

Research on impact of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte doped with a small amount of Al_2O_3 on the proton conducting solid oxide fuel cell

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Abstract. Make the composite electrolyte by doping Al_2O_3 powders, in the ratios of 1:0.02 and 1:0.04 respectively to the electrolyte masses, into initial powders of the electrolyte- BaZrCeYO made in the method of Pechini. After 10 hours sintered at 1400°C , the composite electrolyte was completed, XRD test carried out, respectively in the range of $500\text{--}800^\circ\text{C}$, Ac impedance spectrum tested, and adopted the composite electrolyte impedance test and output characteristic. The results showed that: Al element in the calcinations process replaced B atoms of ABO_3 perovskite structure into the crystal lattice; electrolyte impedance and cell impedance increased significantly when the doping of Al_2O_3 increased, and the output characteristic performance of single cell was significantly reduced.

Introduction

Solid Oxide Fuel Cell (SOFC) as an energy conversion device labeled by highly efficiency and green attracts more and more attentions. Firstly, it overcome the restraint of Carnot cycle heat engine by directly transferring chemical energy into electrical energy by which increases the availability ratio of energy; secondly, the SOFC can be widely used, for it is suitable for all kinds of hydrocarbons energy; thirdly, the SOFC hardly emit harmful gases, it is an environmentally friendly energy conversion devices. Due to the great demand of energy and the shortage of fossil fuels, the US and developed European countries spent enormous human forces and funds in seeking or researching sources of alternative energy, thus the SOFC will be a good choice, for example, United States Department of Energy established Solid Energy Conversion Alliance in 2000 and made a long-term financial scheme to support SOFC commercialized, dozens of corporations took part in this scheme, like Siemens-Westinghouse, General Electric, FuelCell Energy and so forth. [1] Though these corporations above have successfully studied on SOFC and the performance of their products seems great, the road that led to completely success is still long because the techniques are still immature and there are so many difficult problems in stage of laboratory.

The most crucial part of SOFC is electrolyte where ions traverse and parts of reactions happen, the merits of the electrolyte material determine the qualities of cells' performance. Good SOFC electrolytes necessarily meet the following characteristics: (1) at its working temperature, the electrolyte must be stable in both oxidative and reductive ambiances; (2) there must be enough ion conductivity or proton conductivity and the very low electronic conductivity; (3) the electrolyte can be made into thick membrane; (4) it must be compatible with the electrode materials at chemical characteristic and thermal expansion. The electrolytes traditionally used are normally operated at a high temperature, for example, YSZ whose operation temperature normally reaches above 1000°C . Seeking for a kind of material which can both decrease the operation temperature and maintain the output efficiency of the cells is a duty that the researchers must face. Iwahara and his partners found that there is a high protonic conductivity when they studied the BaCeO_3 group compounds. Moreover, mixing some kinds of rare metals into the material, the conductivity will be higher even the operation temperature below 800°C . [2] However, BaCeO_3 was also found that in the presence of CO_2 and H_2O , the material is unstable, fortunately, recent studies have found that, by doping Zr element to replace part of Ce element can resolve this problem, and Zuo et al found that, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ is a stable proton conductor in atmosphere with CO_2 , and has a high protonic conductivity [3]. Yang

and his partners found that doping element Y and Yb can acquire higher conductivity [4]. It is reported that $\text{BaZr}_x\text{Ce}_{0.5}\text{Y}_{0.5}\text{O}_{3-\delta}$ doped with a small amount of ZnO while sintering can reach the electrolyte sintered density of 93-97% [5-6]. Visibly, the method of doping substances by a small amount can significantly change some qualities of the electrolyte. This study choose doping a small amount of Al_2O_3 into the electrolyte in order to study its effect on the qualities of electrolyte and cell, using Penchini method to prepare $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte powder, then mixing the electrolyte powder and Al_2O_3 powder with mass ratio of 1: 0.02, 1: 0.04 ratio to make the composite electrolyte powder. After 10 hours sintered, then pure and composite electrolyte films and single cells are tested by XRD method to research the crystal structure, and by AC impedance spectroscopy measuring electrolyte and impedance of single cells, then linear sweep voltammetry described power curve.

Method

The single cell preparation of Composite Electrolyte. In this experiment, the preparation of electrolyte adopts Penchini method. The raw material $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Y_2O_3 were weighed according to the ratio, mixed with deionized water, stirred and heated to clear solution, add EDTA (ethylenediamine tetraacetic acid) and citric acid with stirring according to the number of metal cation mol ratio (1:2:2), adjusted the PH value of solution reaching to 8 by adding ammonia solution, heated and stirred continually until the solution became viscous wet gel. Put the gel into the oven, and dried at 200 °C within 10 hours to obtain a black foamed xerogel, and then sent to muffle furnace at 800 °C sintering in 4 hours to get a kind of yellow powder. Then the yellow powder above was doped with Al_2O_3 powder according to the mass ratio 1:0.02, 1:0.04. The powder pressed at 300MPa pressure and became the original film with the thickness of the films equal to 1mm, brought to muffle furnace at 1400 °C sintering in 10 hours to obtain a composite electrolyte sheet. The experiment uses anode supported cell to research. Mixed the above yellowish powder with NiO powder with the weight corresponding to the mass ratio of 35:65[7], and added 10% of the pore forming agent, after full balling became anode powder. Used dust pressing method to make the single cell, put a small amount of electrolyte powder evenly laying on the surface of the anode, pressed the powders with 300 MPa pressure, then brought the films into muffle furnace sintering at 1400 °C. After 10 hours sintering, the single cell of supported by anode was completed.

The determination of electrolyte and single battery. The Japanese Rigaku - D - Max - RB - 12 kw transfer target X ray diffraction analysis electrolyte phase structure, tube is 40 kv voltage, tube current 30 ma, 10-90 ° scan range, Angle step 0.02 °, Cu target, for CuK α X-ray line, the wavelength of 0.15418 nm. Using British SolartonSI-1260, Solarton-1287 tester measuring electrolyte electrochemical impedance frequency response 0.1Hz-106Hz, AC amplitude 10mV, test temperature 500-800 °C. Using electrochemical analyzer CHI604C measure the impedance of the single battery and the IV curve, test temperature 500-800 °C.

Results and Discussion

XRD results and discussion. Figure 3.1 is XRD patterns with the standard card comparison chart which the $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte after sintered at 1400 °C. We can see in this figure, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte has been formed in a single perovskite structure. Figure 3.2 is a composite electrolyte sintered under the same conditions after diffraction pattern of FIG comparison with the standard card, in this figure, after 1400 °C sintering, composite electrolyte appears a mixture of a perovskite structure compound and a fluorite structure compound, we speculate that during the high temperature reaction process, Al atom substituted for the B atoms of ABO_3 perovskite structure into the lattice, and the B atoms substituted generated into an fluorite structure, so even doping a small amount of Al_2O_3 , the effect on synthesis still have a non-negligible impediment.

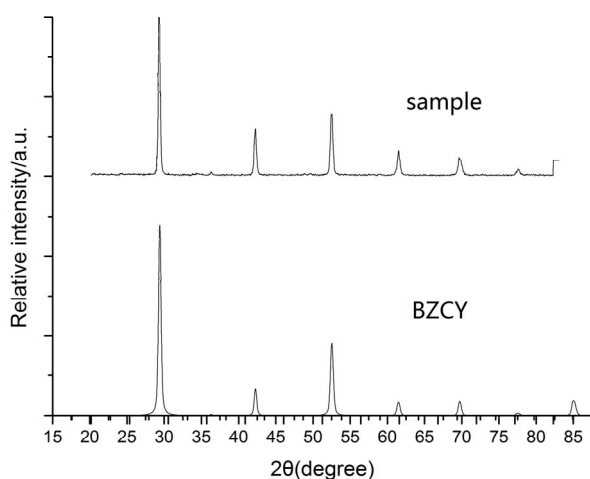


Figure 3.1 BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} electrolyte and the standard card comparison chart

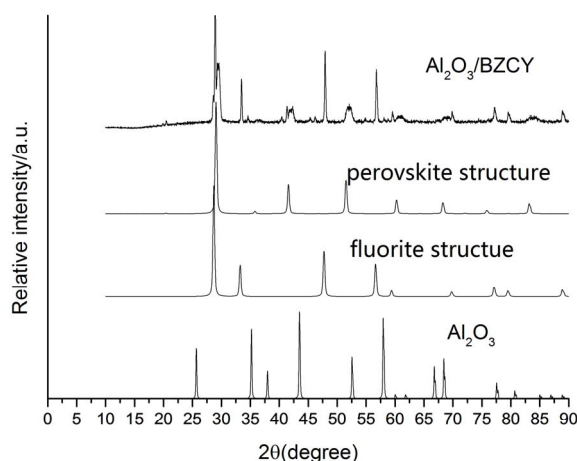


Figure 3.2 Composite electrolytes and the standard card comparison chart

Electrolyte impedance results and discussion. AC impedance spectroscopy is a kind of method which use a small-amplitude AC voltage perturbation as the signal and observe the relationship between the impedance and frequency to characterize the electrochemical properties of the sample. This method was originally applied by the Bauerle using to study the solid electrolyte [8]. Due to the nonuniform of the solid electrolyte and the effect of impedance response of electrode part, when used ac conductivity measure the electric conduction, the electrical resistance changed with frequency, so you need to do thoroughly analysis of the impedance change of cells with the change of frequency. Generally, research the relationship between the different frequency impedance (Z') and capacitive reactance (Z'') using the plural floor plan. Polycrystalline solid electrolyte resistance are complex, including grain resistance, grain boundaries resistance, grain capacitance and grain boundaries capacitance, and have an impedance characteristic related to the measurement of frequency. Figure 3.3 is BZCY electrolyte impedance and comparison charts with composite electrolytes:

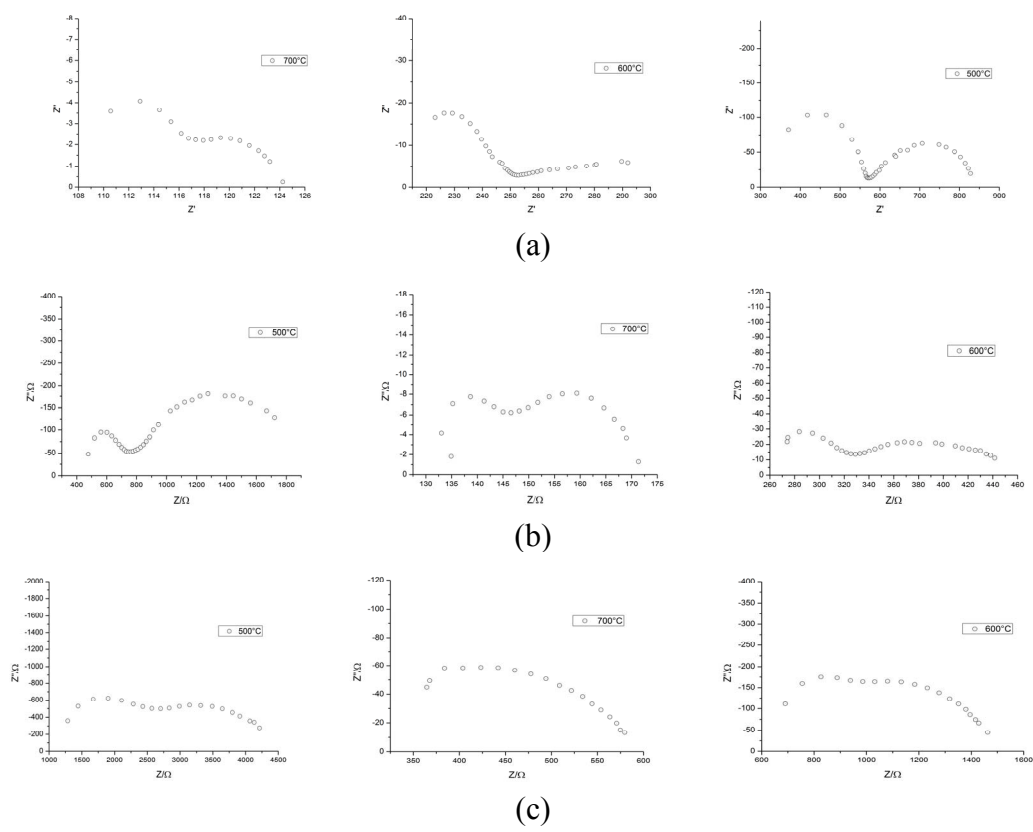


Figure 3.3 (a) impedance spectroscopy of BZCY electrolyte at 700 °C, 600 °C, 500 °C ; (b) impedance spectroscopy of 1: 0.02 composite electrolyte at 700 °C, 600 °C, 500 °C ; (c) impedance spectroscopy of 1: 0.04 composite electrolyte in °C, 600 °C, 500 °C

In figure 3.3, EIS has two semi-circular structures representing the grain boundaries resistance and interface resistance, the grain impedance can be obtained from FIG fitting, the results show that with the increase of doping Al₂O₃ powder, three kinds of impedance increased significantly.

Using the formula $\sigma = \frac{L}{RS}$ can be obtained three kinds of electrolyte conductivity, and by the Arrhenius equation can get the relationship between conductivity and temperature, thus obtain the activation energy $E_a = \Delta H$. And the activation energy can be acquired by these curves which are approximately equal to 0.68eV. Using conductivity and temperature, fit curve of Arrhenius, as shown in figure 3.4:

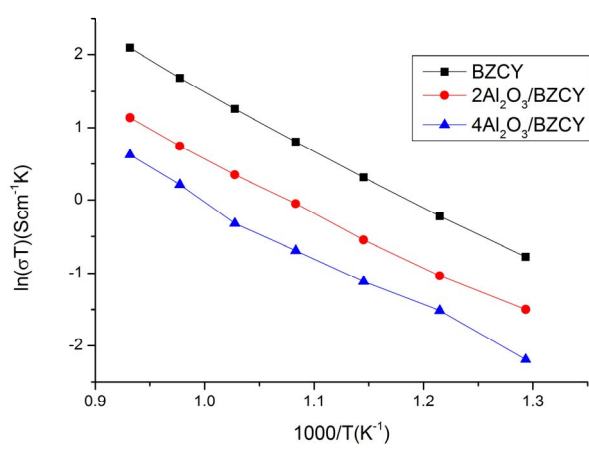


Figure 3.4 curves of Arrhenius

The step that impedance measurement of single cell decomposed into accurately individual loss is very important, but the actual cell impedance spectrum can only show parts of its decomposition. However, because of too many factors combining the impedance, the actual impedance spectra obtained are generally difficult to interpret [9], but from the impedance spectra we can still decompose the impedance into ohmic resistor (including electrolyte resistance and contact resistance of the poles) and polarization resistance in general. Three and a half arc respectively represent ohmic resistance, polarization resistance and resistance related to gas conversion and diffusion. The part of high frequency end correspond to ohmic resistance which can be obtained by impedance spectroscopy accurately, the mid part correspond to the polarization resistance, the part of low-frequency end of the semicircle correspond to relation on gas conversion and diffusion. As shown in Figure 3.5 are three kinds of electrolyte single cell impedance spectroscopy:

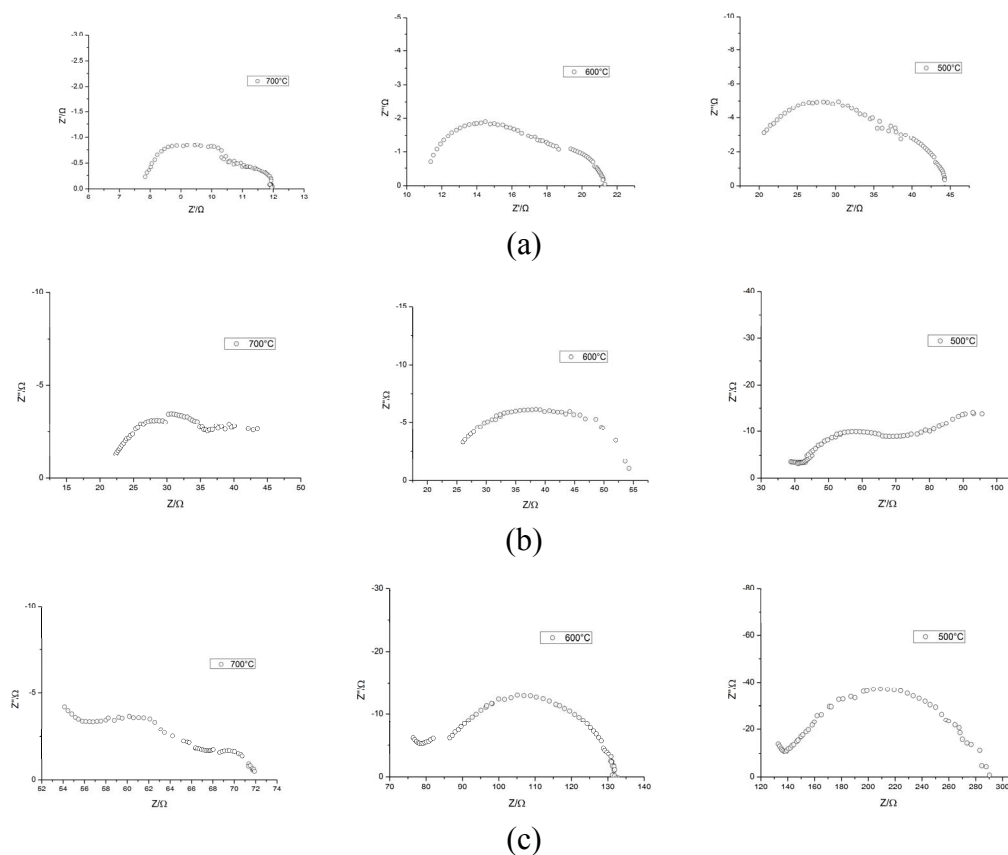
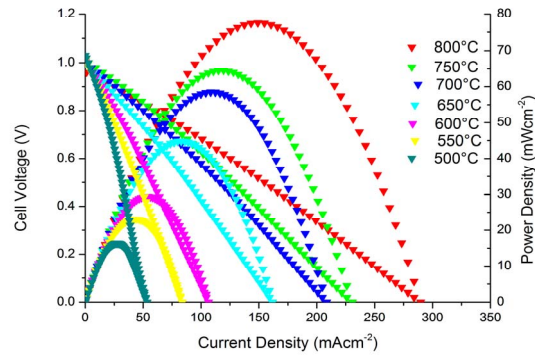


Figure 3.5 (a) Impedance spectrum of cells with pure electrolyte at 700 °C, 600 °C, 500 °C ; (b) cells with 1: 0.02 composite electrolyte at 700 °C, 600 °C, 500 °C ; (c) cells with 1: 0.04 composite electrolyte at 700 °C, 600 °C, 500 °C

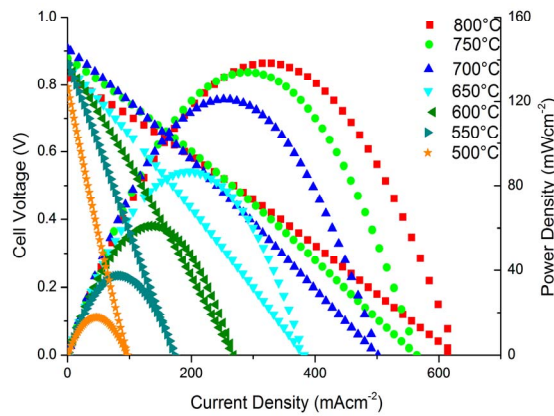
The more quality of Al_2O_3 was added, the higher cell's impedance it is showed, the polarization resistance and gas diffusion resistance changed with the temperature is obvious. So according to the impedance spectra, the influence on single cell mainly is no more than the cell ohmic resistance, but polarization resistance and diffusion resistance cannot be ignored.

Single cell output performance results and discussion. (a) BZCY single cell output performance curve can be seen from Figure 3.6, cell power density and output current change obviously with the increasing temperature, At 800 °C, reaching the maximum short-circuit current density which is equal to 610mA / cm^2 and the power density can be up to 140mW / cm^2 . The open circuit voltage (OCV) namely the Nernst potential theoretical value is approximately 1.2 V [10-11], but the actual open-circuit voltage of cell was influenced by activation polarization, ohmic polarization, concentration polarization. At low current density, activation polarization significantly increases at high current densities; it is steadily increasing [12]. The open circuit voltage is up to 0.92 V at 700 °C, that is because in 700-800 °C, SOFC is affected obviously by concentration polarization,

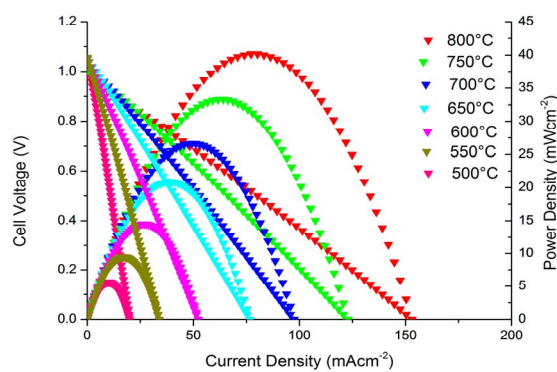
but in the 500-700 °C range the performance was mainly influenced by activation polarization. From Figure 3.7 (b), 3.7 (c) , we can make sure that when doped Al₂O₃ with a larger proportion , the measurement of current output power decreases, however, the open circuit voltage of mixed single cells were significantly higher than undoped one, the cell voltage is relatively more stable, probably because doping Al₂O₃ can reduce the impact of activation polarization on the cell.



(a)



(b)



(c)

Figure 3.6 (a) Output power curve of single cell of BZCY (b) output power curve of single cell of 1:0.02 composite electrolyte;(c) output power curve of single cell of 1:0.04 composite electrolyte

Summary

This paper takes BaZr_{0.1} Ce_{0.7} Y_{0.2} O_{3-δ} electrolyte which is relatively stable as the study object. Pechini method is applied to prepare fluffy electrolyte powder which was doped with Al₂O₃ powder later to synthesis composite electrolyte. By testing with XRD method, it is showed that the Al element can obstruct the process of synthesis. By fitting Arrhenius curve, we find that the conductance

activation energy rarely changed, the activation energy is approximately 0.68eV. The cell test shows that the cell is largely influenced by polarization, much lower than theoretical open-circuit voltage of 1.2V, however, the composite electrolyte with Al₂O₃ can effectively reduce the polarization loss of voltage.

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