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Zr doped $BaFeO_{3-\delta}$ as a robust electrode for symmetrical solid oxide fuel cells

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Abstract

A $BaFe_{0.9}Zr_{0.1}O_{3-\delta}$ (BFZ) is successfully synthesized and its characteristics are investigated. The oxide exhibits high stability and a cubic perovskite structure in a reducing atmosphere. A $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) supported symmetrical solid oxide fuel cell (SOFC) with BFZ electrode demonstrates a maximum power density of 1097 mW cm^{-2} using humidified H_2 as the fuel and ambient air as the oxidant at 800°C. And as low as 0.190 Ω cm^2 of polarization resistance of single cell is observed at 650°C. Moreover, the electrode demonstrates high stability in 100 h test, as well as redox stability in both oxidizing and reducing atmospheres. The high electrochemical property and good stability suggest that the BFZ is promising candidate for symmetrical SOFC electrode.

Keywords: Symmetrical solid oxide fuel cells; Electrode; High performance; Stability.

1 Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention due to their advantages of high conversion efficiency, less emissions and fuel flexibility[1,2]. A typical single cell comprises of a densified electrolyte and two porous ceramic layers of cathode and anode. Different materials are normally applied as the cathode and anode because of the different operation conditions in those two sides. Recently, a symmetrical configuration SOFC with same material for both cathode and anode has been proposed and investigated[3-5]. This type of symmetrical cell demonstrates many advantages compared with conventional cells: facilitating fabrication with enhanced compatibility between electrode and electrolyte, minimizing cost, and eliminating coke formation and sulfur poisoning by switching the supply gas flows.

Due to the unique configuration of symmetrical SOFCs, the electrode material is required to possess structural and chemical stability, sufficient electrical conductivity and favorable electrocatalytic activity in both oxidizing and reducing atmospheres. However, a few materials meet the requirements, and most of them are mixed-ionic-electric-conductive (MIEC) perovskite-based oxides. To enhance the redox stability, some cations with high valence (Cr, Ti, Mo, Nb, Zr and so on) have been doped in these perovskite-based oxides (ABO_3) and which have been applied in symmetrical SOFC, such as $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, $La_{0.5}Sr_{0.5}Co_{0.5}Ti_{0.5}O_{3-\delta}$, $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$, $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$, $SrFe_{0.75}Zr_{0.25}O_{3-\delta}$ and so on[3, 6-9]. It is also reported that the Zr doped perovskite showed a better electrochemical performance in reducing atmosphere[9].

$BaFeO_{3-\delta}$ has been regarded as a potential iron-rich cathode due to its high electrocatalytic activity and fast surface exchange kinetics[10]. However, there is a mismatch of ionic radius between Ba and Fe, the $BaFeO_{3-\delta}$ usually exists as a multiphase compound, depending on the synthesis conditions[11, 12]. To stabilize the cubic lattice structure, a few cations like La, Sm, Zr, Nb, Sn have been doped into $BaFeO_{3-\delta}$. For instance, the $Ba_{0.95}La_{0.05}FeO_{3-\delta}$, $Ba_{0.95}Sm_{0.05}FeO_{3-\delta}$, $BaFe_{0.975}Zr_{0.025}O_{3-\delta}$, $BaFe_{0.95}Nb_{0.05}O_{3-\delta}$ and $BaFe_{0.95}Sn_{0.05}O_{3-\delta}$ have been successfully synthesized and applied as oxygen permeation membrane or SOFC cathode[13-19]. Specially, the $BaFe_{0.95}Zr_{0.05}O_{3-\delta}$ as a SOFC cathode shows fast ion diffusion kinetics because of its high oxygen vacancy concentration[16]. Therefore, a proper amount Zr doped $BaFeO_{3-\delta}$ with enhanced stability in reducing atmosphere could be a promising electrode for symmetrical SOFC. Besides, Zr substitution may introduce the proton conductivity[20, 21], which can improve the electrocatalytic activity in reducing atmosphere.

Herein, we present Zr doped perovskite oxide of $BaFe_{0.9}Zr_{0.1}O_{3-\delta}$ (BFZ) for the application as a symmetrical SOFC electrode. The BFZ demonstrated a high electrocatalytic activity and remarkable stability in both oxidizing and reducing atmospheres, indicating a promising electrode candidate in symmetrical SOFCs, particularly in a lower operation temperature.

2 Experimental

2.1Powder synthesis: BFZ powders were synthesized by a combined EDTA-citrate complexing so-gel method. Stoichiometric ratio of $Ba(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ were mixed in deionized water, then the complexing of ethylenediaminetetraacetic acid (EDTA) and citric acid were added in the solution. After the extra acid was neutralized by $NH_3 \cdot H_2O$, a neutral aqueous solution formed. The gel obtained by evaporation of water was pretreated in oven at 250°C to form a precursor. Finally, the precursor was calcined at 1100°C for 5 h in air and the resulting perovskite oxides were attained. The $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) was prepared by a convenient solid-state reaction method[22].

2.2 Cell fabrication: LSGM electrolyte supported symmetrical cells were fabricated by dry pressing with spray method. The LSGM powers were dry pressed and subsequently sintered at 1450°C for 5h to form the densified substrates. The slurry containing cathode powders were sprayed on the substrate and the symmetrical cells were obtained after calcination at 900°C for 0.5 h.

2.3 Materials Characterization: The BFZ crystal structure in room temperature was indexed by X-ray diffraction (XRD, Rigaku Smartlab) and the elevated temperature one was probed by X'Pert PRO MPD. The morphology of the symmetric cells was obtained by a scanning electron microscope (SEM, JEOL 6490). The electrical conductivity was tested by a four-probe DC method (Keithley 2420 source meter) using the bar-shaped dense samples. The cell electrochemical impedance spectra (EIS) were measured by a Solartron 1260A frequency response analyzer with a Solartron 1287 potentiost at an open circuit condition, and the frequency was from 0.1 Hz to 1 MHz with AC amplitude of 10 mV. Single cell performances were investigated by a homemade testing system with the humidified H_2 (50 mL min^{-1}) as fuel and the ambient air as oxidant, and the *I-V* curves were collected by a Keithley 2420 digital source meter over a range of 650-800°C.

3 Results and discussion

The in-situ XRD patterns of the BFZ at different temperatures in air are shown in Fig. S1. The 10% Zr substitution for Fe at B site fails to stabilize a cubic perovskite structure at room temperature, as described in Ref[23]. The BFZ trends to form the symmetry structure at elevated temperatures. For further investigation, the pattern at 800°C is refined as an example and the result is found in Fig. 1a. It is noted that the BFZ at 800°C mainly exist as a cubic perovskite structure (space group *P m 3 m*) with a unit cell parameter of a = 4.09 Å. The converged reliability factors are Rp = 11.4%, Rwp = 15%, $\chi 2 = 2.60$, which indicate that the purity of the BFZ can be further improved. After annealing in humidified H_2 atmosphere at 800°C for 10 h, no additional phase is found and the cubic perovskite structure is retained even at room temperature, implying sufficient chemical structural stability. Fig. 1b is the refined patterns of BFZ after annealing at room temperature. The cell parameter enlarges to be 4.17 Å, and the fitness tests (Rp = 5.49%, Rwp = 6.96 %, $\chi 2 = 1.94$) indicate a good agreement between calculated and experimental data.

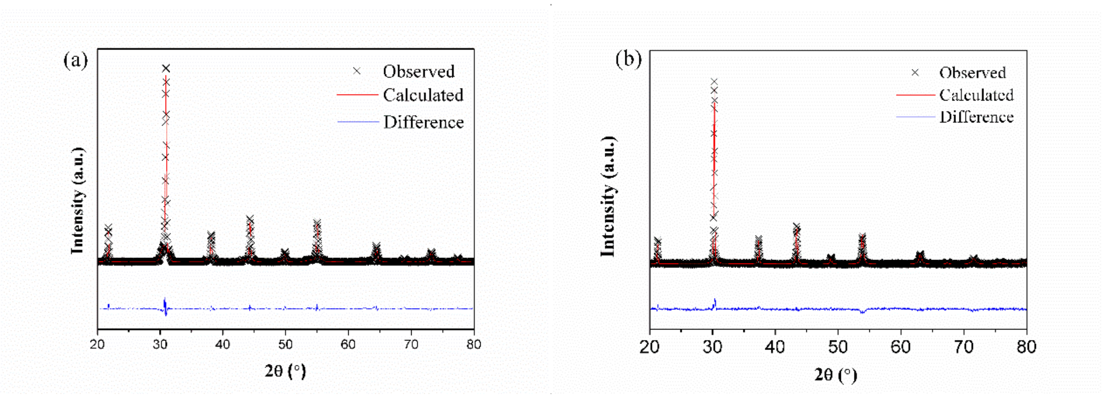

Fig.1 XRD patterns of (a) BFZ powders at 800°C in air, (b) BFZ powders after annealing.

In ABO_3 type perovskite oxides, the stability can be briefly justified by the Goldschmidt tolerance factor $t = (r_A + r_O)/\sqrt{2}\,(r_B + r_O)$, and the cubic structure is preferable while t is in the range of 0.75-1[24]. The t in $BaFeO_{3-\delta}$ is estimated to be ~1.066[25], therefore, the substitution of larger Zr ion ($r_{Zr^{4+}}$ = 0.72 Å) for smaller Fe ion($r_{Fe^{3+}}$ = 0.645 Å, $r_{Fe^{4+}}$ = 0.585 Å) favors the construction of cubic structure. However, the 10% Zr substitution may not guarantee the cubic structure at room temperature. It is likely that the Fe at the B-site is reduced at elevated temperatures and in reducing atmosphere, and the Fe ionic radius with the lower valence enlarges average ionic size of B-site [15], which contributes to the cubic structure of pervoskite.

The electrical conductivities of BFZ in air and humidified H_2 atmosphere are presented in Fig. S2. The oxide demonstrates lower values in reducing atmosphere, which may be attributed to the electronic holes loss in reducing condition[26]. Particularly, the values in both atmospheres are not high but achieve the minimum required conductivity of 0.01 S cm^{-1} [27]. The electrochemical properties in different atmospheres are tested in symmetrical cell configuration with thick LSGM electrolyte (BFZ|LSGM|BFZ). The Fig. 2 shows the area specific resistances (ASRs) of BFZ at various temperatures in air and humidified H_2. The sample delivers excellent electrocatalytic activity in oxidizing atmosphere, and the ASRs of 0.005, 0.02 and 0.14 Ω cm^2 are obtained at 800, 700 and 600°C respectively, which are better than some representative cathode materials in similar condition, such as $SmBaCo_2O_{5+\delta}$ (0.054 Ω cm^2 at 750°C)[28], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (0.04 Ω cm^2 at 800°C)[29] and $SrCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ (0.091 Ω cm^2 at 700°C)[30]. While the atmosphere is switched to humidified H_2, the ASRs increase to 0.43, 1.89 and 7.76 Ω cm^2 at 850, 750 and 650°C, respectively.

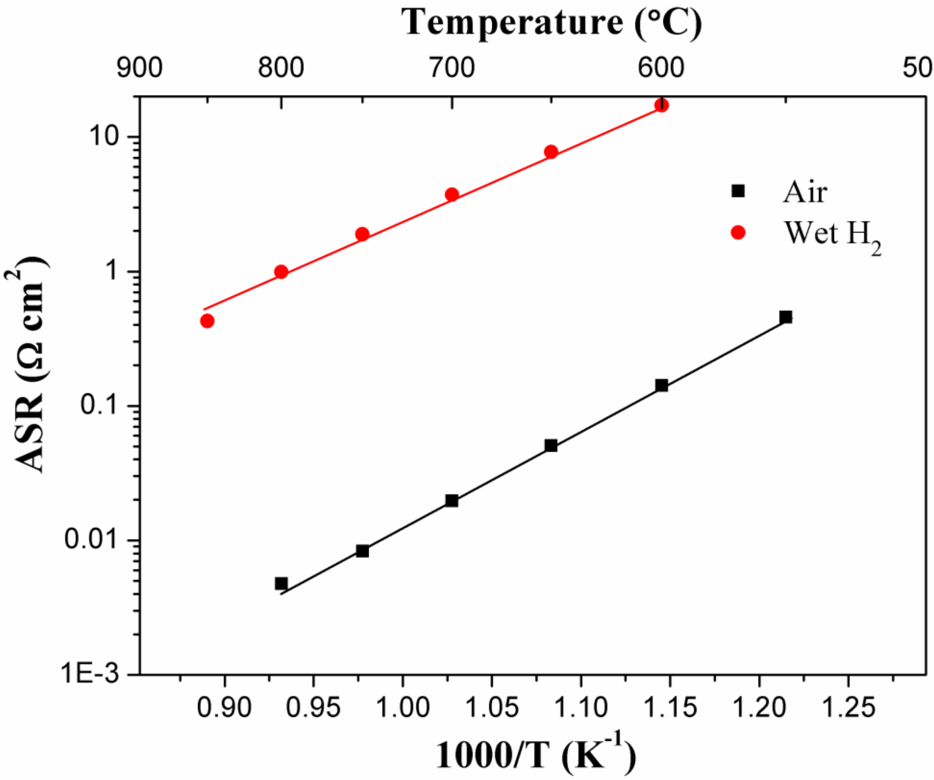

Fig.2 Arrhenius plots of ASR values of BFZ electrode in air and wet H_2.

The Fig. 3a presents the electrochemical performance of symmetrical cell with BFZ electrode using ambient air as oxidant, humidified H_2 as fuel. The LSGM electrolyte is about 200 μm thick and well adhered by the electrodes, as shown in Fig. S3. It is noted that the open circuit voltages (OCVs) of single cell is around 1.05 V at the temperature range of 650-800°C, which is close to the theoretical values. Peak power densities of 1097, 886, 636 and 398 mW cm^{-2} are obtained at 800, 750, 700 and 650°C, respectively. Despite of the thick electrolyte with relatively high ohmic resistances, the excellent performance is mainly ascribed to the low polarization resistances, which are shown in Fig. 3b. The polarization resistances of 0.105, 0.111, 0.137 and 0.190 Ω cm^2 are observed under open circuit condition at 800, 750, 700 and 650°C respectively, which include the cathode and anode polarization resistances. The electrochemical performance is higher than some other oxides in the same condition, like $PrBaMn_{1.5}Fe_{0.5}O_{5+\delta}$ (0.25Ω cm^2 at 750°C) and $PrBa(Fe_{0.8}Sc_{0.2})_2O_{5+\delta}$ (0.35Ω cm^2 at 750°C) [26, 31]. The polarization resistances obtained in single cell are approximately equal to the anode side resistances since the polarization resistances in air presented in Fig. 2 are extremely low. $BaZrO_3$ is a typical parent material for proton conductor, and doped $BaZrO_3$ has been applied widely in proton conducting SOFCs[32]. Recently, triple charge ($H^+/O^{2-}/e^-$) conducting $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ was successfully applied as cathode and electrolyte in proton conducting SOFC, and as the Co/Fe doped derivative of H^+/O^{2-} conducting $BaZr_xY_{1-x}O_{3-\delta}$, the $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ demonstrated high catalytic activity and triple conduction[20, 33]. Rao also investigated cobalt doped $BaZrO_3$ as cathode, which showed electronic and protonic conductivity[34]. In this case, it is considered that the Zr doping may introduce the proton conductivity to improve the catalytic activity of anode due to the small ionic size of proton.

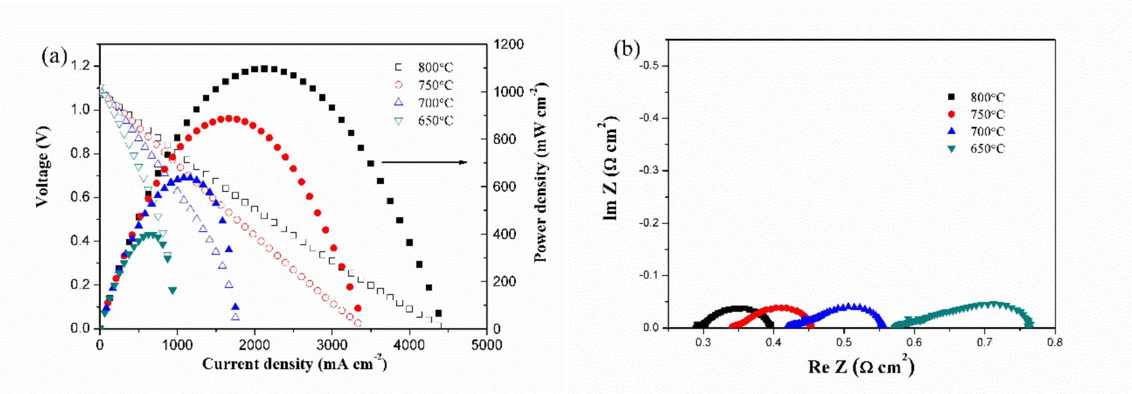

Fig. 3 (a) *I–V* and *I–P* curves for symmetrical cells with BFZ electrode, (b) Impedance spectra of symmetrical cell measured under open circuit conditions.

Fig. 4a reveals the stability of operation voltage at a constant current density of 800 mA cm^{-2} in the short-term test under a fuel cell testing condition. A stable voltage of around 0.75 V is observed during the 100 h test period at 700°C. Since the electrode needs to be functional in both oxidizing and reducing atmospheres, the redox stability is another critical aspect for evaluating electrode in symmetrical SOFC. The redox stability is measured at 700°C after durability test by switching the supply gas. In one cycle, the anode is reduced and oxidized by the wet H_2 and the air, respectively. And the impedance spectra collected in wet H_2 are demonstrated in Fig. 4b. The interfacial polarization resistances are maintained at around 0.115 Ω cm^2 after one cycle, indicating remarkable redox stability.

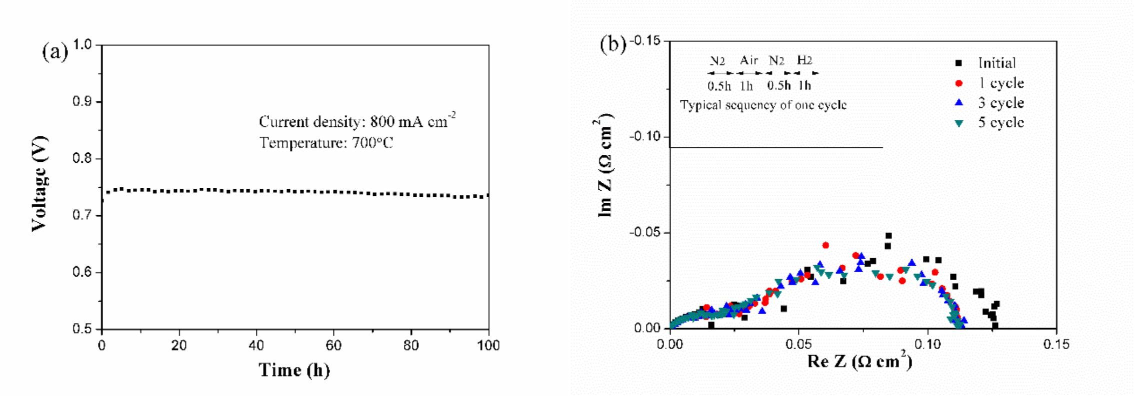

Fig. 4 (a) Short term stability under a constant current load of 0.8 A cm^{-2} at 700°C, (b) Polarization impedance of single cell at 700°C after each cycling test.

4 Conclusions

In summary, the BFZ was successfully synthesized and applied as both cathode and anode in symmetrical SOFC. The BFZ electrode demonstrated favorable catalytic activity in both oxidizing and reducing atmospheres and a peak powder density of 1097 mW cm^{-2} was obtained at 800°C in single cell. Meanwhile, the BFZ had shown high stability in short-term and redox test. The superior electrochemical activity and stability indicate that the BFZ represents potential candidate as the electrode in symmetrical SOFCs.

Acknowledgements

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Captions

Fig. 1. XRD patterns of (a) BFZ powders at 800°C in air, (b) BFZ powders after annealing.

Fig. 2. Arrhenius plots of ASR values of BFZ electrode in air and wet H_2.

Fig. 3. (a) *I–V* and *I–P* curves for symmetrical cells with BFZ electrode, (b) Impedance spectra of symmetrical cell measured under open circuit conditions.

Fig. 4. (a) Short term stability under a constant current load of 0.8 A cm-2 at 700°C, (b) Polarization impedance of single cell at 700°C after each cycling test.

Supplementary materials

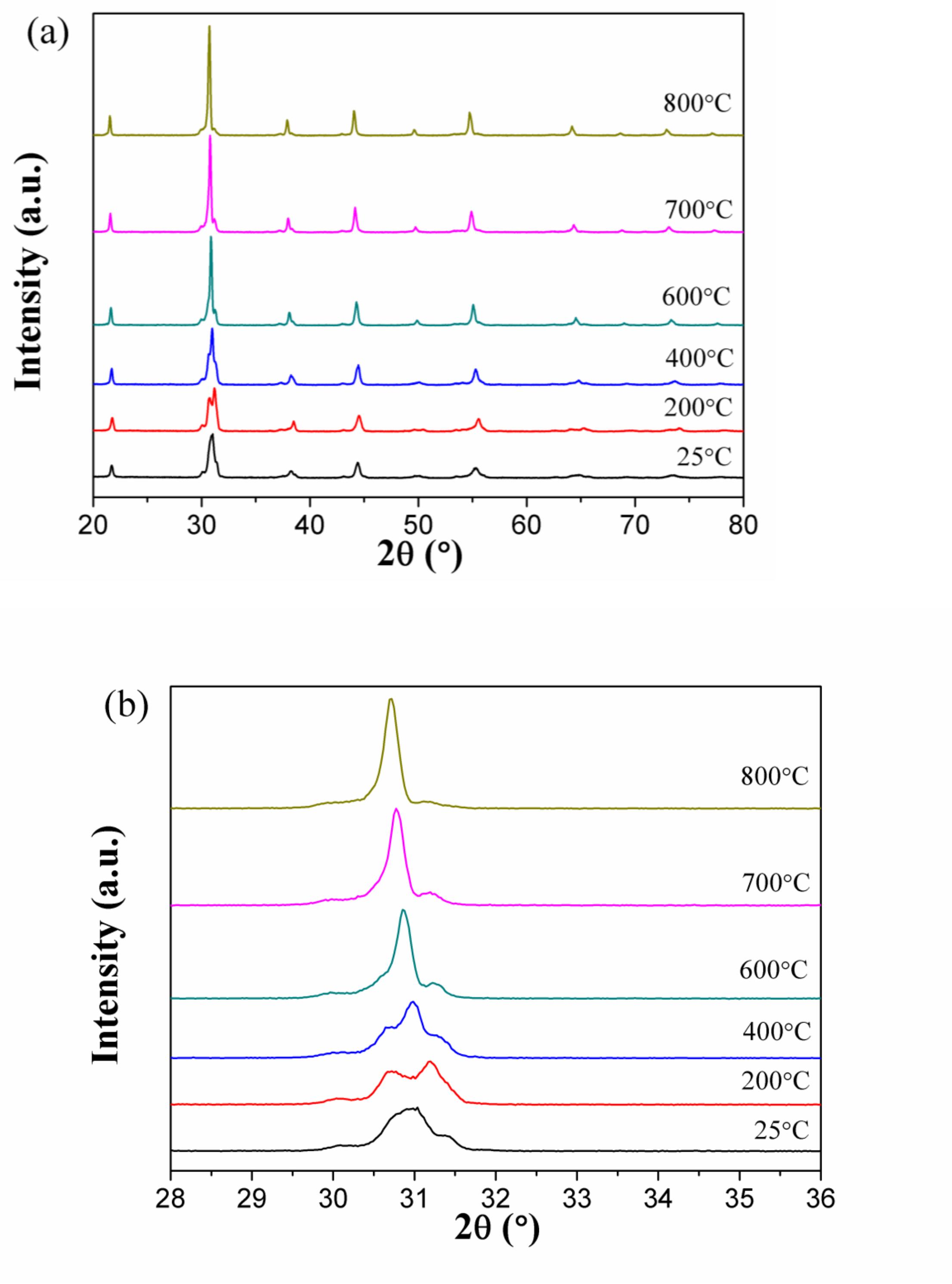

Fig. S1 (a) In-situ XRD patterns of BFZ over the temperature range between room temperatur and 800°C in air; (b) magnified in-situ XRD patterns from 28 to 36°.

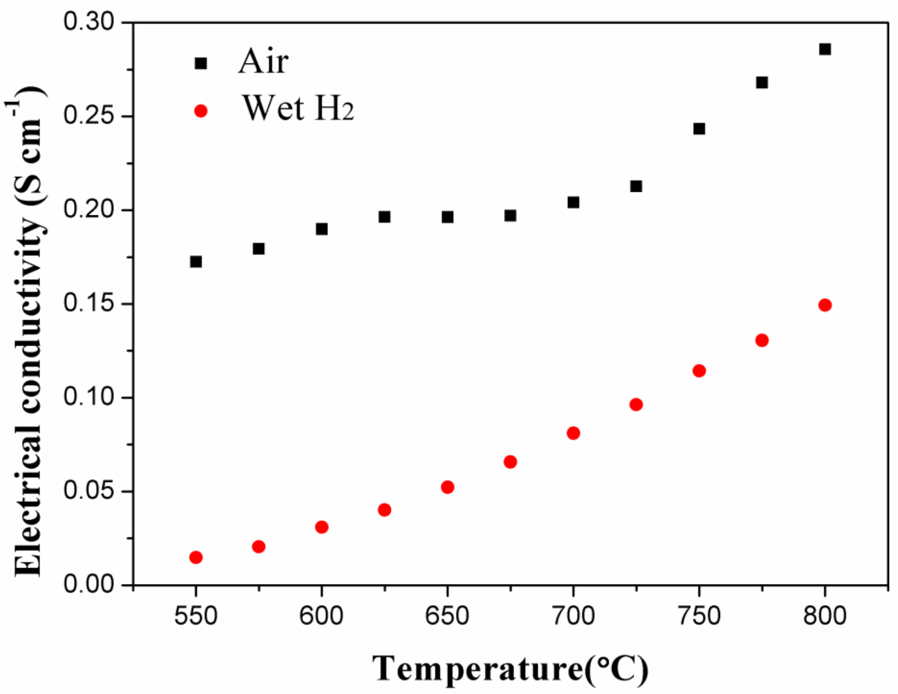

Fig. S2 Electrical conductivity of BFZ in air and wet H_2 as a function of temperature.

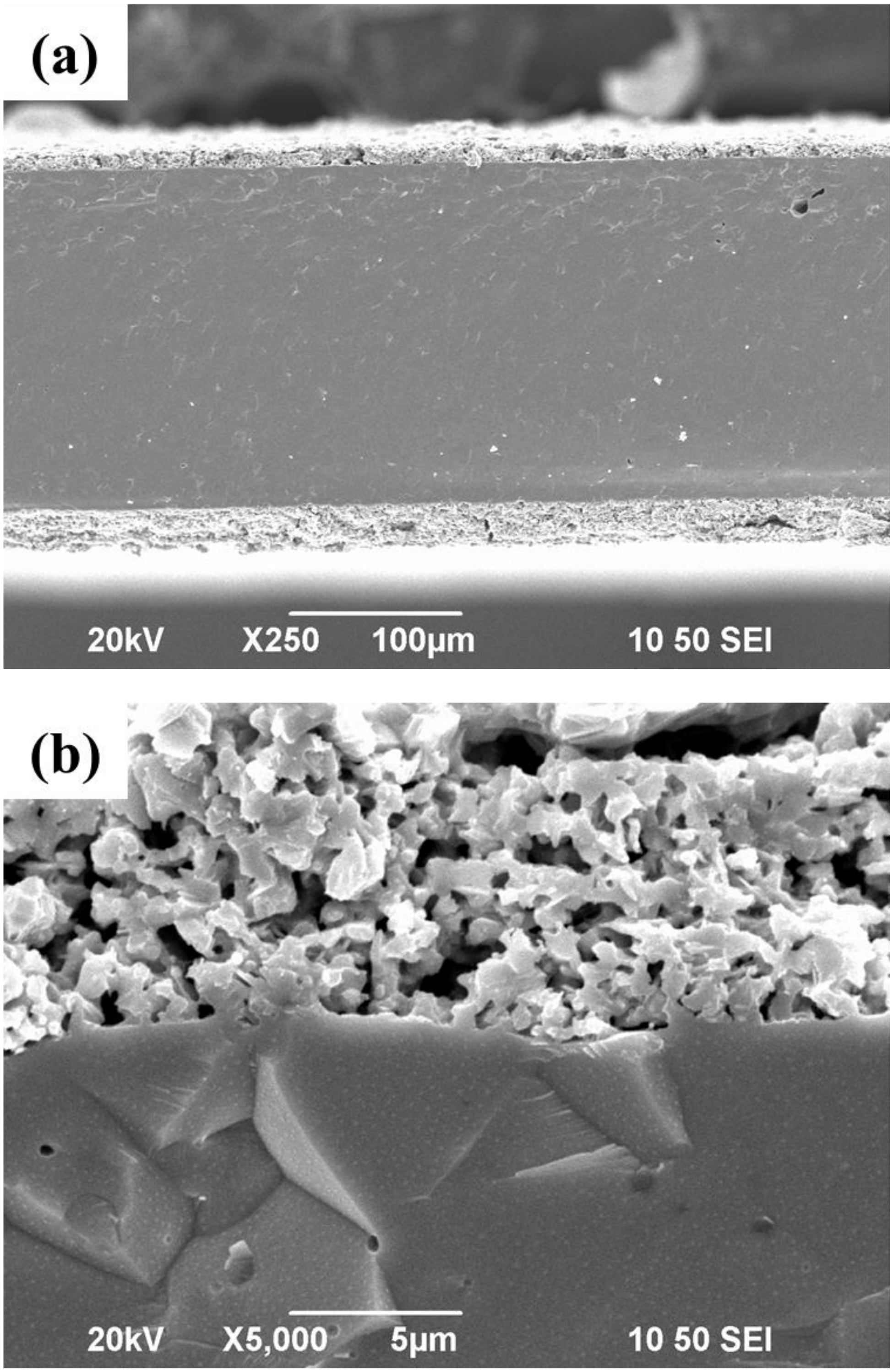

Fig. S3 SEM image of the single cell (a) cross section view, (b) close-up image of the interface of electrode and electrolyte.