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

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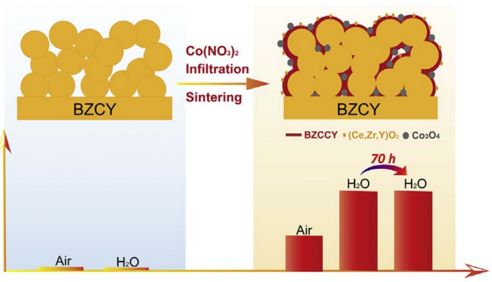
HIGHLIGHTS

- 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 Ω cm² at 600 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

$BaZr_xCe_yY_{1-x-y}O_{3-\delta}$ 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 $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-\delta}$ (BZCY) scaffold to generate a 3D core-shell and triple-conducting ($H^+/O^{2-}/e^-$) electrode in situ via infiltrating and reactive sintering. The core is the bulk BZCY scaffold, while the shell is composed of the cubic $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$, cubic spinel Co_3O_4 and cubic fluorite $(Ce, Zr, Y)O_2$. 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% H_2O) 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 $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$ in the shell.

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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 °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. 500–750 °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 resistance over oxygen-conducting SOFCs [34,35]. Among various proton conductors for H^+-SOFCs, $BaZr_xCe_yY_{1-x-y}O_{3-\delta}$ combines the advantages of barium cerate-based materials (high proton conductivity) and barium zirconate-based materials (outstanding chemical stability in H_2O- and CO_2-containing conditions), displaying relatively high proton conductivity and sufficient chemical stability over a wide range of fuel cell operation conditions [30,36,37]. However, it is unexpected that H^+-SOFCs assembled with the developed $BaZr_xCe_yY_{1-x-y}O_{3-\delta}$ proton conductors still fail to delivery satisfactory performance as expected based on the high intrinsic conductivity of those proton-conducting electrolytes [28]. The reasons why H^+-SOFCs lags far behind the oxygen-conducting SOFC are mainly due to the lack of proper cathode materials and poor compatibility between the existing cathode and the electrolyte.

Cathode materials applied for H^+-SOFCs are generally what have been initially and successfully designed for traditional SOFCs with doped ceria or $LaGaO_3$-based electrolytes [36,38–41]. Unfortunately, the cathodic overpotentials/polarization resistances in H^+-SOFCs are much larger than what are obtained in traditional SOFCs. For example, many well-studied mixed ionic and electronic materials, e.g. $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [36], $PrBaCo_2O_{5+\delta}$ [38], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [40], and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [41] have been extensively selected as cathodes for H^+-SOFCs, but they showed larger polarization resistances than those when assembling them on doped ceria electrolyte or $LaGaO_3$-based electrolyte. Lin et al. reported that the electrode polarization resistance of the $PrBaCo_2O_{5+\delta}$ cathode on $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ at 600 °C was 0.73 $\Omega\,cm^2$ [38], while a smaller polarization resistance of ∼0.4 $\Omega\,cm^2$ for $PrBaCo_2O_{5+\delta}$ 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. $NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$) 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 $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ 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 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode on $BaCe_{0.9}Y_{0.1}O_{2.95}$ 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 an 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 $Sm_{0.2}Ce_{0.8}O_{1.9}$ (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 $\Omega\,cm^2$ at 700, 650, 600, and 550 °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 °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, $Ba(NO_3)_2$, $Zr(NO_3)_4{\cdot}5H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, and $Y(NO_3)_3{\cdot}6H_2O$ in analytical grade (Sinopharm Chemical Reagent Co.,