

H₂S Solid oxide fuel cell based on a modified Barium cerate perovskite proton conductor

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Abstract Urea combustion method was adopted to prepare precursor powder, MCeO₃ doped with Zr (M is alkaline earth element, such as barium, strontium, and calcium). The precursor powder has typically perovskite structure after being calcined at 873 K. In 773 K~1,273 K, BaCe_{0.425}Zr_{0.475}Y_{0.1}O₃ has the highest conductivity above 10⁻² S cm⁻¹ and good chemical stability, while the phase transition may exist in H₂S atmosphere for the proton conductors. In the single fuel cell composed of MoS₂-BaCe_{0.425}Zr_{0.475}Y_{0.1}O_{3-σ}-Ag with BaCe_{0.425}Zr_{0.475}Y_{0.1}O_{3-σ} as electrolyte, the best performance is obtained. The open circuit voltage of fuel cell is all about 0.72 V, the max power density, 1.55 mW cm⁻². The performance drop is attributed to ohmic loss resulting from the separation of electrolyte and electrode, and improvement is required to bring out new anode materials compatible to the proton conductor, BaCe_{0.425}Zr_{0.475}Y_{0.1}O_{3-σ}, as electrolyte.

Keywords Hydrogen sulfide · Solid oxide fuel cell · Proton conductor

H₂S is a corrosive, noxious gaseous pollutant with displeased smell, which is produced from coal gasification,

oil refining industry, natural gas industry, and so on. Furthermore, H₂S may be oxidized into SO₂ and may promote the pollution of acid rain. At present, the main processes to remove H₂S include the Claus process [1] and Tannin extract method [2]. However, these conventional processes only reclaim the sulfur component, while hydrogen component is oxidized into stream, in which a great deal of heat is released in vain.

In 1987, Pujare et al. [3] adopted YSZ as electrolyte to construct the single H₂S solid oxide fuel cell (H₂S-SOFC), and demonstrated the potential application of H₂S-SOFC. And from then on, Pujare et al. and Slavov et al. [4, 5] paid more attention on the electrolyte membrane and anode catalysts applied in H₂S-SOFC, considering the extreme corrosion of H₂S. Iwahara et al. [6–9] reported in succession the high temperature proton conductors (HTPCs) with perovskite structure, such as SrCeO₃, BaCeO₃. The doped cerium is favorable to the conductivity of proton because of the proton charge carriers, while the chemical stability was not obtained. Katahira et al. [10, 11] investigated the endurance against CO₂ of barium cerates with doped ionics. Afterwards, Peterson and Jack [12, 13] found that strontium cerates is easily poisoned by H₂S, and that the formation of strontium sulfate may result in descent of conductivity of electrolyte greatly and may deteriorate the run of fuel cell.

In this paper, alkaline earth cerates doped Zr were synthesized successfully, and Zr as doped element was added into MCeO₃ (M is alkaline earth element, such as barium, strontium, and calcium) to enhanced chemical stability of MCeO₃ against H₂S. Considering the effect on conductivity, the Zr addition of chosen amount is 0.475. In addition, the electrical performance of H₂S-SOFC with the concerned electrolyte was examined.

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Experiment

Preparation of $\text{M}\text{Ce}_{0.9-x}\text{Zr}_x\text{Y}_{0.1}\text{O}_3$ precursor powder

The urea combustion method was adopted to prepare precursor powder of electrolyte specimens. The following metal nitrate solution, $\text{M}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$, $\text{Zr}(\text{NO}_3)_2$, and $\text{Y}(\text{NO}_3)_3$, were mixed in the required stoichiometric ratios. Before the powder was pressed into electrolyte pellet with thinner than 1 mm and in 30 mm diameter, the precursor powder of $\text{BaCe}_{0.425}\text{Zr}_{0.475}\text{Y}_{0.1}\text{O}_3$, $\text{SrCe}_{0.425}\text{Zr}_{0.475}\text{Y}_{0.1}\text{O}_3$, $\text{CaCe}_{0.425}\text{Zr}_{0.475}\text{Y}_{0.1}\text{O}_3$ (respectively notated BCZY, SCZY, and CCZY) were calcined at 873 K. All of specimens were then sintered at 1,473 K. The densification of consequent electrolytes determined by Archimedes method was 92% above.

Preparation of membrane-electrode assemble

MoS_2 slurry as anode was screen printed on one side of electrolyte membrane substrate. And then the assemble membrane was heated at 973 K in N_2 atmosphere for 1 h. The anode thickness is about 4 mm. The same approach was followed to prepare the Ag cathode on the other side of the electrolyte. The configuration of single cell reactor was constructed like this, $\text{MoS}_2/\text{BCZY}/\text{Ag}$. Ni mesh was used as current collector to adhere to electrode surface with Ag paste, and anode chamber was fed with H_2S while cathode chamber was fed with air.

Characterization and electrochemical test

The precursor powder were characterized by XRD (Bruker D8 ADVANCE, Germany), CuK α radiation. The conductivity of electrolyte in humidity H_2 was measured by four-probe method, and the electrochemical test of fuel cell was recorded by potentiostat (TD 3691, China).

Results and discussion

XRD of precursor powder

Cubic perovskite structures for BCZY, SCZY, and CCZY are obtained. To demonstrate the chemical stability of the Zr-doped, the two specimens, Zr-doped and the Zr-free BaCeO_3 , were both held in H_2S atmosphere for 4 h and then sintered in tube furnace at 1,073 K. For comparison, the XRD patterns of Zr-free BaCeO_3 were showed in Fig. 1 while the patterns of Zr-doped BaCeO_3 in Fig. 2. From the difference, the chemical stability of Zr-doped BaCeO_3 is superior to that of the Zr-free BaCeO_3 because BCY was reacted with H_2S and new product can be observed in XRD

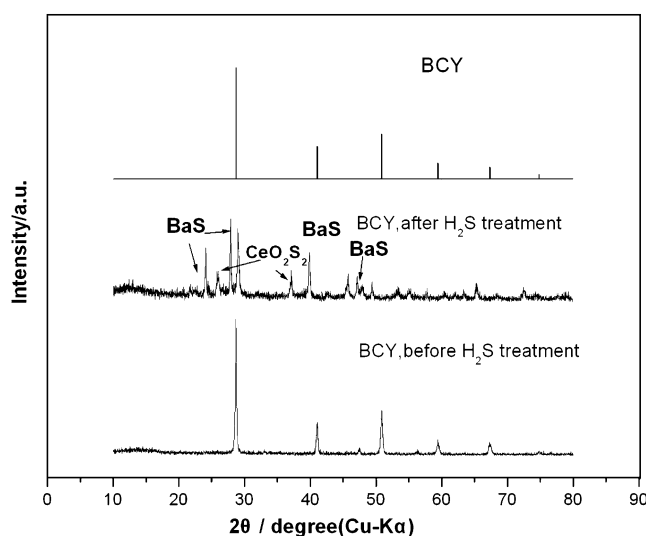


Fig. 1 XRD patterns of Zr-free BaCeO_3 before and after H_2S treatment

patterns. The results show that doped Zr can improve the H_2S endurance of proton conductor. The main peaks in BCZY were labelled in Figs. 1 and 2. The crystal structure was verified as perovskite, and the cell parameters of BCZY and BCY were listed in Table 1. The unit-cell parameters decrease with the addition of Zr ionic, because of the smaller Zr^{4+} ionic radius (7.2 nm), $r_{\text{Zr}^{4+}}$ than the Ce^{4+} ionic radius (9.4 nm), $r_{\text{Ce}^{4+}}$, while the Y^{3+} ionic radius is greatly smaller than the Ce^{4+} ionic radius [14–16]. According to the unit-cell parameters, subtle changes were also observed between the BCZY without treatment and the modified BCZY. Proton originated from H_2S decomposition at certain temperature inserts into the perovskite structure and the modification of unit-cell parameters can

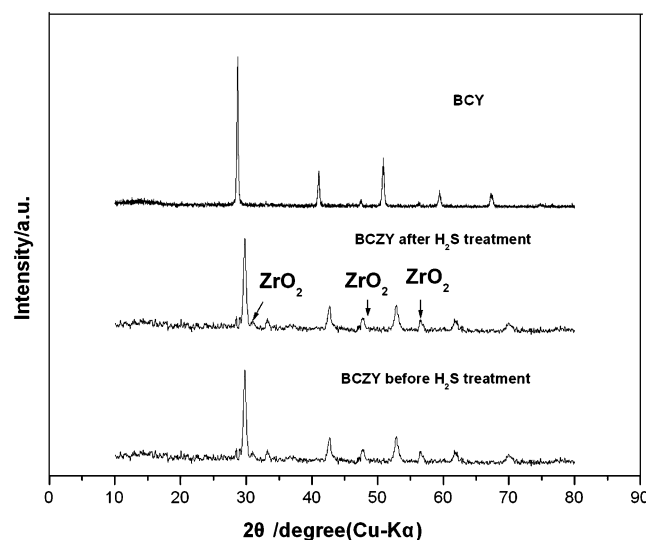


Fig. 2 XRD patterns of Zr-doped BaCeO_3 before and after H_2S treatment

Table 1 The unit-cell parameters of BCZY and BCY

Specimens	a/10 ⁻¹ nm	b/10 ⁻¹ nm	c/10 ⁻¹ nm
BCY	7.341	6.038	6.031
BCZY(before H ₂ S treatment)	6.024	5.162	5.159
BCZY(after H ₂ S treatment)	6.033	5.170	5.163

be seen herein. Slodczyk et al. has proved the proton insertion may contribute to the changes of unit-cell parameter by the Raman spectra patterns at different pressure [17].

Conductivity

Considering the Zr addition effect on conductivity, it is necessary for these conductors to determine the conductivity at different temperature. The results of conductivity were obtained as Fig. 3 showed. The conductivity of three kinds of proton conductors almost increases with the elevated temperature. It is noted that conductivity of BCZY can reach 10⁻² S cm⁻¹ in the range of mid-temperature. We attempted to demonstrate that the conductivity of proton conductors in humidity H₂ accords with the Arrhenius equation generally in Fig. 3. However, it is mentionable that some exceptional points depart from the curve of conductivity vs. temperature, especially for below 1,000 K (ie. 1,000 × T⁻¹ ≈ 1). Various views were found to explain the deflection of proton conductivity or total conductivity in the literature, such as the annealed condition [18], doped ionic

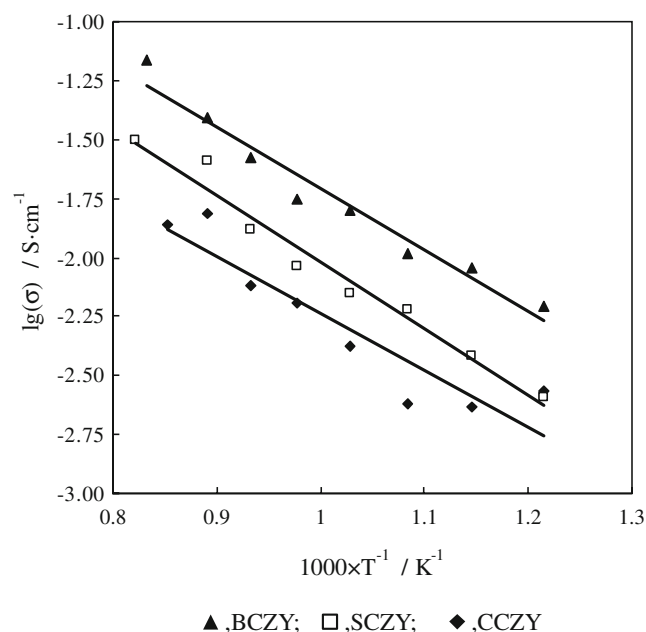


Fig. 3 Curve of temperature dependence of the total conductivities for BCZY, SCZY, and CCZY measured in humidity H₂ (in 773 K~1,273 K)

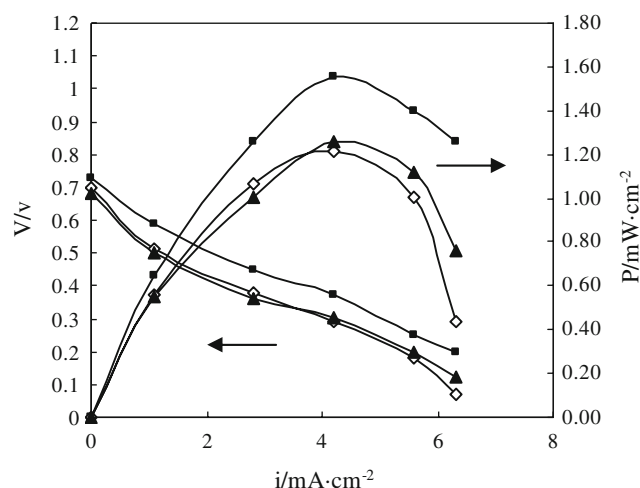


Fig. 4 $i \sim V$ & $i \sim P$ curve for H₂S-SOFC at 1,023 K, MCZY as solid electrolyte

concentration and variety [19], etc. In our work, the obvious deflection occurs with the turning of temperature, which may infer that the related phase transitions happen. In the humidity H₂ atmosphere, water vapor favors the proton production and transfer. Below 1,000 K, the decreased conductivity may result from the low proton concentration. For barium cerate as proton conductor in experiments, there are rhombohedral and orthorhombic phases in the perovskite type structure at least. Elevated temperature in the tests may contribute to phase transitions, and the rhombohedral phase existing in the temperature does not advantage the total conductivity upgrade [20].

In contrast to the conductivity of oxide ion solid electrolyte, such as ceria-doped samarium (SDC), MCZY (M=barium, strontium) and SDC are in the same magnitude [21]. The result indicates that SCZY and BCZY are potential electrolyte even in mid-temperature.

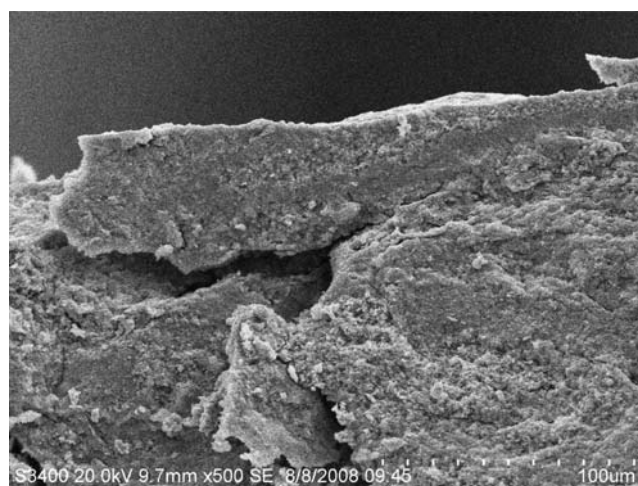


Fig. 5 SEM morphology of degraded anode-electrolyte section

Fuel cell test

To investigate the applicability of the proton conductors in fuel cell, three kinds of proton conductors, BCZY, SCZY, and CCZY, are adopted to carry out electrochemical test at 1,023 K. The temperature selected is to evaluate the feasibility of H₂S fuel cell in mid-temperature, such as 973 K–1,123 K. The current density (*i*) vs. potential (*V*) and vs. power density (*P*) curve are showed in Fig. 4. It seems that the voltage output of the three fuel cells decreases rapidly with the increase of current density without exception, especially in the range of low current density. The voltage of the SOFC with BCZY electrolyte decreases nearly in linearity, while the fuel cells with SCZY and CCZY electrolyte are both performed worse, and it is deemed that there is a great voltage drop in the high current density region. The obtained max current density is less than 8 mA cm⁻², which results from the ohmic loss. After the run of fuel cell, the severe separation has been found at the connection between the electrode and the electrolyte, as Fig. 5 showed herein, which may contribute to the ohmic loss. The weak match of thermal expansion between the anode and electrolyte can be seen easily. Anyway, the performance persisted for 10 h and the test was ended on purpose without voltage drop in evidence. It is not observed that electrolyte deterioration resulting from H₂S poisoning [12].

At 1,023 K, the highest open circuit voltage (noted as OCV) among the concerned fuel cells is the one with BCZY as electrolyte, 0.72 V, and the max power density is 1.55 mW cm⁻². Although poorer performance than that of fuel cell with oxide conducting electrolyte in reference [21], it can be concluded that the SOFC with BCZY as proton electrolyte exhibits more suitable for H₂S feed. The performance descent is attributed to the separation between the electrode and electrolyte, and something should be done to improve the compatibility between the electrolyte and electrode.

Conclusion

Proton conductor, BCZY prepared by urea combustion method are suitable for H₂S-SOFC. BCZY pretreated in H₂S atmosphere may induce the structure changes, and further influences the conductivity of potential electrolyte at low temperature. Because of the highest conductivity

among three proton conductors prepared, BCZY was selected to construct the fuel cell with the configuration like MoS₂-BCZY-Ag, and the best performance is obtained with OCV 0.72 V, the max power density 1.55 mW cm⁻² at 1,023 K. The ohmic loss resulting from the separation between the electrode and electrolyte is the main cause influencing performance of the fuel cell. It suggests that a new anode material compatible to the BCZY in H₂S-SOFC is required.

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