Short communication

A novel cobalt-free layered GdBaFe$_2$O$_{5+\delta}$ cathode for proton conducting solid oxide fuel cells

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ABSTRACT

While cobalt-containing perovskite-type cathode materials facilitate the activation of oxygen reduction, they also suffer from problems like poor chemical stability in CO$_2$ and high thermal expansion coefficients. In this research, a cobalt-free layered GdBaFe$_2$O$_{5+\delta}$ (GBF) perovskite was developed as a cathode material for protonic ceramic membrane fuel cells (PCMFCs) based on proton conducting electrolyte of stable BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY7). The button cells of Ni–BZCY7|BZCY7|GBF were fabricated and characterized using complex impedance technique from 600 to 700 °C. An open-circuit potential of 1.007 V, maximum power density of 417 mW cm^{-2}, and a low electrode polarization resistance of 0.18 Ω cm^2 were achieved at 700 °C. The results indicate that layered GBF perovskite is a good candidate for cobalt-free cathode material, while the developed Ni–BZCY7|BZCY7|GBF cell is a promising functional material system for solid oxide fuel cells.

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1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) could potentially circumvent problems induced by high temperature operating conditions in yttria stabilized zirconia (YSZ) electrolyte based SOFCs, such as long term stability and durability of material systems [1]. In order for IT-SOFC performance to be comparable to its high temperature counterpart, two technical barriers have to be overcome, e.g., high ohmic resistance of electrolyte and low catalytic activity of electrodes under intermediate temperature conditions (550–750 °C).

Recently, proton conducting SOFCs have attracted much attention and show great advantages over oxide-ion conducting SOFCs, such as low activation energy [2] and high energy efficiency [3]. The state-of-the-art proton conducting materials are barium-based perovskite-type oxides, e.g., BaCeO$_3$ and BaZrO$_3$. By suitable doping, these materials may obtain both adequate proton conductivity as well as sufficient chemical and thermal stabilities over a wide range of SOFC operating conditions, e.g., BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY7) [4]. This material can be used as an electrolyte for proton conducting IT-SOFC development.

In a typical proton conducting electrolyte based SOFC, hydrogen molecules release electrons and are dissociated into protons at anode active layer. The protons then migrate into cathode side through the proton electrolyte. At cathode side, oxygen molecules are changed into ions with a supply of external electrons; water molecules are then formed through the combination of protons and ions. Essentially three charge species are involved in cathode electrode, i.e., protons, ions, and electrons. Consequently, cathode electrode development is very critical for high performance proton conducting SOFCs. Furthermore, intermediate temperature operating condition imposes additional challenges on cathode material selections [5]. Many cobalt-containing perovskite-type mixed ionic-electronic conductors (MIEC), such as La$_x$Sr$_{1-x}$Co$_y$Fe$_{1-y}$O$_{3-\delta}$ (LSCF) [6], Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) [7] and Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC) [8], have been extensively studied as possible cathodes due to the fact that cobalt is beneficial to the activation of oxygen reduction. These cobalt-based cathodes, however, often suffer from problems like poor chemical stability in CO$_2$, high thermal expansion coefficients (TECs), ease of evaporation, as well as high cost of cobalt element [9,10]. Clearly, it is significant to develop cobalt-free cathodes with sufficient catalytic activity at reduced temperatures for IT-SOFCs. Several cobalt-free oxides with simple perovskite structure, such as La$_x$Sr$_{1-x}$FeO$_{3-\delta}$ (LSF) [11], and Ba$_{0.5}$Sr$_{0.5}$Zn$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (BSZF) [9] have been reported as IT-SOFC cathodes.

Recently, layered perovskites have attracted much attention because their A-sites are ordered. The ordering A-sites are recognized to be able to greatly enhance the diffusivity of oxygen ion in the bulk of the material by orders of magnitude [12–15], and consequently improve cathode performance. In this paper, we present the development of a novel cobalt-free material GdBaFe$_2$O$_{5+x}$ (GBF) with a layered perovskite structure for proton conducting SOFCs based on proton conducting BZCY7 electrolyte.

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2. Experimental

2.1. Sample preparation, cell fabrication, and X-ray diffraction measurement

The $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) powders were synthesized using modified Pechini method, where citrate and ethylenediamine tetraacetic acid (EDTA) were employed as parallel complexing agents. Y_2O_3 was first dissolved in nitric acid under heating; the calculated amount of $Ba(NO_3)_2 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Zr(NO_3)_4 \cdot 4H_2O$ was dissolved in EDTA–NH_3 aqueous solution. After agitation for a certain time, a proper amount of citric acid was introduced, the molar ratio of EDTA:citric acid:total of metal cations was controlled around 1:1.5:1. After converted into viscous gel under heating and stirring conditions, the solution ignited to flame and resulted in ash. The resulting ash-like material was calcined afterwards in air at 1100 °C for 5 h to form a pure perovskite oxide, and the synthesized BZCY7 powders were then obtained.

The anode-supported BZCY7 bi-layer (Φ = 15 mm) was prepared by a dry-pressing method. The mixture of NiO + BZCY7 + starch (60%:40%:20% in weight) was pre-pressed at 200 MPa and formed into an anode substrate. The anode functional layer (mixture of NiO and BZCY7, NiO:BZCY7 = 60%:40% in weight) was then pressed onto the substrate. Finally loose BZCY7 powder synthesized above was uniformly distributed onto the anode substrate, co-pressed at 250 MPa, and subsequently co-sintered at 1400 °C for 5 h to obtain dense BZCY7 membrane.

Layered $GdBaFe_2O_{5+\delta}$ (GBF) powder was synthesized using Pechini process with Gd_2O_3, $Ba(NO_3)_2 \cdot 9H_2O$, and $Fe(NO_3)_3 \cdot 5H_2O$ as precursors, followed by calcinations at 1000 °C for 10 h. Fine GBF powders were then mixed thoroughly with a 6 wt% ethylcellulose–terpineol binder to prepare the cathode slurry. The slurry was painted on BZCY7 electrolyte films, which was then sintered at 1000 °C for 3 h in air to form single cells of NiO–BZCY7/BZCY7/GBF.

The phase identification of the sintered anode-electrolyte bi-layer and prepared cathode powders were studied with the powder X-ray diffraction by Cu-$K\alpha$ radiation (D/Max-gA, Japan).

2.2. Electrochemical characterization

Single cells were tested from 600 to 700 °C with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. The flow rate of fuel was controlled at 30 ml min^{-1} using a precision flow meter (APEX). The voltage–current curves were recorded by Scribner 890 ZV at the scanning rate of 30 mV s^{-1}. The electrochemical impedance spectra (EIS) were obtained using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat over the frequency range from 0.01 to 10^5 Hz under open-circuit conditions. A scanning electron microscope (SEM) was used to observe the microstructure of the post-test cells

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of GBF exhibits a pure layered perovskite phase structure without any peaks attributable to impurities [16]. The diffraction peaks are identical with $GdBaCo_2O_{5+\delta}$ reported in the literature by Tarancón et al. [17]. The replace of Fe at B site did not affect the formation of layered perovskite phase. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1400 °C for 5 h. It can be clearly seen that there are only peaks corresponding to BZCY7 in electrolyte membrane (Fig. 1(b)) and to NiO and BZCY7 in anode substrate (Fig. 1(c)). There is no evidence pointing to the formation of other substance.
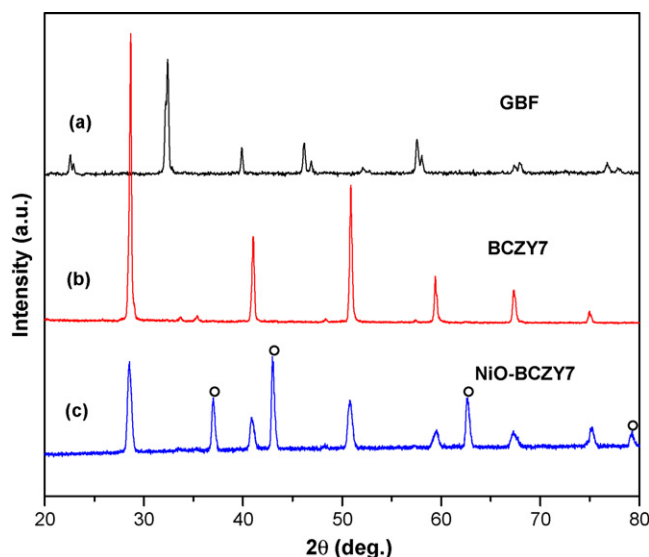

Fig. 1. XRD patterns for (a) the layered $GdBaFe_2O_{5+\delta}$ (GBF) perovskite powders, the bi-layer of (b) BZCY7 membrane and (c) NiO–BZCY7 anode substrate. (○): NiO.

After electrochemical test, the microstructure of as-prepared tri-layer cell is examined using SEM. One can see from Fig. 2 that the BZCY7 electrolyte membrane is completely dense, and there are no pores or cracks. The relatively uniform porosity distribution in anode support layer can be observed due to the well mixed powder materials of NiO, BZCY7 and starch. The anode functional layer between anode support layer and electrolyte layer is used to avoid the formation of macro-pores at the electrode/electrolyte interface, otherwise, the ohmic resistance at the interface will increase. It can also be seen from the cross-section view of tri-layer cell Ni–BZCY7|BZCY7|GBF that the thickness of fabricated BZCY7 membrane is only about 20 μm, and that of GBF cathode layer is about 20 μm. No cracks can be found in SEM image of tri-layer cell. The cathode adheres to the electrolyte fairly well, which is probably due to the replacement of cobalt element with Fe element. The reduction of cobalt element from high valence state to low valence state and the loss of lattice oxygen lead to the high TEC of cobalt-containing cathode material [18], as a result, the replacement of cobalt element with Fe element can potentially mitigate such a high thermal expansion.

The electrochemical performance of the as-prepared cell is experimentally obtained and shown in Fig. 3 under different oper-
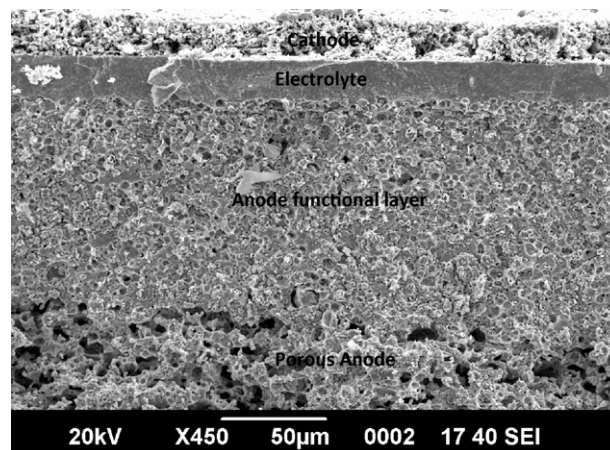

Fig. 2. SEM micrographs of cell after testing: the cross-section of tri-layer cell with a 20-μm thick BZCY7 membrane.
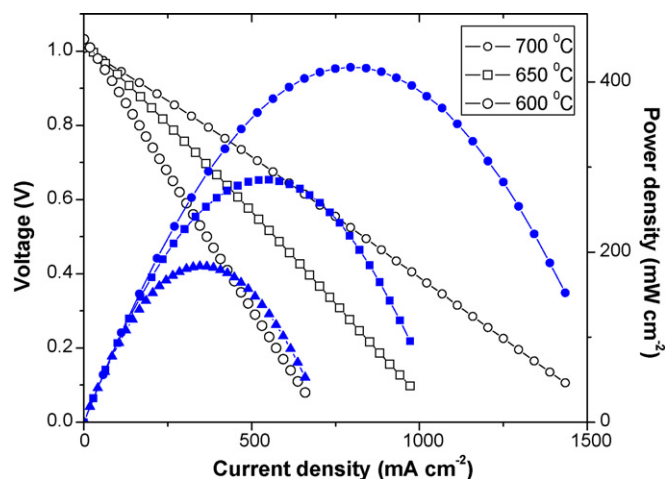
Fig. 3. Performance of the as-prepared cell with hydrogen at different temperatures.

ating temperatures, including *I–V* curve and *I–P* curve. In general, the open-circuit voltage (OCV) of the cell should be close to its theoretic value of 1.1 V, and is slightly influenced by operating conditions. Since BZCY7 electrolyte is a mix conductor membrane, a slight electron cross-flow (current leakage) might exist through the membrane, consequently leads to that the practical OCV is lower than its theoretical value. The higher the current leakage exists, the lower the cell OCV will be. On the other hand, if the electrolyte membrane is not dense, fuel/gas cross-flow might take place, causing lower OCV value as well. One can see from Fig. 3 that peak power densities are 417, 286 and 183 mW cm^{-2} at 700, 650 and 600 °C, respectively; whereas the high open-circuit voltages (OCV) of 1.007 V at 700 °C, 1.019 V at 650 °C, 1.032 V at 600 °C indicate that the electrolyte membrane is sufficiently dense, and the current leakage is negligible. It is worth noting that *I–V* curves are almost linear implying that there is a little activation loss related to the high catalytic activity of GBF. Since the conductivity of both anode and cathode materials is higher than that of electrolyte in the as-prepared cell, it can be deduced that the voltage drop of the cell is mainly attributed to the *IR* loss across the BZCY7 electrolyte.

The performance of GBF perovskite as cathode material in PCMFC settings is examined using electrochemical impedance spectra. The impedance spectra of the as-prepared cells are obtained under open-circuit conditions at different temperatures, and are shown in Fig. 4(a). The impedance spectra consisted of two arcs. This indicates that there are at least two electrode processes
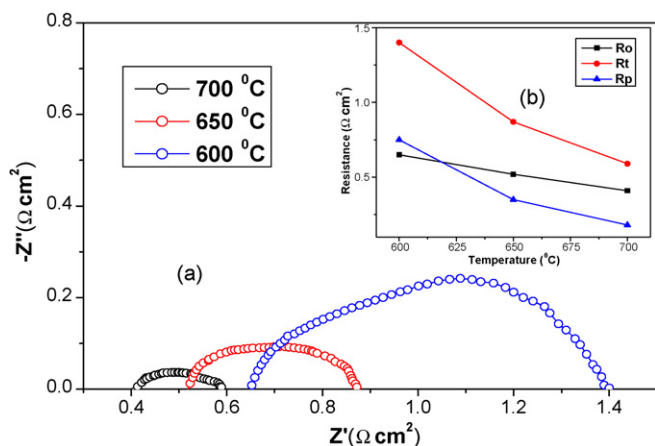
corresponding to the two arcs during oxygen molecule reduction. The high frequency arc can be attributed to polarization during charge transfer process. The low frequency arc can be attributed to the oxygen adsorption and desorption on the cathode surface and the diffusion of the oxygen ions [19]. The total cell resistance (R_t), ohmic resistance (R_o), as well as interfacial polarization resistance (R_p) are then determined from the impedance spectra in Fig. 4(a), the results are shown in Fig. 4(b). As one can see that increase in operating temperature leads to significant reduction of interfacial polarization resistance R_p, typically from 0.75 Ω cm^2 at 600 °C to 0.18 Ω cm^2 at 700 °C, respectively. It is worth noting that the R_p values of GBF are well comparable to cobalt-containing cathodes with the same anode and electrolyte, such as GdBaCo$_2$O$_{5+\delta}$ [20] (0.16 Ω cm^2 at 700 °C) and PrBaCo$_2$O$_{5+\delta}$ [21] (0.15 Ω cm^2 at 700 °C).

The experimental results of the cell Ni–BZCY7|BZCY7|GBF can be understood using the microstructure characteristic of layered perovskite cathode GBF. It is well known that the ionic conductivity is dependent on both the chemical diffusion coefficient and the surface exchange coefficient. Due to the ordering of A-sites in the layered perovskite oxides, the rate of the oxygen up-taking is much faster than that in simple ABO$_3$-type perovskite. Similarly it is also much easier to release oxygen from the layered oxides. Taskin et al. have established that the ordering of the A-site sub-lattice in layered structure significantly enhances the oxygen relaxation rate since oxygen atoms can be partially or even completely removed from the Gd^{3+} planes, generating numerous oxygen vacancies in the crystal lattice [15].

4. Conclusions

A cobalt-free layered perovskite oxide, GdBaFe$_2$O$_{5+\delta}$ (GBF), was investigated as a novel cathode for PCMFC. The dense BZCY7 electrolyte was fabricated on a porous anode support by a simple dry-pressing/co-firing process. The performance of the lab-scale tri-layer cell Ni–BZCY7|BZCY7|GBF was tested and characterized under intermediate temperature range from 600 to 700 °C with humified H$_2$ (~3% H$_2$O). The results show that the open-circuit potential of 1.007 V and maximum power density of 417 mW cm^{-2} are achieved at 700 °C. The polarization resistance of the electrodes was 0.18 Ω cm^2 at 700 °C. With temperature increases, the total cell resistance decreases, among which electrolyte resistance becomes increasingly dominant over polarization resistance. The results indicate that layered GBF perovskite is a promising cobalt-free cathode for intermediate temperature PCMFC development.

Acknowledgement

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Fig. 4. (a) Impedance spectra and (b) R_p, R_o, and R_t from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures.

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