



Optimizing the Manufacturing Method of Half-Cell Fuel Cell Based on Solid Electrolyte with Hydrogen Ion Conductivity

Naghmeh Mirab, Zahra Sherafat and Mohammad Hossein Paydar

Department of Materials Science and Engineering, Faculty of Engineering, Shiraz University, Shiraz, Iran

Abstract: Barium cerate-based perovskite oxides are protonic conductor candidates for intermediate temperature solid oxide fuel cells due to their high ionic conductivity and good sinterability. The aim of the present study is to fabricate a half-cell single-cell includes substrate, anode and electrolyte layers. The exact composition of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) has been selected as a proton conducting electrolyte. The fabrication process of a dense electrolyte membrane on a NiO- $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (NiO-BZCY7) anode substrate has been studied by a co-pressing process after co-firing at 1400°C. BZCY7 powders were synthesized by solid-state reaction method after calcinations at 1150°C. A single phase was obtained at this low temperature. The phase composition of the resulting specimens was investigated using X-ray diffraction (XRD) analysis. Scanning electron microscope (SEM) was used to evaluate the features of the synthesized powders and also the condition of connected layers in half-cell.

Key words: Solid oxide fuel cell; Proton conducting electrolyte; Solid-state synthesis; Dry pressing.

INTRODUCTION

There is an increasing worldwide interest for energy supply due to population growth and industrialization in developing countries. But fossil fuels that are the main energy source cannot properly respond to this growing demand. Moreover, excessive fuel consumption will lead to increasing pollution and global warming. Therefore, discovering of an alternative energy source is very important and many researches have been done in this field [1]. In this scenario, solid oxide fuel cells (SOFCs), which are electrochemical devices that are able to directly convert chemical into electrical energy, are promising candidates. They have high-energy conversion efficiency, wide application range (stationary and mobile applications are both possible), and fuel flexibility [2].

Most SOFCs are based on ceramic electrolyte materials with oxygen ion conductivity, which require operation temperatures in the range of 800–1000 °C [3, 4]. These conditions lead to high costs due to the need for using ceramic interconnects, expensive raw materials and materials degradation [5]. In addition, this high operating temperature represents the main drawback for SOFC practical applications, because of long start-up time, large energy input to warm up the cell, and the occurrence of thermal stresses that reduce the cell lifetime. Lowering the operating temperature of SOFCs is required not only to reduce the costs, but also to develop miniaturized SOFCs for portable-power supply [2].

In the attempt to develop SOFCs with the ability of operating at intermediate-temperature (IT) range, 500–700 °C, the ohmic resistance of the electrolyte needs to be reduced. This can be achieved with the aim of using alternative materials as electrolyte that have a higher ionic conductivity than that of oxygen ion conductors in the IT range [2].

At the intermediate temperature range, the ionic conductivity of proton conductors is more than oxygen ion conductors. Because of the activation energy for proton transfer with smaller ionic radius is generally lower than that for oxygen-ion conducting electrolytes [5]. Therefore proton conducting ceramics have the capability to be used as an electrolyte in IT fuel cells [3, 4]. These compounds show proton conductivity when exposed to hydrogen or water-vapor containing atmospheres, achieving suitable conductivity values in the IT range [2]. Furthermore, the use of proton conductors in fuel cells presents other advantages with respect to oxygen ion conductors. For instance in the conventional oxygen ion conductor electrolytes, the fuel concentration is unduly diluted at the anode by the formation of oxidation products such as water vapor and carbon dioxide.

The Nernst potential difference falls reducing the cell efficiency, while for protonic electrolytes the fuel can be fully depleted in the anode reaction, and the system operates 'dead-ended' maintaining the fuel pressure to compensate for hydrogen flux as ions through the electrolyte. Therefore, the use of proton conductors as electrolytes is a promising alternative that might solve the limits of SOFCs [5].

Many acceptor doped perovskites exhibit proton conductivity in an intermediate temperature range between 300 and 700 °C and thus are good candidate electrolyte materials for intermediate-temperature SOFCs. In these compounds, presence of dopant is necessary. In fact oxygen vacancies generated by doping, play an important role in the formation of proton conducting properties including the formation and transport of protons [6, 7]. However, these compounds usually do not combine the three important requirements for electrolyte materials including high ionic conductivity, chemical stability, and good sinter ability [8]. Doped barium cerate electrolytes represent high protonic conductivity and satisfactory sinterability, but they react with acidic gases (e.g., CO₂ and SO₂) and steam [9, 10]. On the other hand, chemically stable doped barium zirconate sintered pellets generally have a low total proton conductivity because of the large volume content of poorly conducting grain boundaries [11, 12].

A proposed solution that is taken by the result of extensive research of a group of researchers including Badwal, is using mixed solid solutions of perovskite structures to achieve a compromise between the properties of both materials [13]. Since both compounds, barium zirconate and barium cerate, are soluble in any proportion, replacement of appropriate amount of Zr into barium cerate could make a compound with suitable chemical stability and high proton conductivity. Between these chemical compositions, BZCY7 is an appropriate choice for using as an intermediate temperature electrolyte because it is shown the desired properties in a wide range of working conditions of the fuel cell [14].

According to the subjects mentioned above, the composition of BZCY7 has been selected as an electrolyte. But up to now, it is still a challenge to prepare fuel cell by a cost-effective and efficient technology. In this work, experiments conducted on an all-solid-state process, which is possible to further simplify the cell preparation. Also dry-pressing method was applied to decrease the cost of cell fabrication. Therefore, the main purpose of this study is to fabricate the layers of fuel cell (includes substrate, anode and electrolyte) with co-pressing method and then optimize fabrication process.

EXPERIMENTAL

Preparation of powders: The BZCY7 powders were synthesized by a solid-state reaction method. Barium carbonate (BaCO₃), zirconium oxide (ZrO₂), cerium oxide (CeO₂) and yttrium oxide (Y₂O₃) powders with the minimum purity of 99.9% and the average grain size of about 1 micron were used as raw materials. The powders were weighed in the stoichiometric ratios and then mixed using an attrition mill with 5 mm in diameter stabilized zirconia ball media in ethanol for 5 h. The resultant mixture was then dried at 100 °C for 1 h, followed by calcination at 1150 °C for 5 h. The

attrition and calcination process under the same mentioned conditions, were repeated twice to obtain pure phase.

These pre-BZCY7 powders were added to pure nickel oxide (NiO), with grain size of less than 10 micron, in a weight ratio of 40:60 to prepare anode powder. This mixture was well mixed by the attrition mill in ethanol for 1 h. To produce a final sample with enhanced strength, due to the low thickness of the anode and the electrolyte, these layers were fabricated on the anode substrate. This substrate was produced in a similar way of the anode production and just to create sufficient porosity in this layer; 20wt% corn starch was added to the anode material as the pore former.

Fabrication of tri-layer anode-supported half-cells:

After producing powders of NiO-BZCY7-Starch/NiO-BZCY7/BZCY7 (substrate/anode/electrolyte), the tri-layer anode-supported half-cells were fabricated by uniaxial dry-pressing method. The thickness of the layers was controlled by varying the amounts of powders used.

First, substrate powders were pressed under 65 MPa pressure with 20 mm in diameter and 0.5 mm in thickness to form the anode substrate with a flat surface and acceptable mechanical strength. Then the anode layer with thickness of 0.1 mm was pressed under 160 MPa on the pressed surface. At the end, a thin and dense electrolyte layer with a thickness of about 0.07 mm was pressed together with the pre-pressed two layers of anode and substrate under 200 MPa pressure. To enhance green strength of electrolyte layer, exact amount of 3wt% of a 2wt% PVA solution was used as a binder.

Finally, a green tri-layer sample from the press, were sintered under a suitable process. The final sintering temperature was selected at 1400 °C for 5 h. The green half-cells were heated to the target temperature, step by step to remove binder and starch at 600 and 800 °C, respectively.

Characterization of the phase composition and microstructure of the cell component:

Phase structure and composition of the produced powders were identified by X-ray diffraction (XRD) analysis using CuK α radiation. The microstructures of the produced powders were investigated by scanning electron microscopy (SEM) and also the fracture surface of a produced half-cell was imaged by SEM to ensure the accuracy of manufacturing process and connectivity of various layers together and also determine the size and percentage of remaining porosities.

In order to examine the densification behavior of various layers in half-cell (substrate/anode/ electrolyte), single-layer samples were prepared and then sintered at different temperatures of 800, 1000, 1200, and 1400 °C for 5 h. Then the changes in volume and the relative density of the samples were investigated. Shrinkage variations during sintering of each layer were calculated with measuring the dimensions of the single-layer samples that were pressed separately, before and after sintering, by caliper. The relative density of the samples was obtained based on Archimedes method.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of BZCY7 and BZCY7+NiO powders. As it can be seen in Fig. 1(a), only the peaks corresponding to BZCY7 with perovskite structure can be found and there are not any peaks attributable to impurities or unwanted phases. In the pattern of anode powder shown in Fig. 1(b), the peaks related to NiO were clearly detectable so it confirms the presence of nickel oxide in anode composition.

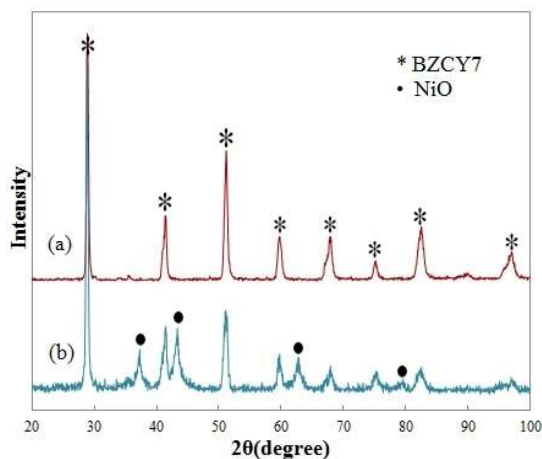


Fig. 1: XRD patterns of BZCY7 (a) and NiO+BZCY7 (b), electrolyte and anode powders respectively.

Fig. 2 shows the morphology of the BZCY7 electrolyte and NiO-BZCY7 anode powders obtained by scanning electron microscope. The powders, consisting of particles about 0.5 microns in size, agglomerate together. This structure is typical for powders prepared via a solid state reaction method.

Fig. 3 shows variations of shrinkage versus sintering temperature, and indicates the shrinkage behavior of each layer.

It is obvious that the shrinkage of anode samples are more than others. Difference in shrinkage behavior of layers will cause disintegration of tri-layer samples, because of the sintering of the thin-film electrolyte on the anode substrate is actually a constraint sintering process.

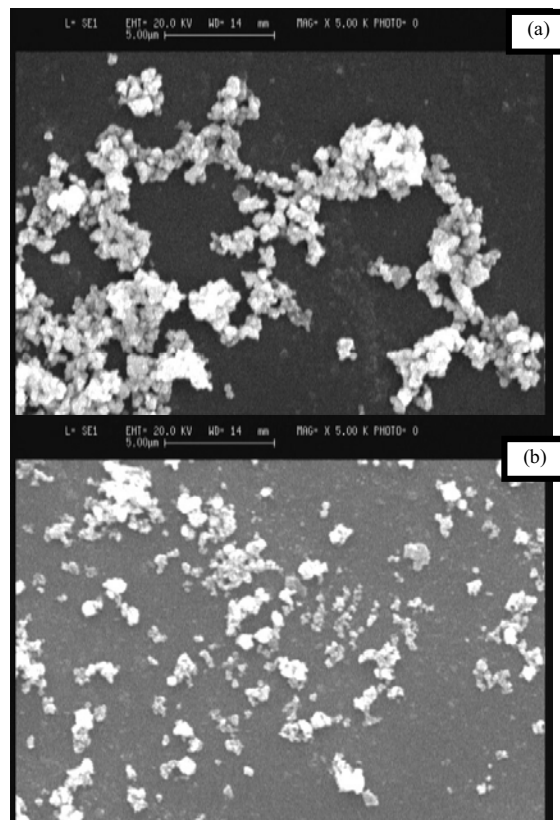


Fig. 2: SEM images of the BZCY7 electrolyte (a) and NiO-BZCY7 anode powders (b)

Since anode and substrate layers together are more than 6 times thicker than electrolyte layer, sintering of electrolyte layer is more affected by anode layer. As the presence of porosity in the anode layer will increase cell efficiency, so introducing porosity in the anode layer in so much that equalize shrinkage behavior of anode and electrolyte layers can help fabrication of tri-layer samples with high quality with no undesirable effect on cell performance. For this purpose, an appropriate percentage of pore former materials (such as starch or graphite) was added to the anode powder. It should be noted that due to the presence of porosity in the substrate layer, its shrinkage will be affected by the anode layer. Therefore, the difference in the sintering behavior of the anode and the substrate layers will not cause a problem. Variations of relative density versus sintering temperature presented in Fig. 4, shows similar trend as shrinkage variations.

To investigate the microstructure and to be ensure about the accuracy of manufacturing process, the fracture surface of a produced half-cell was imaged after sintering using SEM. Fig. 5 shows the cross-sectional view of the tri-layer half-single-cell after co-firing at 1150 °C.

As shown in Fig. 5, the three distinct layers (the anode substrate, the active anode layer and the electrolyte), can be easily distinguished. The smooth and recognizable interfaces between the layers

represent no inter diffusion between the different layers.

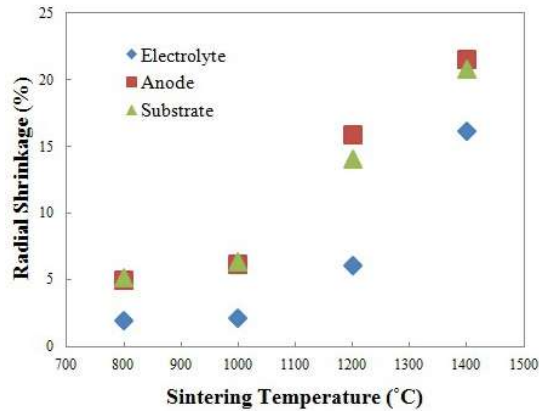


Fig. 3: Shrinkage variations in separate layers of electrolyte, anode and anode-substrate during sintering at different temperatures for 5 h

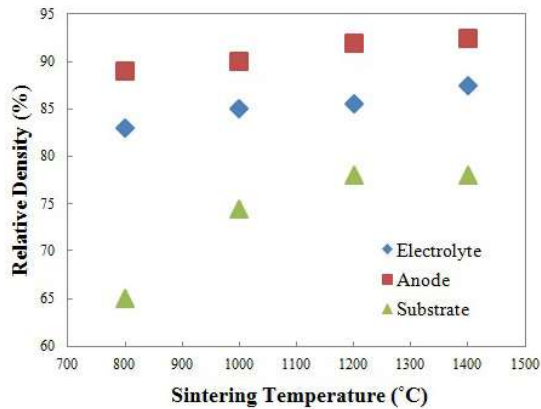


Fig. 4: Relative density variations in separate layers of electrolyte, anode and anode-substrate during sintering at different temperatures for 5 h

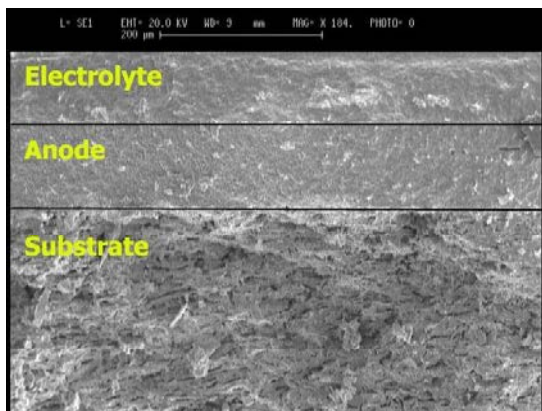


Fig. 5: SEM images of the fracture surface of the tri-layer sample

Figs. 6 and 7 show the fracture surface images of the sample at higher magnifications. Therefore, only two layers of them are visible and as the result, the connection of layers can be investigated more accurately.

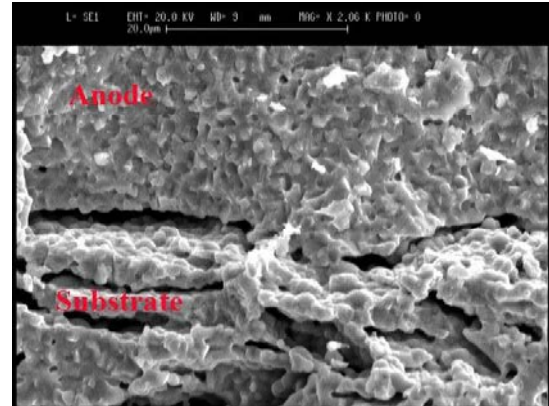


Fig. 6: The fracture surface SEM images of the interface between the anode active layer and substrate

As these images show clearly, the layers connected to each other very well and no porosity observed in the interfaces. Fig. 7 indicates that the BZCY7 membrane is quite dense, without any obvious cracks or pores, which points that the BZCY7 membrane can reach dense after sintering at the relatively low temperature of 1150 °C.

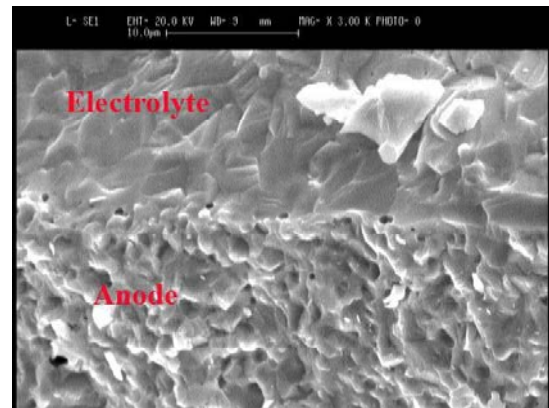


Fig. 7: The fracture surface SEM images of the interface between the anode active layer and electrolyte

The microstructure of anode observed by SEM was not porous enough. Since the porosity of the active anode layer increase the single cell efficiency. Therefore, a material which produces porosity can be added but with far less percentage of what added to substrate. Fig. 8 shows SEM image of a single-layer anode in which 5wt.% of 2wt.% PVA solution was added in order to create porosity.

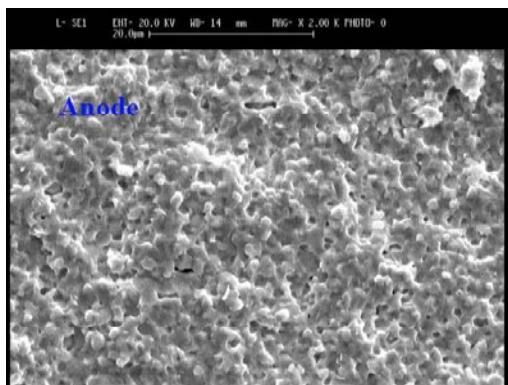


Fig. 8: SEM image of fracture surface of the single-layer anode sample

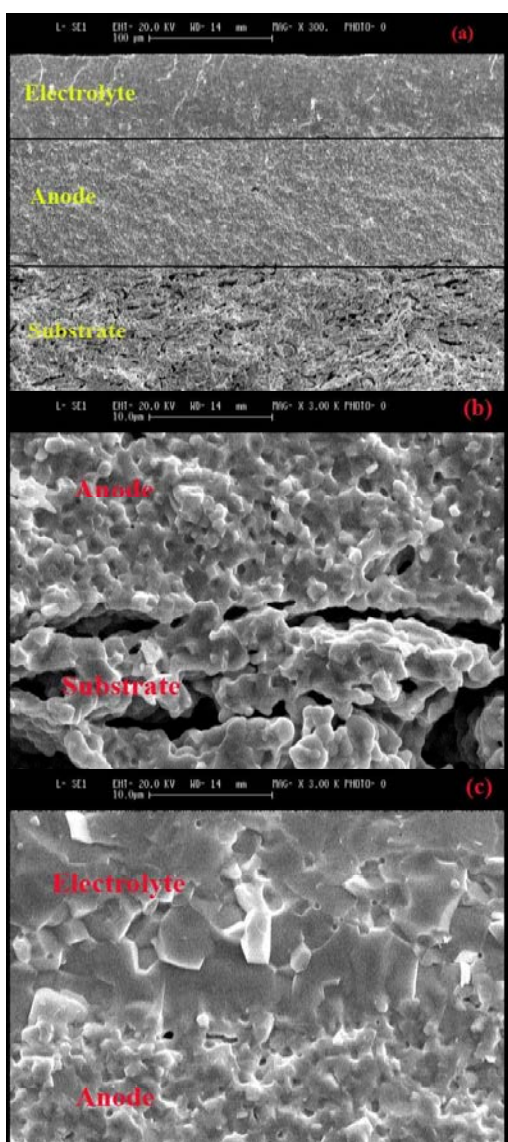


Fig. 9: SEM images of fracture surface of (a) the tri-layer sample, (b) the interface of substrate-anode (c) the interface of anode-electrolyte

As it is clear in the image and it was expected, the addition of PVA solution lead to increase the percentage of porosity in the anode layer. In this condition, not only a tri-layer sample was not broken during sintering, but also the connection of the layers improved. Due to increasing porosity, the cell will produce a better performance. The image of the tri-layer sample produced with this composition of anode, which is more porous, is shown in Fig. 9. In this sample, due to better pressability and sinterability, the connectivity of layers improved which is visible at higher magnifications in Fig. 9 (b) and (c).

CONCLUSION

- Based on the XRD analysis, BZCY7 and NiO-BZCY7 compositions were produced successfully by using solid-state synthesis as a simple and cost-effective method.
- By the SEM images, it can be distinguished that solid-state synthesis, to produce powders, and the uniaxial dry-pressing method can be used to fabricate half of the single-cell and thus the production costs can be significantly reduced.
- By adding the appropriate amounts of PVA as the pore former materials to the anode powder, the shrinkage of this layer was controlled and disintegration of a tri-layer sample during sintering was avoided.
- By increasing the percentage of PVA to the anode powder, in addition to preventing the disintegration of three layers, pressability and sinterability also increased and thus the connectivity of layers improved.

REFERENCES

1. Bose, A.C., 2009. Inorganic Membranes for Energy and Environmental Applications, Springer, Pittsburgh.
2. Fabbri, E., L. Bi, H. Tanaka, D. Pergolesi and E. Traversa, 2010. Chemically Stable Pr and Y Co-Doped Barium Zirconate Electrolytes with High Proton Conductivity for Intermediate-Temperature Solid Oxide Fuel Cells. *Advanced Functional Materials*, 1-9.
3. Kreuer, K., 2003. Proton-conducting oxides. *Annual Review of Materials Research*, 33(1): 333-359.
4. Steele, B.C.H. and A. Heinzel, 2001. Materials for fuel-cell technologies. *Nature*, 414(6861): 345-352.
5. Epifanio, A.D., E. Fabbri, E. Di Bartolomeo, S. Licocchia and E. Traversa, 2008. Design of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ Protonic Conductor to Improve the Electrochemical Performance in Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). *fuel cells*, 8(1): 69-76.
6. Iwahara, H., et al., 1981. Proton conduction in sintered oxides and its application to steam

- electrolysis for hydrogen production. *Solid State Ionics*, 3: 359-363.
7. Iwahara, H., et al., 1993. Performance of Solid Oxide Fuel Cell Using Proton and Oxide Ion Mixed Conductors Based on $\text{BaCe}_{1-x}\text{Sm}_x\text{O}_{3-\alpha}$. *Journal of the Electrochemical Society*, 140(6): 1687-1691.
 8. Zuo, C., S. Zha, M. Liu, M. Hatano and M. Uchiyama, 2006. Doping and Defect Structure of Mixed Conducting Ceramics for Gas Separation. *Advanced Materials*, 18: 3318-3320.
 9. Wu, T., Y. Rao, R. Peng and C. Xia, 2010. Fabrication and evaluation of Ag-impregnated $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{2.9}$ composite cathodes for proton conducting solid oxide fuel cells. *Power Sources*, 195: 5508-5513.
 10. Bi, L., S. Fang, Z. Tao, S. Zhang, R. Peng and W. Liu, 2009. Influence of anode pore forming additives on the densification of supported $\text{BaCe}_{0.7}\text{Ta}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte membranes based on a solid state reaction. *the European Ceramic Society*, 29: 2567-2573.
 11. Sun, W., L. Yan, Z. Shi, Z. Zhu and W. Liu, "Fabrication and performance of a proton-conducting solid oxide fuel cell based on a thin $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte membrane," *Power Sources*, Vol.195, pp. 4727-4730, 2010.
 12. Peng, C., J. Melnik, J. Li, J. Luo, A.R. Sanger and K.T. Chuang, 2000. ZnO-doped $\text{BaZr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ proton-conducting electrolytes: Characterization and fabrication of thin films. *Power Sources*, 190: 447-452.
 13. Phair, J.W. and S.P.S. Badwal. 2006. Review of Proton Conductors for Hydrogen Separation. *Ionics*, 12: 103-115.
 14. Huang, C., D. Chen, Y. Lin, R. Ran and Z. Shao, 2010. Evaluation of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ mixed conductor as a cathode for intermediate-temperature oxygen-ionic solid-oxide fuel cells. *Power Sources*, 195: 5176-5184.