In situ formation of a 3D core-shell and triple-conducting oxygen reduction reaction electrode for proton-conducting SOFCs

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Abstract: $\text{BaZr}_x\text{Ce}_{1-x}\text{Y}_2\text{O}_{7-\delta}$ compositions are recognized proton-conducting electrolyte materials for proton-conducting solid oxide fuel cells (H⁺-SOFCs) below 650 °C. Here Co cations are incorporated into the $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) scaffold to generate a 3D core-shell and triple-conducting (H⁺/O²-/e⁻) electrode in situ via infiltrating and reactive sintering. The core is the bulk BZCY scaffold, while the shell is composed of the cubic $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$, cubic spinel Co_3O_4 and cubic fluorite $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$. The obtained electrode exhibits an excellent compatibility with the BZCY electrolyte, and performs well in yielding a low and stable polarization resistance for oxygen reduction reaction for intermediate-temperature H⁺-SOFCs. In particular, it achieves polarization resistances as low as 0.094 and 0.198 Ω cm² at 650 and 600 °C in wet air (3 % H₂O) when the sintering temperature for the electrode is 900 °C. In addition, a symmetrical cell also exhibits operation stability of 70 h at 650 °C. Furthermore, a fuel cell assembled with the 3D core-shell and triple-conducting electrode delivers a peak power density of ~330 mW cm⁻² at 650 °C. The substantially improved electrochemical performance and high stability are ascribed to the unique core-shell structure and the formation of $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ in the shell.

Highlights

- A 3D core-shell and triple-conducting ($H^+ / O^{2-} / e^-$) electrode is in situ formed.
- An optimal sintering temperature for the construction of the electrode is 900 °C.
- The constructed electrode is promising for the oxygen reduction reaction.
- A low polarization resistance is as low as $0.198 \Omega \text{ cm}^2$ at 600 °C.

**In situ formation of a 3D core-shell and triple-conducting oxygen
reduction reaction electrode for proton-conducting SOFCs**

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Abstract

BaZr_xCe_yY_{1-x-y}O_{3-δ} compositions are recognized proton-conducting electrolyte materials for proton-conducting solid oxide fuel cells (H⁺-SOFCs) below 650 °C. Here Co cations are incorporated into the BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-δ} (BZCY) scaffold to generate a 3D core-shell and triple-conducting (H⁺/O²⁻/e⁻) electrode in situ via infiltrating and reactive sintering. The core is the bulk BZCY scaffold, while the shell is composed of the cubic Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-δ}, cubic spinel Co₃O₄ and cubic fluorite (Ce, Zr, Y)O₂. The obtained electrode exhibits an excellent compatibility with the BZCY electrolyte, and performs well in yielding a low and stable polarization resistance for oxygen reduction reaction for intermediate-temperature H⁺-SOFCs. In particular, it achieves polarization resistances as low as 0.094 and 0.198 Ω cm² at 650 and 600 °C in wet air (3 % H₂O) when the sintering temperature for the electrode is 900 °C. In addition, a symmetrical cell also exhibits operation stability of 70 h at 650 °C. Furthermore, a fuel cell assembled with the 3D core-shell and triple-conducting electrode delivers a peak power density of ~330 mW cm⁻² at 650 °C. The substantially improved electrochemical performance and high stability are ascribed to the unique core-shell structure and the formation of Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-δ} in the shell.

Keywords: Proton-conducting solid oxide fuel cell; Triple-conducting electrode; Core-shell structure; Infiltration; Reactive sintering

1. Introduction

Solid oxide fuel cells (SOFCs), among various types of fuel cells, have a great potential to combine the benefits of the high energy conversion efficiency, fuel flexibility, and relatively low cost (without using precious catalysts). The particularly high operating temperature (i.e. $>800\text{ }^{\circ}\text{C}$) hinders the further commercialization of SOFCs due to the high operation cost and materials degradation caused by chemical and/or mechanical incompatibility [1-8]. During the last decade, great efforts have been made to maintain high electrochemical performance while lowering the operating temperatures of SOFCs to the intermediate-temperature to low-temperature range, e.g. $500\text{-}750\text{ }^{\circ}\text{C}$ [8-19]. This operation temperature range could make this efficient electrochemical conversion device more economically competitive and prolong its lifetime.

Recently, SOFCs employing proton-conducting electrolytes (H^+ -SOFCs) have received increasing attention on developing the electrolyte composition, thin-film fabrication, mechanism understanding and so on [20-28]. Proton-conducting electrolytes with the prominent advantage of the low activation energy for the proton transport show a great potential to lower the operation temperature of SOFCs [28, 29]. Moreover, H^+ -SOFCs can prevent water evolution and fuel dilution on the anode side during the operation, leading to higher fuel utilization and a higher Nernst potential in comparison to traditional SOFCs based on oxygen ion conductors [30-33]. Furthermore, H^+ -SOFCs have advantages of higher CH_4 conversion efficiency and higher carbon coking

1 resistance over oxygen-conducting SOFCs [34, 35]. Among various proton
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3 conductors for H⁺-SOFCs, BaZr_xCe_yY_{1-x-y}O_{3-δ} combines the advantages of barium
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5 cerate-based materials (high proton conductivity) and barium zirconate-based
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7 materials (outstanding chemical stability in H₂O- and CO₂-containing conditions),
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9 displaying relatively high proton conductivity and sufficient chemical stability
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11 over a wide range of fuel cell operation conditions [30, 36, 37]. However, it is
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13 unexpected that H⁺-SOFCs assembled with the developed BaZr_xCe_yY_{1-x-y}O_{3-δ}
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15 proton conductors still fail to delivery satisfactory performance as expected based
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17 on the high intrinsic conductivity of those proton-conducting electrolytes [28].
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19 The reasons why H⁺-SOFCs lags far behind the oxygen-conducting SOFC are
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21 mainly due to the lack of proper cathode materials and poor compatibility
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23 between the existing cathode and the electrolyte.
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27 Cathode materials applied for H⁺-SOFCs are generally what have been
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29 initially and successfully designed for traditional SOFCs with doped ceria or
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31 LaGaO₃-based electrolytes [36, 38-41]. Unfortunately, the cathodic
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33 overpotentials/polarization resistances in H⁺-SOFCs are much larger than what
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35 are obtained in traditional SOFCs. For example, many well-studied mixed ionic
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37 and electronic materials, e.g. Sm_{0.5}Sr_{0.5}CoO_{3-δ} [36], PrBaCo₂O_{5+δ} [38],
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39 Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} [40], and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} [41] have been
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41 extensively selected as cathodes for H⁺-SOFCs, but they showed larger
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43 polarization resistances than those when assembling them on doped ceria
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45 electrolyte or LaGaO₃-based electrolyte. Lin et al. reported that the electrode
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polarization resistance of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode on $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ at 600 °C was $0.73 \Omega \text{ cm}^2$ [38], while a smaller polarization resistance of $\sim 0.4 \Omega \text{ cm}^2$ for $\text{PrBaCo}_2\text{O}_{5+\delta}$ on samarium-doped ceria was achieved at 600 °C [42]. The unsuccessful use of these superior mixed oxygen ion and electron conducting (MIEC) cathode materials on proton electrolytes is mainly due to the limited electrochemically reaction active sites on the interface [30, 43]. Therefore, designing a mixed proton (H^+), oxygen ion (O^{2-}), and electron conducting (e^-) conducting (triple conducting) cathode is a reasonable approach for the development of H^+ -SOFCs [20, 28, 30, 41]. Traditionally, incorporating proton electrolytes into MIEC oxides was reported to produce active sites. Recently, Kim et al. proposed a layered perovskite oxide (i.e. $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$) as a triple-conducting electrode due to the better proton-conducting properties than other perovskite-related materials [30]. Very Recently, Duan et al. developed a new cathode with the composition of $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ for high-performance low-temperature H^+ -SOFCs, which exhibited a simultaneous conduction of H^+ , O^{2-} and e^- in a single phase [20]. Applying these triple-conducting materials, the electrochemically reaction active sites can extend from the interface between the electrode and the electrolyte to the entire surface of the electrode [20, 30].

The chemical and mechanical compatibility between cathode materials and proton conductors (e.g. BZCY) is another critical issue for the development of practical SOFCs. It has been reported that the formation of interfacial phase

between two phases would significantly block the proton transportation. Lin et al, found that the interfacial phase was formed when sintering the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathode on $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ at 1100 °C, and they also observed that this undesirable reaction could greatly degrade the electrochemical performance [40]. The high content of Co cations in some designed perovskite oxides to increase electrochemical performance could also result in a large thermal expansion coefficient. To eliminate the formation of undesired phases, mediate the thermal expansion mismatch, and enhance the durability of the H^+ -SOFCs, applying the infiltration method to fabricate a cathode layer on a electrolyte scaffold could be a promising approach [44-46]. Traditionally, nano-structured particles will be deposited by infiltration and sintering at a relatively low temperature (e.g. 800 °C) to alleviate the undesirable reactions and to enhance the electrochemical activity, but this technique is not suitable for the development of cathodes for H^+ -SOFCs since no triple-conducting phase is formed if low-sintering temperature was applied. As suggested, a cathode with proton, oxygen ion, and electron conductivity is the preference for the enhancement of the electrochemical performance. Recently, Chen et al. employed a new approach combined the infiltration and high-temperature sintering to construct an efficient oxygen reduction electrode on $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) with a 3D core-shell architecture [47]. The resultant electrode is composed of a stable porous scaffold as the core for bulk oxygen ion diffusion, and a connective thin film as the shell with both ionic and electronic conductivity for the efficient

oxygen reduction reaction. Following the combined infiltration and high-temperature sintering approach, a cathode with a stable porous scaffold as the core for bulk proton diffusion, and a connective thin film as the shell for the simultaneous conduction of proton, oxygen ion, and electron, might be designed for H^+ -SOFCs by replacing SDC with $BaZr_xCe_yY_{1-x-y}O_{3-\delta}$.

In this study, a unique 3D electrode with proton, oxygen ion, and electron conductivity (a triple-conducting electrode) were in situ prepared by infiltration and high-temperature sintering. The solid state reaction between Co^{2+} and $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$ (BZCY) after firing at a relatively high temperature leads to beneficial oxide products, including $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$, $(Ce, Zr, Y)O_2$, and Co_3O_4 . $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$ offers conducting pathways for proton, electron, and oxygen ion. $(Ce, Zr, Y)O_2$ and Co_3O_4 additionally help conducting oxygen ion and electron, respectively. Therefore this triple-conducting electrode greatly increases the number of active sites, facilitating the electrochemical oxygen reduction reaction. A typical symmetrical cell with the 3D cathode has demonstrated low polarization resistances of 0.058, 0.094, 0.198, and 0.409 Ωcm^2 at 700, 650, 600, and 550 $^{\circ}C$, respectively, in wet air atmosphere. In addition, a typical symmetrical cell with the 3D cathode has also exhibited operation stability of 70 h at 650 $^{\circ}C$.

2. Experimental

2.1. Powder Synthesis

$BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$ powder was synthesized by modified sol-gel method with

both ethylene diamine tetraacetic acid (EDTA) and citric acid (CA) as complexing agents [38, 48]. According to the cation stoichiometry, $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in analytical grade (Sinopharm Chemical Reagent Co., Ltd) were weighted as raw materials and added into the deionized water to form a clear solution. EDTA and CA were added to the heated and stirred solution at a molar ratio of 1: 1: 2 for total metal ions : EDTA : CA. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to adjust the pH of the solution to ~6. A transparent gel was obtained by continuously evaporating H_2O from the solution under stirring and heating, and the obtained gel was pre-fired at 250 °C in an oven. The solidified product was calcined at 1100 °C for 10 h in air to finally obtain pure-phase powders with the nominal composition of BZCY and a desired cubic structure.

2.2. Fabrication of Symmetrical Cell and Complete Fuel Cell

Fabrication of a symmetrical cell with the configuration of electrode|BZCY|electrode was divided into 3 sub-steps, as schematically shown in Fig. S1. First, a dense BZCY electrolyte with a thickness of 0.6 mm and diameter of 11.5 mm was fabricated by pressing and sintering in air at 1550 °C for 5 h. Second, porous BZCY scaffold was fabricated by symmetrically spraying deposition of BZCY powder on the both surfaces of the dense electrolyte, and then they were sintered in air at 1200 °C for 5 h to obtain a well-connected scaffold with a porosity of ~50%. The solution for spraying deposition was prepared by mixing 90 wt.% BZCY and 10 wt.% starch with an appropriate amount of alcohol, glycerol, ethylene glycol and isopropyl under high-energy ball milling (Fritsch, Pulverisette 6) at a rotation speed

of 400 rpm for 30 min. Third, the solution infiltration and high-temperature sintering was applied to in situ prepare the 3D core-shell electrode consisted of desired compositions and phases. The solution contained $\text{Co}(\text{NO}_3)_2$ with the concentration of 0.8 mol L^{-1} for infiltration was dissolved in the solution of water and ethanol with a volume ratio of 3: 1, and glycine at a molar ratio of glycine to Co^{2+} of 2 : 1 was also added in the solution. The infiltration (where microliter syringe was used) and low-temperature firing (400°C) procedures were repeated for several times until the final loading reached about 35 wt.% of the electrode. The porous BZCY|dense BZCY|porous BZCY pellet was put on a hot plate (80°C) to accelerate the gas expulsion and to enhance the liquidity of solution in the porous scaffold. After the infiltration, the pellets were fired in air for 2 h at 800, 900 and 1000°C , respectively. Silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins) was used as current collector for electrochemical performance evaluation, while a mesh-like silver current collector is applied to electrode for the stability test. The electrode area is 1.04 cm^2 .

Anode-supported fuel cells with thin BZCY electrolyte ($\sim 25 \mu\text{m}$) and 40 wt.% BZCY + 60 wt.% NiO + 10 wt.% starch composite anode were prepared via dry-pressing and subsequent high-temperature sintering. The preparation of the infiltrated BZCY cathode was same to the fabrication of the electrode for symmetrical cells, but the effective surface area of cathode for fuel cells is 0.48 cm^2 .

2.3. Characterizations

Room-temperature phase structure of as-prepared powder was determined using

1 X-ray diffraction (XRD, Bruker D8 Advance) with Cu-K α radiation at 40 kV and 100
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3 mA in the scan range of 20-80°. Rietveld refinement on the zero point, lattice
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5 parameters, optimized scale factor, and peak shape was carried out by the GSAS
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7 software. The phase structure and microstructure were further determined by scanning
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9 transmission electron microscope (STEM) and the corresponding energy-dispersive
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11 X-ray (EDX) mappings, which were collected using a FEI TITAN transmission
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13 electron microscope equipped with an EDX detector. Microstructure of prepared
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15 electrodes was illustrated using environmental scanning electron microscopy (ESEM,
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17 QUANTA-2000) and the elemental distribution in electrodes was clarified by EDX
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19 spectroscopy (EDAX GENESIS 2000). The thermal expansion of the dense BZCY
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21 and infiltrated BZCY pellets was tested using a dilatometer (NETZSCH DIL402C).
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23 The electrical conductivity was determined using a four-probe DC technique on the
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25 sintered pellets within the temperature range from 300 to 900 °C.
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35 **2.4. Electrochemical Measurement**

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37 Electrochemical performance of symmetrical cells was studied via
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39 electrochemical impedance spectra (EIS) using Solartron 1287 and 1260A
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41 electrochemical workstation. Frequency range for EIS was from 0.1 to 10⁶ Hz and
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43 amplitude of 10 mV was applied. Electrodes were tested from 600 to 750 °C in both
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45 synthetic air and H₂O-containing air with a flow rate of 100 mL min⁻¹. The stream
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47 content of 3 vol.% was controlled by heating the beaker at 25 °C. The stability of a
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49 symmetrical cell was examined at 650 °C for 70 h in synthetic air with a flow rate of
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51 100 mL min⁻¹. Current-voltage (*IV*) and current-power (*IP*) curves of anode-supported
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fuel cells with the infiltrated BZCY electrode were collected using a digital source meter (Keithley 2420) based on a four-terminal configuration. During the test, the cathode side was exposed to ambient air, while H₂ was fed into the anode side as the fuel gas at the flow rate of 80 mL min⁻¹.

3. Results and Discussion

The phase structure of the synthesized BZCY was first examined by room-temperature XRD. Typical XRD patterns of the powder BZCY, dense BZCY membrane, and porous BZCY/dense BZCY (p/d BZCY) are presented in Fig. 1a. As seen, no detectable impurities are found in all samples and the obtained patterns are in line with literatures [49, 50]. In order to obtain more information on the phase structure, dense BZCY membrane as a representative was subjected to Rietveld refinement (Fig. 1b). The XRD pattern is well refined based on a cubic structure with the space group of *Pm-3m*. The obtained lattice parameters are $a = b = c = 4.3043$ (1) Å, which agree well with the literatures for BZCY [49, 50]. These results suggest that a single-phase BZCY was successfully synthesized via sol-gel method.

Fig. 1 XRD patterns of the powder BZCY, dense BZCY, and porous BZCY/dense BZCY at room temperature (a), and XRD pattern with Rietveld refinement of the dense BZCY (b). The reliability factors for the dense BZCY are $R_{wp} = 9.06\%$, $R_p = 6.85\%$ and $\chi^2 = 13.11$.

Fig. 2 XRD patterns of the $\text{Co}(\text{NO}_3)_2$ precursor infiltrated BZCY after sintering at 800, 900 and 1000 °C (a), and XRD pattern with Rietveld refinement of the infiltrated electrode after sintered at 900 °C (b).

The impregnation method has been widely applied to develop efficient electrodes for SOFCs [44-46]. Determining phases in the electrode after infiltration and sintering is of importance for the clarification of the active phases for electrochemical performance. Typical room-temperature XRD patterns of the $\text{Co}(\text{NO}_3)_2$ precursors infiltrated porous BZCY scaffold after heat treatment at different temperatures are exhibited in **Fig. 2a**. As observed, newly formed reflection peaks appear in the XRD patterns, suggesting the phase reaction between BZCY and $\text{Co}(\text{NO}_3)_2$ occurs after high-temperature calcination. Meanwhile, the characteristic peaks of the infiltrated p/d BZCY, e.g. (110), (111), and (200), shift to a higher 2θ after heat treatment when compared to the peaks of the fresh p/d BZCY. This strongly suggests that Co^{2+} cations from the infiltration solution diffuse into the lattice structure of BZCY. The right shift of peaks is closely related to the ionic radius of cations in BZCY since the ionic radius of Co^{m+} (VI) ($m = 2, 3$, and 4) is much smaller than those of B-site cations in BZCY according to the database (Co^{m+} (VI, 0.530-0.745 Å), Zr^{4+} (VI, 0.72 Å), Ce^{x+} (VI, 0.87-1.01 Å), and Y^{3+} (VI, 0.90 Å)). The diffusion of Co^{m+} from cathode materials to

electrolytes has been widely recognized during the calcination, which agrees well with previous reports [51-53]. It should be noted that a higher heat treatment temperature shows limited influence on the peak shift, suggesting that the amount of cation diffusion is limited under such conditions.

To acquire more in-depth information on the phase structures after infiltration and sintering, the infiltrated electrode fired at 900 °C was selected as a representative to perform Rietveld refinement (Fig. 2b). The XRD pattern is indexed as a mixture of 54.3 wt.% $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$, 29.5 wt.% Co_3O_4 and 16.2 wt.% $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$. $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ shows a cubic structure with the space group of $Pm-3m$ and lattice parameters of $a = b = c = 4.2339(4) \text{ \AA}$. Co_3O_4 presents a cubic spinel structure with the space group of $Fd-3m$. $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$ exhibits a cubic fluorite phase with the space group of $Fm-3m$. A low error ($R_p = 4.43\%$, $R_{wp} = 5.73\%$, and $\chi^2 = 1.564$) suggests a goodness of the fitting. Therefore we conclude that the infiltrated electrode contains BZCY (proton conductor), $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (triple-conducting composition), $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$ (ionic conductor), and Co_3O_4 (electronic conductor).

The morphological structure of electrodes is important for achieving high electrochemical performance [54]. Therefore, all prepared electrodes were subjected to ESEM observations to investigate the adhesion between the dense BZCY electrolyte and electrodes, as well as the microstructure of symmetrical cells. As presented in Fig. S2, it is obviously found that the thicknesses of all prepared electrodes are ~20 μm . Meanwhile, the electrodes are porous, providing channels for the gas diffusion and providing active sites, thus able to minimize the polarization

resistance [54]. Noted that no cracks are observed between the BZCY electrolyte and infiltrated electrodes, which could reduce the interfacial polarization and ensure an efficient charge transfer.

The electrocatalytic activity of the infiltrated BZCY electrodes was examined in a symmetrical cell with a BZCY electrolyte by EIS under air and wet air. Fig. 3 summarizes temperature-dependent polarization resistances of typical symmetrical cells with the pure silver paste, fresh porous BZCY, and infiltrated BZCY as electrodes. As shown in Fig. 3a, the polarization resistances of the electrode with a porous BZCY layer are much higher than those of pure silver as the electrode, indicating that a porous BZCY layer itself cannot be regarded as an efficient electrode since only protons are transferred. Obviously, infiltrated electrodes exhibit much lower polarization resistances than the porous BZCY electrode. Among them, the electrode fired at 900 °C displays the lowest polarization resistances, i.e., 0.030, 0.078, 0.196, and 0.471 $\Omega \text{ cm}^2$ in dry air at 750, 700, 650, and 600 °C, respectively. As shown in Fig. 3b, polarization resistances of the symmetrical cells are further lowered in wet air (3% H_2O). For example, the electrode fired at 900 °C shows polarization resistances of 0.058, 0.094, 0.198, and 0.409 $\Omega \text{ cm}^2$ at 700, 650, 600, and 550 °C in wet air (3% H_2O). The decreased polarization resistances in wet atmosphere have successfully demonstrated that the designed electrode is a proton conductor under wet atmosphere [55-57]. These polarization resistances are comparable to the optimized electrode with a similar configuration and preparation method based on the SDC electrolyte and scaffold, where 0.04, 0.076, 0.17, and 0.39 $\Omega \text{ cm}^2$ at 700, 650, 600,

and 550 °C were achieved respectively [47]. Furthermore, the electrode fired at 900 °C shows much lower polarization resistances than those of well-known electrodes on proton conductors, e.g. LSCF/BZCY/LSCF (0.19, 0.47, and 1.34 $\Omega \text{ cm}^2$ at 650, 600, and 550 °C, respectively) [41] and PBC/BZCY/PBC (0.17, 0.28, 0.49, and 1.05 $\Omega \text{ cm}^2$ at 700, 650, 600, and 550 °C, respectively) [38]. The electrode fired at 800 °C shows obviously large polarization resistances of 0.149/0.125, 0.373/0.259, 0.961/0.560, and 2.321/1.117 $\Omega \text{ cm}^2$ in dry air/wet air at 700, 650, 600, and 550 °C, respectively. When the electrode was fired at 1000 °C, polarization resistances are 0.095/0.080, 0.237/0.151, 0.644/0.305, and 1.668/0.756 $\Omega \text{ cm}^2$ in dry air/wet air at 700, 650, 600, and 550 °C, respectively. The lack of the beneficial reaction should be the main cause for the large polarization resistance of the electrode fired at 800 °C, whereas the loss of active sites or active surface area due to change of the microstructure might be responsible for the reduced electrochemical performance of the electrode fired at 1000 °C [47].

Fig. 3 Temperature-dependent polarization resistances of typical symmetrical cells with the pure silver paste, fresh porous BZCY, and infiltrated BZCY as electrodes in air (a) and wet air (b).

It is interesting that the polarization resistances of symmetrical cells at 750 °C unusually increase though slightly after introducing 3% H₂O in air, i.e., 0.061 vs. 0.062 Ω cm² (800 °C), 0.030 vs. 0.032 Ω cm² (900 °C), and 0.040 vs. 0.042 Ω cm² (1000 °C), indicating the change of the oxygen reduction reaction mechanism. One plausible explanation is that Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-δ} is a triple-conducting oxide, and the dominant conductivity is transferred from the proton conductivity to the oxygen ionic conductivity at 750 °C. Therefore the intentionally introduced H₂O cannot accelerate the rate of the oxygen reduction reaction because of the competitive adsorption on the active site.

STEM was applied to determine the composition and microstructure. The BZCY soaked with the Co(NO₃)₂ solution and sintered at 900 °C in air for 2 h was subjected to the characterization since it shows relatively low polarization resistances compared to other electrodes. Fig. 4a&b show the STEM and magnified STEM images of the infiltrated BZCY. The lattice fringes with an interplanar spacing of 0.242 nm was obtained, in line with the diffraction plane (111) of Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-δ}. For a better visualization, an inverse fast Fourier transform (FFT) image of Fig. 4b is also exhibited in Fig. 4c. Additionally, all elements are homogenously distributed in the Co-infiltrated BZCY sintered at 900 °C in air for 2 h (Fig. 4d).

Fig. 4 STEM (a), magnified STEM (b) images, FFT of the STEM image (c), and corresponding EDS elemental distribution of BZCY soaked with the $\text{Co}(\text{NO}_3)_2$ solution and sintered at 900 °C in air for 2 h.

Fig. 5 A typical cross-sectional ESEM image (a) and corresponding SEM/EDS mappings (b) of the $\text{Co}(\text{NO}_3)_2$ -infiltrated electrode sintered at 900 °C in air for 2 h, and the magnified ESEM image (c) from the electrode layer.

To check the elemental distributions in the electrode layer and the electrolyte layer, a typical cross-section ESEM image and the corresponding EDS mappings of the $\text{Co}(\text{NO}_3)_2$ -infiltrated electrode sintered at 900 °C in air for 2 h are shown in **Fig. 5a and 5b**. Homogeneous distributions of Co, Ba, Zr, Ce, and Y in the electrode layer are displayed (**Fig. 5b**), suggesting the successful diffusion of $\text{Co}^{\text{m}+}$ ions into the BZCY lattice as demonstrated with the XRD and STEM results. Due to the limited diffusion distance, a thin film with a composition of $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ is suggested to be formed on the surface of the porous scaffold. As shown in **Fig. 5c**, the magnified part of the ESEM image of the electrode in **Fig. 5a**, in addition to the $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ thin film, nano/micro-sized particles are found on the surface of the scaffold, which indicates that the cation exchange leads to the formation of $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$ on the surface. According to XRD results, these particles may also include Co_3O_4 from the direct decomposition of $\text{Co}(\text{NO}_3)_2$ at the high temperature. Therefore a 3D core-shell triple-conducting oxygen reduction reaction electrode is proposed, which includes a bulk $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ scaffold, a thin-film $\text{Ba}(\text{Zr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2})_{1-x}\text{Co}_x\text{O}_{3-\delta}$ layer, and minor $(\text{Ce}, \text{Zr}, \text{Y})\text{O}_2$ and Co_3O_4 nano/micro-sized particles.

As electrode for H^+ -SOFCs, high electrical conductivity is a basic requirement to achieve high electrochemical performance. Although BZCY was reported to be a proton conductor with total conductivity of less than 0.01 S cm^{-1} at evaluated temperatures [**56, 58**], Co-infiltrated BZCY and the formed Co_3O_4 may contribute to additional conductivity to the overall conductivity. Rectangular bars ($\sim 2 \text{ mm} \times 5 \text{ mm}$

$\times 10$ mm) with the porosity of ~ 50 % were applied to measure the total conductivity. As shown in **Fig. 6**, the total conductivity of the infiltrated BZCY fired at 900 $^{\circ}\text{C}$ increases with the **increasing** temperature, and the total conductivity of the infiltrated BZCY is much higher than the fresh porous BZCY. Due to the negligible electronic conductivity of BZCY and high porosity, the total conductivity is still quite low in all investigated temperatures. Nevertheless, the increase of the total conductivity suggests that $\text{Co}^{\text{m}+}$ ions diffuse into the BZCY scaffold to in situ form a triple-conducting thin film.

Fig. 6 Electronic conductivity of porous BZCY, and $\text{Co}(\text{NO}_3)_2$ -infiltrated BZCY electrodes sintered at 900 $^{\circ}\text{C}$ in air for 2 h.

Fig. 7 Thermal expansion behavior of dense BZCY and $\text{Co}(\text{NO}_3)_2$ -infiltrated BZCY bars sintered at 900 $^{\circ}\text{C}$ in air for 2 h.

1 A good compatibility between the electrolyte and the electrode is critical for
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3 achieving excellent operational stability for H⁺-SOFCs. The mismatch in the thermal
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5 expansion coefficient (TEC) between layers could create a large internal strain during
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7 the heating and cooling processes, leading to the delamination, thus the rapid
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9 degradation in outputs of H⁺-SOFCs. As reported, the thermal behavior of the
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11 composite electrode prepared by the infiltration was mainly determined by the
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13 scaffold [47, 59, 60]. Fig. 7 shows the thermal expansion plots of dense BZCY and
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15 the infiltrated BZCY bars fired at 900 °C. The calculated TEC values of the infiltrated
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17 BZCY and dense BZCY in the temperature range of 200-900 °C are 9.93×10^{-6} and
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19 $9.27 \times 10^{-6} \text{ K}^{-1}$, respectively, which are similar to the reported values in literatures [61,
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21 62]. For the infiltrated electrode, the TEC value is only slightly larger than that of the
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23 dense BZCY, which suggests that the introduction of Co ions via infiltration and
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25 sintering might not change TEC. The similar TEC values between the dense BZCY
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27 and infiltrated BZCY have demonstrated good thermo-mechanical compatibility, thus
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29 ensuring operational stability.
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42 The operational stability evaluation thus was carried out on the in situ formed
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44 3D core-shell triple-conducting oxygen reduction reaction electrode. The good
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46 compatibility of the electrode and electrolyte and the limited phase reaction at the
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48 operation temperature (if the phase reaction was existed, the formed phase is
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50 beneficial for the oxygen reduction reaction) may help maintain the stability during
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52 the operation. Fig. 8 displays polarization resistances of the symmetrical cell at
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54 650 °C for 70 h under the open circuit condition. A mesh-like silver current collector
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is applied considering its stable behavior [63]. The polarization resistance is relatively stable and there is no obvious degradation after 70 h, implying superior stability of the 3D core-shell structure from the infiltration and high-temperature sintering. Fig. 8b shows typical impedance spectra after the operation for 0, 38, and 70 h at 650 °C. No obvious changes of the spectra features suggest that the oxygen reduction reaction mechanism is unchanged during the operation.

Fig. 8 Time-dependent polarization resistance of the infiltrated BZCY at 650 °C (a), and typical impedance spectra of the infiltrated BZCY during the stability measurement.

For potential practical application, we assembled the core-shell triple-conducting electrode fired at 900 °C with an anode-supported thin-film BZCY electrolyte (~25 μm) to form a fuel cell. Fig. S3 shows typical *IV* and *IP* curves of a fuel cell operated at 650 and 600 °C, using H₂ as fuel gas and ambient air as oxidant gas. A high open circuit voltage is recorded, which is close to the theoretical value, suggesting high reliability of the fabricated fuel cell. A peak power density of ~330 and ~220 mW cm⁻² is achieved at 650 and 600 °C, respectively. The peak power density is comparable or even better than that of the recently reported H⁺-SOFCs [29, 58, 64], suggesting great potential of the core-shell triple-conducting electrode for H⁺-SOFCs. A higher power output might be obtained by further optimizing anode microstructure

[54], electrolyte and scaffold composition [34], and interfacial contact [65].

4. Conclusions

In this work, a 3D core-shell and triple-conducting oxygen reduction reaction electrode for intermediate-temperature H^+ -SOFCs is presented. The core is the bulk BZCY scaffold, while the shell consists of the cubic $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$, cubic spinel Co_3O_4 and cubic fluorite (Ce, Zr, Y) O_2 . Outstanding electrochemical oxygen reduction activity and favourable stability are obtained with the in situ formed electrode. The enhanced oxygen reduction activity is mainly due to the formed $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$ on the shell, which conducts protons in wet atmosphere. The unique 3D core-shell structure ensures excellent compatibility with the electrolyte and outstanding stability during the operation. In particular, the designed electrode sintered at 900 °C exhibits polarization resistances as low as 0.094 and 0.198 $\Omega\text{ cm}^2$ at 650 and 600 °C in wet air (3% H_2O) in a symmetrical cell. A fuel cell delivers a peak power density of $\sim 330\text{ mW cm}^{-2}$ at 650 °C when assembling the developed core-shell and triple-conducting electrode. Our results suggest that the infiltration and reactive sintering method is a promising strategy for constructing efficient electrodes for intermediate-temperature H^+ -SOFCs.

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References

- [1] W. Wang, C. Su, Y. Wu, R. Ran, Z. Shao, Progress in solid oxide fuel cells with nickel-based anodes operating on methane and related fuels, *Chem. Rev.* 113 (2013) 8104-8151.
- [2] A. J. Jacobson, Materials for solid oxide fuel cells, *Chem. Mater.* 22 (2009) 660-674.
- [3] D. Chen, C. Chen, Z. Zhang, Z. M. Baiyee, F. Ciucci, Z. Shao, Compositional engineering of perovskite oxides for highly efficient oxygen reduction reactions, *ACS Appl. Mater. Interfaces* 7 (2015) 8562-8571.
- [4] S. Sengodan, S. Choi, A. Jun, T. H. Shin, Y. W. Ju, H. Y. Jeong, J. Shin, J. T. S. Irvine, G. Kim, Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells, *Nat. Mater.* 14 (2015) 205-209.
- [5] Z. Zhang, Y. Zhu, Y. Zhong, W. Zhou, Z. Shao, Anion doping: A new strategy for developing high-performance perovskite-type cathode materials of solid oxide fuel cells, *Adv. Energy Mater.* 7 (2017) 1700242.
- [6] E. D. Wachsman, C. A. Marlowe, K. T. Lee, Role of solid oxide fuel cells in a balanced energy strategy, *Energy Environ. Sci.* 5 (2012) 5498-5509.
- [7] P. I. Cowin, C. T. G. Petit, R. Lan, J. T. S. Irvine, S. Tao, Recent progress in the development of anode materials for solid oxide fuel cells, *Adv. Energy Mater.* 1 (2011) 314-332.
- [8] J. Wang, M. Saccoccio, D. Chen, Y. Gao, C. Chen, F. Ciucci, The effect of A-site and B-site substitution on $\text{BaFeO}_{3-\delta}$: An investigation as a cathode material for intermediate-temperature solid oxide fuel cells, *J. Power Sources* 297 (2015) 511-518.
- [9] E. D. Wachsman, K. T. Lee, Lowering the temperature of solid oxide fuel cells, *Science* 334 (2011) 935-939.
- [10] Z. Shao, S. M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, *Nature* 431 (2004) 170-173.
- [11] J. G. Lee, J. H. Park, Y. G. Shul, Tailoring gadolinium-doped ceria-based solid oxide fuel cells to achieve 2 W cm^{-2} at 550°C , *Nat. Commun.* 5 (2014) 4045.
- [12] Y. Zhang, R. Knibbe, J. Sunarso, Y. Zhong, W. Zhou, Z. Shao, Z. Zhu, Recent progress on advanced materials for solid-oxide fuel cells operating below 500°C , *Adv. Mater.* 29 (2017) 1700132.
- [13] S. Yoo, A. Jun, Y. W. Ju, D. dkhuu, J. Hyodo, H. Y. Jeong, N. Park, J. Shin, T. Ishihara, G. Kim, Development of double-perovskite compounds as cathode

- materials for low-temperature solid oxide fuel cells, *Angew. Chem. Int. Ed.* 53 (2014) 13064-13067.
- [14] W. Zhou, R. Ran, Z. Shao, Progress in understanding and development of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -based cathodes for intermediate-temperature solid-oxide fuel cells: a review, *J. Power Sources* 192 (2009) 231-246.
- [15] M. Li, M. Zhao, F. Li, W. Zhou, V. K. Peterson, X. Xu, Z. Shao, I. Gentle, Z. Zhu, A niobium and tantalum co-doped perovskite cathode for solid oxide fuel cells operating below 500 °C, *Nat. Commun.* 8 (2017) 13990.
- [16] Y. Chen, J. Shen, G. Yang, W. Zhou, Z. Shao, A single-/double-perovskite composite with an overwhelming single-perovskite phase for the oxygen reduction reaction at intermediate temperatures, *J. Mater. Chem. A* 5 (2017) 24842-24849.
- [17] D. Ding, X. Li, S. Y. Lai, K. Gerdes, M. Liu, Enhancing SOFC cathode performance by surface modification through infiltration, *Energy Environ. Sci.* 7 (2014) 552-575.
- [18] J. Wang, K. Y. Lam, M. Saccoccio, Y. Gao, D. Chen, F. Ciucci, Ca and In co-doped $\text{BaFeO}_{3-\delta}$ as a cobalt-free cathode material for intermediate-temperature solid oxide fuel cells, *J. Power Sources* 324 (2016) 224-232.
- [19] Y. Gao, D. Chen, M. Saccoccio, Z. Lu, F. Ciucci, From material design to mechanism study: nanoscale Ni exsolution on a highly active A-site deficient anode material for solid oxide fuel cells, *Nano Energy* 27 (2016) 499-508.
- [20] C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almansoori, R. O'Hayre, Readily processed protonic ceramic fuel cells with high performance at low temperatures, *Science* 349 (2015) 1321-1326.
- [21] L. Bi, E. Fabbri, Z. Sun, E. Traversa, A novel ionic diffusion strategy to fabricate high-performance anode-supported solid oxide fuel cells (SOFCs) with proton-conducting Y-doped BaZrO_3 films. *Energy Environ. Sci.* 4 (2011) 409-412.
- [22] T. Wei, L. A. Zhang, Y. Chen, P. Yang, M. Liu, Promising proton conductor for intermediate-temperature fuel cells: $\text{Li}_{13.9}\text{Sr}_{0.1}\text{Zn}(\text{GeO}_4)_4$, *Chem. Mater.* 29 (2017) 1490-1495.
- [23] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Towards the next generation of solid oxide fuel cells operating below 600 °C with chemically stable proton-conducting electrolytes, *Adv. Mater.* 24 (2012) 195-208.
- [24] Z. Wang, M. Liu, W. Sun, D. Ding, Z. Lü, M. Liu, A mixed-conducting $\text{BaPr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$ cathode for proton-conducting solid oxide fuel cells, *Electrochem. Commun.* 27 (2013) 19-21.

- [25] K. D. Kreuer, Annu. Proton-conducting oxides, Rev. Mater. Res. 33 (2003) 333-359.
- [26] E. Fabbri, D. Pergolesi, E. Traversa, Electrode materials: a challenge for the exploitation of protonic solid oxide fuel cells, Sci. Techno. Adv. Mater. 11 (2010) 044301.
- [27] K. Xie, Q. Ma, B. Lin, Y. Jiang, J. Gao, X. Liu, G. Meng, An ammonia fuelled SOFC with a $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\delta}$ thin electrolyte prepared with a suspension spray, J. Power Sources 170 (2007) 38-41.
- [28] S. Choi, C. J. Kucharczyk, Y. Liang, X. Zhang, I. Takeuchi, H. I. Ji, S. M. Haile, Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells, Nat. Energy 3 (2018) 202-210.
- [29] Y. Chen, S. Yoo, K. Pei, D. Chen, L. Zhang, B. deGlee, R. Murphy, B. Zhao, Y. Zhang, Y. Chen, M. Liu, An in situ formed, dual-phase cathode with a highly active catalyst coating for protonic ceramic fuel cells, Adv. Funct. Mater. 28 (2018) 1704907.
- [30] J. Kim, S. Sengodan, G. Kwon, D. Ding, J. Shin, M. Liu, G. Kim, Triple-conducting layered perovskites as cathode materials for proton-conducting solid oxide fuel cells, ChemSusChem 7 (2014) 2811-2815.
- [31] A. Zhu, G. Zhang, T. Wan, T. Shi, H. Wang, M. Wu, C. Wang, S. Huang, Y. Guo, H. Yu, Z. Shao, Evaluation of $\text{SrSc}_{0.175}\text{Nb}_{0.025}\text{Co}_{0.8}\text{O}_{3-\delta}$ perovskite as a cathode for proton-conducting solid oxide fuel cells: The possibility of in situ creating protonic conductivity and electrochemical performance, Electrochim. Acta 259 (2018) 559-565.
- [32] T. Norby, The promise of protonics, Nature 410 (2001) 877-878.
- [33] Z. Wang, W. Yang, S. P. Shafi, L. Bi, Z. Wang, R. Peng, C. Xia, W. Liu, Y. Lu, A high performance cathode for proton conducting solid oxide fuel cells, J. Mater. Chem. A 3 (2015) 8405-8412.
- [34] L. Yang, S. Wang, K. Blinn, M. Liu, Z. Liu, Z. Cheng, M. Liu, Enhanced sulfur and coking tolerance of a mixed ion conductor for SOFCs: $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Yb}_x\text{O}_{3-\delta}$, Science 326 (2009) 126-129.
- [35] W. Wang, Y. Chen, F. Wang, M. O. Tade, Z. Shao, Enhanced electrochemical performance, water storage capability and coking resistance of a $\text{Ni}+\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ anode for solid oxide fuel cells operating on ethanol, Chem. Eng. Sci. 126 (2015) 22-31.
- [36] L. Yang, C. Zuo, S. Wang, Z. Cheng, M. Liu, A novel composite cathode for low-temperature SOFCs based on oxide proton conductors, Adv. Mater. 20 (2008) 3280-3283.

- [37] C. Zuo, S. Zha, M. Liu, M. Hatano, M. Uchiyama, $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ as an electrolyte for low-temperature solid-oxide fuel cells, *Adv. Mater.* 18 (2006) 3318-3320.
- [38] Y. Lin, R. Ran, C. Zhang, R. Cai, Z. Shao, Performance of $\text{PrBaCo}_2\text{O}_{5+\delta}$ as a proton-conducting solid-oxide fuel cell cathode, *J. Phys. Chem. A* 114 (2009) 3764-3772.
- [39] Y. Lin, R. Ran, D. Chen, Z. Shao, A novel $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathode for protonic solid-oxide fuel cells, *J. Power Sources* 195 (2010) 4700-4703.
- [40] Y. Lin, R. Ran, Y. Zheng, Z. Shao, W. Jin, N. Xu, J. Ahn, Evaluation of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as a potential cathode for an anode-supported proton-conducting solid-oxide fuel cell, *J. Power Sources* 180 (2008) 15-22.
- [41] L. Yang, Z. Liu, S. Wang, Y. Choi, C. Zuo, M. Liu, A mixed proton, oxygen ion, and electron conducting cathode for SOFCs based on oxide proton conductors, *J. Power Sources* 195 (2010) 471-474.
- [42] D. Chen, R. Ran, K. Zhang, J. Wang, Z. Shao, Intermediate-temperature electrochemical performance of a polycrystalline $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode on samarium-doped ceria electrolyte, *J. Power Sources* 188 (2009) 96-105.
- [43] L. Fan, P. C. Su, Layer-structured $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$: A new triple ($\text{H}^+/\text{O}^{2-}/\text{e}^-$) conducting cathode for low temperature proton conducting solid oxide fuel cells, *J. Power Sources* 306 (2016) 369-377.
- [44] S. P. Jiang, Nanoscale and nano-structured electrodes of solid oxide fuel cells by infiltration: advances and challenges, *Int. J. Hydrogen Energy* 37 (2012) 449-470.
- [45] Z. Jiang, C. Xia, F. Chen, Nano-structured composite cathodes for intermediate-temperature solid oxide fuel cells via an infiltration/impregnation technique, *Electrochim. Acta* 55 (2010) 3595-3605.
- [46] J. M. Vohs, R. J. Gorte, High- performance SOFC cathodes prepared by infiltration, *Adv. Mater.* 21 (2009) 943-956.
- [47] D. Chen, G. Yang, F. Ciucci, M. O. Tadé, Z. Shao, 3D core-shell architecture from infiltration and beneficial reactive sintering as highly efficient and thermally stable oxygen reduction electrode, *J. Mater. Chem. A* 2 (2014) 1284-1293.
- [48] Y. Guo, Y. Lin, R. Ran, Z. Shao, Zirconium doping effect on the performance of proton-conducting $\text{BaZr}_y\text{Ce}_{0.8-y}\text{Y}_{0.2}\text{O}_{3-\delta}$ ($0.0 \leq y \leq 0.8$) for fuel cell applications, *J. Power Sources* 193 (2009) 400-407.
- [49] Y. Song, W. Wang, L. Ge, X. Xu, Z. Zhang, P. S. B. Julião, W. Zhou, Z. Shao, Rational design of a water-storable hierarchical architecture decorated with amorphous barium oxide and nickel nanoparticles as a solid oxide fuel cell anode with excellent sulfur tolerance, *Adv. Sci.* 4 (2017) 1700337.

- [50] R. R. Chien, C. S. Tu, V. Hugo Schmidt, S. -C. Lee, C. -C. Huang, Synthesis and characterization of proton-conducting $\text{Ba}(\text{Zr}_{0.8-x}\text{Ce}_x\text{Y}_{0.2})\text{O}_{2.9}$ ceramics, *Solid State Ionics* 181 (2010) 1251-1257.
- [51] Z. Zhang, D. Chen, Y. Chen, Y. Hao, M. O. Tade, Z. Shao, Facile fabrication and improved carbon dioxide tolerance of a novel bilayer-structured ceramic oxygen permeating membrane, *J. Membr. Sci.* 472 (2014) 10-18.
- [52] S. W. Tao, J. T. Irvine, J. A. Kilner, An efficient solid oxide fuel cell based upon single-phase perovskites, *Adv. Mater.* 17 (2005) 1734-1737.
- [53] S. Uhlenbruck, T. Moskalewicz, N. Jordan, H. J. Penkalla, H. P. Buchkremer, Element interdiffusion at electrolyte–cathode interfaces in ceramic high-temperature fuel cells, *Solid State Ionics* 180 (2009) 418-423.
- [54] T. Suzuki, Z. Hasan, Y. Funahashi, T. Yamaguchi, Y. Fujishiro, M. Awano, Impact of anode microstructure on solid oxide fuel cells, *Science* 325 (2009) 852-855.
- [55] R. Peng, T. Wu, W. Liu, X. Liu, G. Meng, Cathode processes and materials for solid oxide fuel cells with proton conductors as electrolytes, *J. Mater. Chem.* 20 (2010) 6218-6225.
- [56] E. Fabbri, D. Pergolesi, E. Traversa, Materials challenges toward proton-conducting oxide fuel cells: a critical review, *Chem. Soc. Rev.* 39 (2010) 4355-4369.
- [57] D. J. Brett, A. Atkinson, N. P. Brandon, S. J. Skinner, Intermediate temperature solid oxide fuel cells, *Chem. Soc. Rev.* 37 (2008) 1568-1578.
- [58] L. Yang, C. Zuo, M. Liu, High-performance anode-supported solid oxide fuel cells based on $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ (BZCY) fabricated by a modified co-pressing process, *J. Power Sources* 195 (2010) 1845-1848.
- [59] X. Kong, Y. Tian, X. Zhou, X. Wu, J. Zhang, Surface tuned $\text{La}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ based anode for direct methane solid oxide fuel cells by infiltration method, *Electrochim. Acta* 234 (2017) 71-81.
- [60] L. Almar, A. Morata, M. Torrell, M. Gong, T. Andreu, M. Liu, A. A. Tarancón, A durable electrode for solid oxide cells: mesoporous $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ scaffolds infiltrated with a $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ catalyst, *Electrochim. Acta* 235 (2017) 646-653.
- [61] Z. Zhu, J. Qian, Z. Wang, J. Dang, W. Liu, High-performance anode-supported solid oxide fuel cells based on nickel-based cathode and $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ electrolyte, *J. Alloy. Compd.* 581 (2013) 832-835.
- [62] Q. Jiang, J. Cheng, R. Wang, Y. Fan, J. Gao, Novel triple-phase composite cathode materials for proton-conducting solid oxide fuel cells, *J. Power Sources* 206 (2012) 47-52.
- [63] Y. Chen, F. Wang, D. Chen, F. Dong, H. J. Park, C. Kwak, Z. Shao, Role of silver current collector on the operational stability of selected

cobalt-containing oxide electrodes for oxygen reduction reaction, J. Power Sources 210 (2012) 146-153.

[64] L. Bi, E. H. Da'as, S. P. Shafi, Proton-conducting solid oxide fuel cell (SOFC) with Y-doped BaZrO₃ electrolyte, Electrochem. Commun. 80 (2017) 20-23.

[65] D. Chen, G. Yang, Z. Shao, F. Ciucci, Nanoscaled Sm-doped CeO₂ buffer layers for intermediate-temperature solid oxide fuel cells, Electrochem. Commun. 35 (2013) 131-134.

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