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Evaluation of $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$ perovskite as a cathode for proton-conducting solid oxide fuel cells: The possibility of *in situ* creating protonic conductivity and electrochemical performance

Ankang Zhu [a], Guilin Zhang [a], Tingting Wan [a], Tingting Shi [a], Hong Wang [a], Mingzai Wu [a], Chunchang Wang [a], Shouguo Huang [a], Youmin Guo [a, *], Hao Yu [b], Zongping Shao [c, d]

[a] *School of Physics and Materials Science, Anhui University, No.111 Jiulong Road, Hefei, 230601 China*
[b] *College of Chemical and Environmental Engineering, Shandong University of Science and Technology, 266590, Qingdao, China*
[c] *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, No.5 Xin Mofan Road, Nanjing, 210009, China*
[d] *Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia*

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ABSTRACT

Proton-conducting solid oxide fuel cells (H^+-SOFCs) have attracted considerable interest recently. However, the overall cell performance of H^+-SOFCs is still low due to the lack of a promising cathode material. In this study, $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$ (SSNC) was synthesized for evaluation as a cathode material in H^+-SOFCs based on a $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte. The chemical compatibility and stability of the SSNC cathode with the BZCY electrolyte in humidified air were studied. In addition, the electrochemical behavior of the SSNC cathode on the BZCY electrolyte was investigated using SSNC/BZCY/SSNC symmetrical cells at 600 °C in dry air and humidified air at various H_2O partial pressures. Promising electrocatalytic activity was observed for the SSNC cathode in humidified air. The area specific resistance obtained on symmetrical cells at 600 °C in a 10% H_2O-air atmosphere was 0.26 Ω cm^2. A promising peak power density of 498 mW cm^{-2} was obtained using an anode-supported cell with a 46 μm-thick BZCY electrolyte layer at 700 °C.

1. Introduction

Solid oxide fuel cells based on proton-conducting electrolytes (H^+-SOFCs) show the competitive advantages of low activation energy and high ionic conductivity of the electrolyte at lower temperatures over SOFCs based on oxygen ion-conducting electrolytes (O^{2-}-SOFCs) [1–3]. This high ionic conductivity of the electrolyte at low temperatures allows H^+-SOFCs to operate at intermediate-to-low temperatures (400–700 °C), which minimizes the thermal degradation of the components of these SOFCs and reduces the duration of start-up and shut-down procedures [4,5]. However, operation at$<$750 °C presents some challenges in terms of the lower electrocatalytic activity of cathode materials for the oxygen reduction reaction [6,7] In addition, unlike O^{2-}-SOFCs, H_2O is formed at the cathode side of H^+-SOFCs. Because of this formed water vapor, cathode materials in H^+-SOFCs may have some specific requirements.

A number of classic mixed ionic (O^{2-}) and electronic (e^-) conducting (MIEC) oxides, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [8–10], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [11], $PrBaCo_2O_{5+\delta}$ (PBC) [12], $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$(BCFN) [13] and $BaFe_{0.6}Co_{0.3}Ce_{0.1}O_{3-\delta}$ (BFCC) [14], have been employed as potential cathode materials for H^+-SOFCs. However, when these MIEC oxides are used, H_2O is formed only at the three-phase boundary (TPB) near the electrolyte/electrode interface and must be flowed out through the electrode. To extend the reaction area, composite electrodes have been made, generally by introducing protons (H^+) into MIEC oxides by mixing of proton-conducting electrolyte materials with MIEC oxides [15–17]. Indeed, the protons (H^+) introduced in the composite cathodes can diffuse from the electrolyte through the cathode bulk, which would promote the active area of the electrochemical reaction from the TPB to the entire cathode surface [18]. However, an interfacial phase reaction may occur between MIEC oxides and proton conducting electrolyte materials, this reaction produces

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* Corresponding author.
E-mail address: youminguo@ahu.edu.cn (Y. Guo).

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undesirable phases and limits the ionic migration through the cathode surface, resulting in the increase of cathode polarization [19]. Therefore, single phase oxides possessing oxygen ionic (O^{2-}), electronic (e^-) and protonic (H^+) conductivities (also known as triple conducting materials) are highly desirable for H^+-SOFCs.

Very recently, triple conducting materials (O^{2-}/e^-/H^+) have been developed as promising cathode materials for H^+-SOFCs, such as $BaZr_{0.1}Co_{0.4}Fe_{0.4}Y_{0.1}O_{3-\delta}$, $NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ and $LiNi_{0.8}Co_{0.2}O_2$, allowing the simultaneous conduction of intrinsic oxygen ions and electrons as well as extrinsic protons [20–23]. However, the development of suitable cathode materials for H^+-SOFCs is still ongoing because of the limited range for cathode materials with triple conducting properties. Interestingly, recent works have demonstrated the possibility of creating *in situ* protonic conductivity in classic MIEC oxides during fuel cell operation via humidification of the cathode by the formed water vapor [9,21,24,25]. For instance, Grimaud et al. reported that proton conductivity was successfully created in BSCF and PBC bulk over a long period of operation and that the created proton conductivity in BSCF and PBC could extend the TPB deep into the entire cathode surface, leading to a decrease in cathode polarization resistance [9,10]. This result suggests that the *in situ* creation of proton conductivity in MIEC oxides by humidifying the cathode using the H_2O formed at the cathode is a feasible strategy.

$SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$(SSNC) perovskite has previously been reported to exhibit a high bulk oxygen diffusion rate below 550 °C and to show good oxygen reduction reactivity when interfaced to an oxygen ion conducting electrolyte [26]. In addition, compared to BSCF, SSNC has demonstrated superior CO_2 tolerance [27]. In this study, the application of SSNC as a cathode for H^+-SOFCs with a proton conducting $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) electrolyte is reported. More importantly, the possibility to *in situ* create proton conductivity in the SSNC cathode by humidification is emphasized, and promising results are reported.

2. Experimental

2.1. Synthesis

Both $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$ (SSNC) and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) powders were prepared by the sol-gel method with citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) as parallel complexing agents. For SSNC, stoichiometric amounts of $Sr(NO_3)_2$ (AR, Sinopharm Chemical Reagent Co., Ltd), $Sc(NO_3)_3$ (AR, Aladdin Reagents), $C_{10}H_5NbO_{20}$ (AR, Aladdin Reagents) and $Co(NO_3)_2\cdot 6H_2O$ (AR, Sinopharm Chemical Reagent Co., Ltd) were dissolved in deionized water under heating and stirring. Appropriate amounts of CA and EDTA were added to the solution at a ratio of 2:1:1. Furthermore, ammonia water was also added to adjust the pH value of the aqueous solution to ~8. The solution was heated and stirred until it was converted to a viscous gel and then was transferred into an oven at 240 °C for 6 h. The obtained ash was then calcined at 1000 °C for 5 h in air to obtain a pure SSNC perovskite phase. For BZCY, the major steps for powder synthesis were similar to those for SSNC, except that the starting materials were $Ba(NO_3)_2$, $Zr(NO_3)_4\cdot 5H_2O$, $Ce(NO_3)_3\cdot 6H_2O$ and $Y(NO_3)_3\cdot 6H_2O$. The calcinations conditions were also the same as those for the SSNC powders. The phase structure of the synthesized SSNC was examined using an X-ray diffractometer (XRD, Smartlab), which was equipped with a CuKα radiation source (1.5406 Å) and operated at 40 kV and 30 mA at a scan rate of 1° min^{-1} between scanning angles (2θ) of 20 and 80°. The pseudo Voigt function was adopted as the profile function in Rietveld refinement computation.

2.2. Chemical compatibility and stability test

The chemical compatibility between the SSNC cathode and the BZCY electrolyte was investigated in a typical cell fabrication process as follows: SSNC and BZCY were first well-mixed in powder form at a mass weight ratio of 1:1 and pressed into a pellet under 200 MPa pressure. Then, the pellet was cut into several pieces and calcined at a temperature range of 700–1100 °C for 2 h, respectively. After sintering, the sample was ground into powder for analysis. To test the chemical stability of SSNC in humidified air, SSNC powder was exposed to 3%H_2O-air or 3%H_2O-O_2 atmospheres at 700 °C for up to 10 h. After the various chemical compatibility and stability tests, the samples were analyzed by X-ray diffraction (XRD, operating at 9 kW with Cu Kα radiation) and Fourier transform-infrared spectroscopy (FT-IR, VERTEX80).

2.3. Preparation of symmetrical cells and single cells

To prepare the symmetrical cells with the configuration of SSNC/BZCY/SSNC, dense ~1 mm thick BZCY disks were first fabricated by uniaxially pressing the synthesized BZCY powder at ~120 MPa and then firing at 1450 °C for 5 h. The SSNC powder was added with proper amounts of ethylene glycol, isopropanol and glycerine in a mortar-pestle and then ground to obtain an SSNC ink with the desired viscosity. Porous SSNC electrodes were prepared by spray coating the SSNC ink onto both sides of BZCY electrolyte disks and firing at 1000 °C for 2 h. Finally, a diluted silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins) was painted on the SSNC electrodes as a current collecting layer. The final symmetrical cells had a geometric surface area of 1.13 cm^2 for each one of electrodes.

Single cells with the configuration of NiO + BZCY/BZCY/SSNC were also fabricated. First, the synthesized BZCY powder was mixed with commercial NiO (AR, Sinopharm Chemical Reagent Co., Ltd) and polyvinyl butyral (PVB) at a weight ratio of 40:60:5 by ball-milling in ethanol for 2 h. The mixture was dried and ground into NiO + BZCY anode powder. Approximately 0.4 g of the NiO + BZCY powder was pressed into a green pellet with a diameter of 15 mm under 100 MPa pressure as an anode substrate, and then 0.04 g of BZCY powder was applied on the NiO + BZCY substrate as a thin-film electrolyte by dual dry pressing. The NiO + BZCY|BZCY dual layer was calcined at 1450 °C for 5 h. Finally, an SSNC cathode was prepared on the surface of the BZCY electrolyte by spray coating and sintered at 1000 ̊Cfor 2 h. Diluted silver paste was also painted on the SSNC cathode as a current collecting layer. The single cells investigated in this study had an active area of 0.4 cm^2. The microstructure of the cross-section of the tested single cells was observed using a scanning electron microscope (SEM, Hitachi S-4800).

2.4. Electrical conductivity and electrochemical characterization

Electrical conductivity measurements of the SSNC electrodes were performed using the standard four-point DC technique on sintered rectangular bars. The SSNC powders were pressed and sintered at 1200 °C for 5 h to obtain the dense bars. Silver paste and silver wires were used as electrical contacts. The measurements were conducted under either dry air or humidified air with various H_2O partial pressures in the temperature range of 350–800 °C at increments of 25 °C. The constant current was supplied by a programmable current source, and the voltage drop through the SSNC samples was detected by a source meter (Keithley 2420).

The prepared SSNC|BZCY|SSNC symmetrical cells were tested via electrochemical impedance spectroscopy (EIS) in two-point configurations. The EIS measurements were performed under dry