was finally calcined at 1200 °C for 10 h to form the desired phases. Similarly, $Gd_{0.1}Ce_{0.9}O_2$ (GDC) and $PrBaCo_2O_{5+\delta}$ (PBC) powders were prepared using the same method. Glycine, however, was used as the chelating agent instead of EDTA and CA.

2.2. Materials characterizations

The powder X-ray diffraction (XRD) was performed on a Rigaku Miniflex X-ray diffractometer using CuK_α radiation ($\lambda = 1.54056$ Å). The 2-theta range was 10-90° with the step size of 0.02° and the scan rate of 2.5° min^{-1}. The morphology of the sample was characterized using a FEI Verios 460 scanning electron microscope (SEM) coupled with an energy-dispersive X-ray (EDX) detector. Transmission electron microscope (TEM) analysis was carried out using a FEI Tecnai Osiris TEM operating at 200 kV. It was equipped with a high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) detector coupled with an EDX spectrometer for elemental analysis. The sample was prepared by spreading a small amount of the powder, dispersed in ethanol, onto the copper grid. Thermogravimetric and differential scanning calorimetric (TGA-DSC) analysis was carried out using the NETZSCH Jupiter® STA 449F3. All the measurements were done in the temperature range of 30–900 °C in air flow with a flow rate of 20 mL min^{-1} at a heating rate of 5 °C min^{-1}.

2.3. Procedures of cerate stability test

The ambient-condition stability test of various cerates was carried out at room temperature (21 °C) in humidified ambient air (relative humidity = 98–100%). The sample powder was placed and sealed in a quartz tube. Humidified air was continuously passed through for 72 h. The stability test of BCZYSn in simulated coal-derived syngas (40% H_2 + 60% CO, certified and provided by Praxair, Inc.) was performed likewise. The tube was mounted in a tubular furnace to be heated to the designed temperatures.

2.4. Procedures of electrochemical test

A detailed PC-SOFC button cells fabrication procedure was reported in our previous work [22]. In brief, the BCZYSn electrolyte ink was spin-coated on the pre-calcined porous NiO-BCZYSn support, a subsequent 5 h sintering at 1420 °C fully densified the electrolyte. Then the PBC-BCZYSn cathode ink was applied onto the opposite side of the dense electrolyte to form the cathode after 2 h calcination at 1000 °C. In the electrochemical test, gold paste was applied onto both electrodes as the current collector. The button cell was mounted between a pair of coaxial alumina tube in the furnace. Before the test, the cell was reduced in a stream of 5% H_2 + N_2 and then conditioned in humidified H_2 (*ca.* 3 vol % water vapor). During the test, the impedance and current–voltage characteristics were determined using a Solartron 1287 electrochemical interface together with a 1255B frequency response analyzer. The hydrogen flow rate was 50 mL min^{-1} whereas the oxygen flow rate at the cathode was also 50 mL min^{-1}. The conductivity of the BCZYSn disc was determined at the designed temperatures in humidified hydrogen environment using the two-electrode configuration via the electrochemical impedance spectroscopy. All the impedance spectra were obtained under open circuit with the AC amplitude of 10 mV and the frequency range from 0.1 Hz to 100 kHz.

2.5. Procedures of hydrogen permeation test

To prepare the hydrogen permeation membrane, equal amount of BCZYSn and GDC powders were homogenized thoroughly by ball milling in isopropanol. The dried mixture was pressed into pellet and densified at 1400 °C for 10 h. The obtained membrane disc was grinded and polished at both sides; the final thickness was controlled at 0.6–0.7 mm. The SOFC test setup was adapted and used to measure the hydrogen permeability. Before mounting to this setup, Pt paste was applied onto both sides of the disc as the porous catalytic layer for hydrogen activation. In the test, hydrogen was separated from both 50% H_2 balanced by He and the simulated coal-derived syngas; Ar was used as the sweep gas at the permeate side. The flow rates were 100 mL min^{-1} at both the feed and permeate sides. All the gas composition analysis was determined by the gas chromatography (GC, Agilent 6890N).

3. Results and discussion

3.1. Surface degradation of doped cerate at ambient conditions

Thermodynamically, pure $BaCeO_3$ and $BaZrO_3$ are both instable below 500 °C (see Fig. 1a). For instance, the ΔG reaches -95 kJ mol^{-1} at 25 °C for the carbonation reaction of $BaZrO_3$. Fortunately, the sluggish kinetics of such degradation at ambient conditions often suppresses the progress of the reaction. However, with the presence of high-level humid, this detrimental reaction might proceed rapidly. To examine the kinetically stability at ambient condition, we selected BCZYYb, one of the classical proton-conducting materials that exhibits high proton conductivity and reasonable chemical stability at high temperatures, as the studying sample. The STEM-HAADF image in Fig. 1b shows the morphologies of BCZYYb powder after the 72 h stability test in humid