

Article

Fluorine Anion-Doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as a Promising Cathode for Protonic Ceramic Fuel Cells

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Abstract: The widespread application of protonic ceramic fuel cells is limited by the lack of oxygen electrodes with excellent activity and stability. Herein, the strategy of halogen doping in a $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCFN) cathode is discussed in detail for improving cathode activity. $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-x-\delta}\text{F}_x$ ($x = 0, 0.05, 0.1$) cathode materials are synthesised by a solid-phase method. The XRD results show that fluorine anion-doped BSCFN forms a single-phase perovskite structure. XPS and titration results reveal that fluorine ion doping increases active oxygen and surface adsorbed oxygen. It also confines chemical bonds between cations and anions, which enhances the cathode's catalytic performance. Therefore, an anode-supported single cell with the configuration of $\text{Ni-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) | BZCYYb | $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-0.1-\delta}\text{F}_{0.1}$ (BSCFN- $\text{F}_{0.1}$) achieved a high peak power density of 630 mW cm^{-2} at 600°C . Moreover, according to the symmetrical cell test, the BSCFN- $\text{F}_{0.1}$ electrode demonstrated a superb stability for nearly 400 h at 600°C . This work focuses on the influence of fluorine anion incorporation upon the performance of cathode materials. It also analyses and discusses the effects of different fluorine ion incorporation amounts to occupy different oxygen positions.

Keywords: protonic ceramic fuel cells; perovskite; halogen doping; cathode; active oxygen



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1. Introduction

The development of new materials and new technologies is a key step towards solving the energy crisis [1–5]. Fuel cells are favoured because they can directly convert the chemical energy of fuels to clean electricity with high efficiency [6–9]. Protonic ceramic fuel cells (PCFCs) have very bright prospects for application within the domain of intermediate and low temperatures for fast proton conduction and low proton activation energy [10–14]. In comparison to typical solid oxide fuel cells (SOFCs) on the basis of oxygen ion conduction (O-SOFCs), PCFCs have two unique advantages. Firstly, the lower activation energy for PCFCs leads to lower operating temperatures than for O-SOFCs, which can improve the operational stability and reduce the complexity and cost of the system. Secondly, during operation, the water formation reaction takes place on the cathode side of the PCFC to avoid fuel dilution, which can not only improve fuel utilisation but also reduce the possibility of nickel anodic oxidation [15–17]. Nevertheless, the key point hindering the development of intermediate- and low-temperature PCFCs is the insufficiency of catalytic activity for oxygen reactions at the oxygen electrode [18–20]. Accordingly, in-depth research and exploration of new high-performance oxygen electrodes makes sense for PCFCs.

To obtain higher power density at a lower temperature range, many promising oxygen electrodes have been investigated [21–27]. For example, $\text{Ba}_{0.95}\text{Fe}_{0.7}\text{Co}_{0.2}\text{Sc}_{0.1}\text{O}_{3-\delta}$ [28], $\text{La}_{1.6}\text{Sr}_{0.4}\text{Cu}_{0.6}\text{Ni}_{0.4}\text{O}_{4+\delta}$ [29], $\text{PrBaCo}_{1.92}\text{Zr}_{0.08}\text{O}_{5+\delta}$ [30], $\text{Pr}_{0.2}\text{Ba}_{0.2}\text{Sr}_{0.2}\text{La}_{0.2}\text{Ca}_{0.2}\text{CoO}_{3-\delta}$ [31]

and other materials applied in the development of PCFCs have attracted extensive attention in recent years because of their outstanding electrochemical activity under intermediate and low temperatures. What these studies have in common is the application of highly active cathode materials due to elemental doping or cationic defects at the A and B sites of perovskite materials, which have good stability for PCFCs [32,33]. In recent years, oxygen site doping of halogen elements in perovskite oxides has become one of the most effective strategies to boost the catalytic performance of materials [34–38]. For example, Xia et al. proposed doping $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_3$ with chlorine ions to improve the chemical stability of the proton conductor electrolyte and then enhance the oxygen incorporation kinetics of the cathode at medium and low temperatures, thereby improving the catalytic performance [39]. It provided a good reference for the developmental direction of proton conductor fuel cell cathodes. Subsequently, Shao et al. demonstrated that anion doping can boost the electrocatalytic activity of perovskite cathodes at an intermediate temperature range. They developed the fluorine ion doping of $\text{SrFeO}_{3-\delta}$, and found that the area specific resistance (ASR) of $\text{SrFeO}_{2.95-\delta}\text{F}_{0.05}$ was $0.393 \Omega \text{ cm}^2$ at 600°C , which is much smaller than that of $\text{SrFeO}_{3-\delta}$ and can be attributed to enhanced bulk diffusion and surface exchange [40].

Herein, we employ the anion-doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BSCFN) strategy, which can significantly promote oxygen reduction activity and mobility, to further explore the development of perovskite cathode materials for PCFC applications. In this work, fluorine ion-doped BSCFN materials, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-x-\delta}\text{F}_x$ (BSCFN- F_x , $x = 0.05, 0.1$), have been developed as potential oxygen electrodes for PCFCs with a $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYb) electrolyte. Compared with BSCFN, the ASR of the BSCFN- $\text{F}_{0.1}$ electrode at 600°C decreased by nearly 50% (0.23 vs. $0.44 \Omega \text{ cm}^2$), and the peak power density of a PCFC with a BSCFN- $\text{F}_{0.1}$ cathode was also increased by 47% (632 vs. 429 mW cm^{-2}). Meanwhile, under a steady current density of 0.16 A cm^{-2} , the PCFC with the BSCFN- $\text{F}_{0.1}$ cathode showed an excellent durability of $\sim 130 \text{ h}$.

2. Results and Discussion

2.1. Structure of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-x-\delta}\text{F}_x$ ($x = 0, 0.05, 0.1$)

We investigated the phase structure of cathode materials at room temperature using X-ray powder diffraction (XRD). As shown in Figure 1a, the crystal diffraction peaks of BSCFN and BSCFN- F_x ($x = 0.05, 0.10$) are piercing and pointed, indicating their high crystallinity. The extra small peak at 27.5° is a $\text{K}\beta$ peak. Based on Rietveld refinement calculations (Figure 1b–d), the materials are cubic perovskite crystal structures with a Pm-3m space group. The calculated lattice parameter of BSCFN is $a = b = c = 4.007(1) \text{ \AA}$. The lattice parameters, χ^2 values, R_{wp} and R_p are derived from the refinement results and displayed in Table 1, and they further confirm the reliability of the Rietveld method ($\chi^2 < 3$; $R_{\text{wp}}, R_p < 10$). Compared to the lattice parameter of BSCFN, BSCFN- $\text{F}_{0.05}$ and BSCFN- $\text{F}_{0.1}$ have smaller lattice parameters, which are in accordance with a very small lattice shrinkage [34]. In addition, the X-ray density of the sample was calculated according to the following formula:

$$\rho_x = n \cdot M_w / N_A \cdot V \quad (1)$$

where n is the number of atoms per unit cell, M_w is the molecular weight of the sample, V is the volume of the unit cell and N_A is Avogadro's number. The values of the estimated density increased slightly from 8.7328 to 8.7522 g/cm^3 (Table 2). This increasing can be attributed to the decreasing of the volume of the unit cell as reported before. The crystallinity is increased and the number of crystals per unit volume is increased.

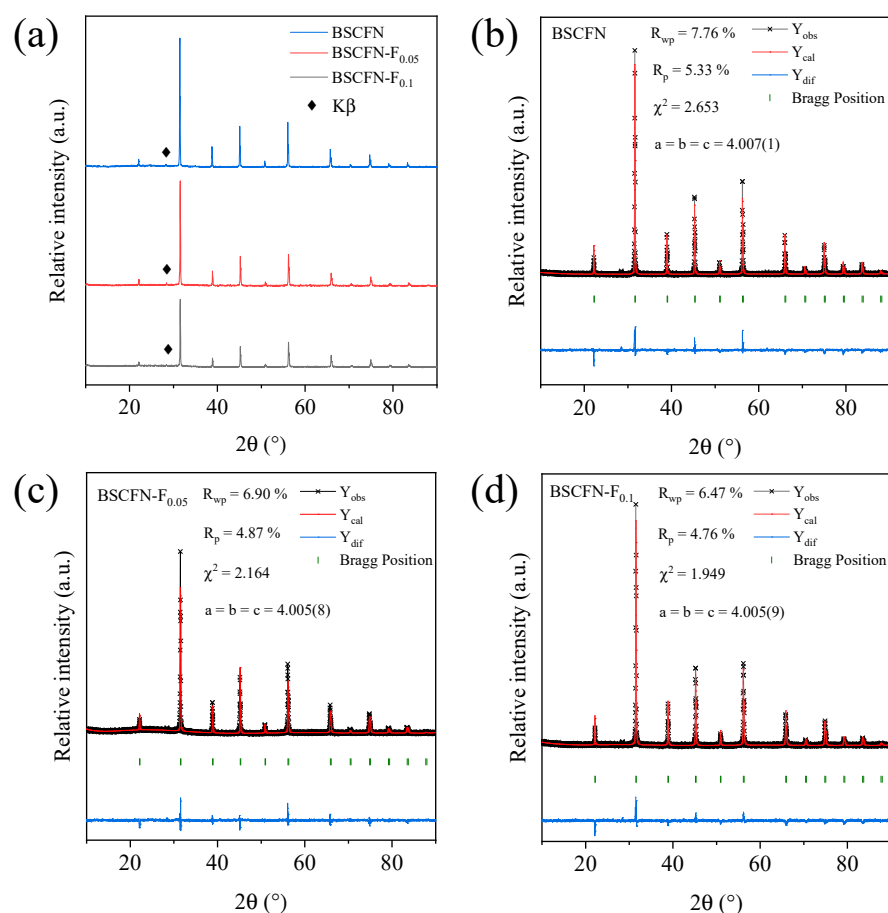


Figure 1. (a) XRD patterns of the synthesised BSCFN and BSCFN-F_x ($x = 0.05, 0.10$) samples. Refined XRD profiles of (b) BSCFN, (c) BSCFN-F_x ($x = 0.05$) and (d) BSCFN-F_x ($x = 0.10$) samples.

Table 1. Refined XRD profiles of BSCFN and BSCFN-F_x ($x = 0.05, 0.10$) samples.

Samples	Space Group	$a = b = c$ (Å)	χ^2	R_{wp}	R_p
BSCFN	Pm-3m	4.007(1)	2.653	7.76	5.33
BSCFN-F _{0.05}	Pm-3m	4.005(8)	2.164	6.90	4.87
BSCFN-F _{0.1}	Pm-3m	4.005(9)	1.949	6.47	4.76

Table 2. The X-ray density of the sample is calculated as a table of values.

Sample	Volume Density (ρ) (g/cm ³)
BSCFN	8.7328
BSCFN-F _{0.05}	8.7471
BSCFN-F _{0.1}	8.7522

The morphology and phase composition of BSCFN-F_{0.1} was observed using high-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) with energy-dispersive X-ray spectroscopy (EDS) mapping, as shown in Figure 2. The lattice spacing of the anion-doped catalyst is about 0.285 nm (Figure 2a), which corresponds to the BSCFN-F_{0.1} (110) lattice width, confirming the formation of the anion-doped BSCFN-F_{0.1} phase structure. The corresponding fast Fourier transformed (FFT) pattern (Figure 2b) indicates the cation-ordering reflections of BSCFN-F_{0.1}. The EDS mapping images of all elements of BSCFN-F_{0.1} are shown in Figure 2c,

in which the uniform distribution of Ba, Sr, Co, Fe, Nb, O and F further reveals that the fluorine anion has been successfully doped into the BSCFN- $F_{0.1}$ perovskite lattice.

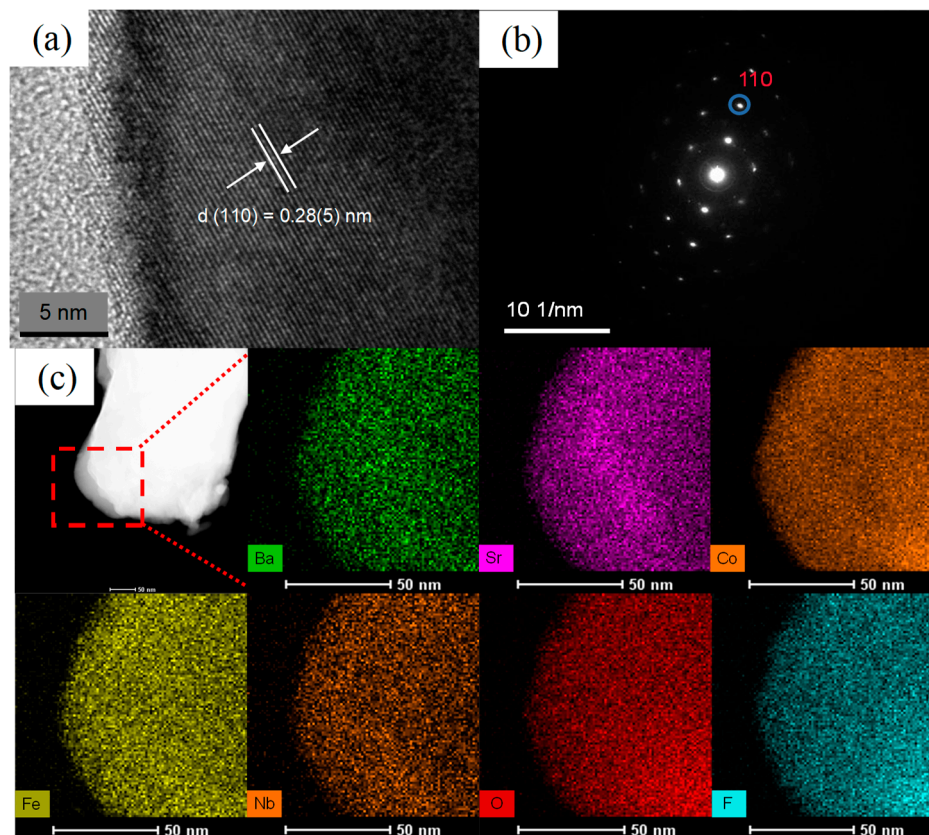


Figure 2. (a) HR-TEM image of BSCFN- $F_{0.1}$ sample and (b) corresponding FFT pattern. (c) HAADF-STEM image of BSCFN- $F_{0.1}$ and corresponding EDS mapping images showing element distribution.

2.2. Properties of BSCFN and BSCFN- F_x

The chemical states and surface elemental compositions of the samples were obtained by X-ray photoelectron spectroscopy (XPS) survey. Figure 3a shows the measured XPS spectra of BSCFN, BSCFN- $F_{0.05}$ and BSCFN- $F_{0.1}$. The signal peaks of Ba, Sr, Co, Fe, Nb and O can be clearly identified on the surface of the sample. As shown in Figure 3b, the characteristic peak of F is located at 683 eV, indicating that the fluorine ion was successfully incorporated into BSCFN. Before peak splitting and fitting of the full spectrum from the XPS, the spectra of all elements were calibrated by the C 1s peak at 284.80 eV, which clearly shows the corresponding peaks of cobalt (Co 2p), iron (Fe 2p) and oxygen (O 1s).

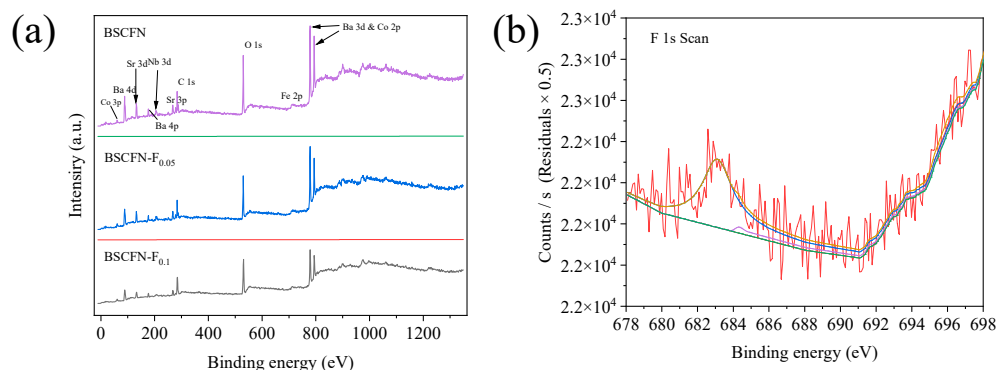


Figure 3. (a) XPS survey spectra of BSCFN, BSCFN- $F_{0.05}$ and BSCFN- $F_{0.1}$. (b) XPS spectrum of F 1s for BSCFN- $F_{0.1}$ (the red box area in Figure 3a).

The XPS spectra of the Co 2p levels of the prepared samples with different compositions are shown in Figure 4a. As can be seen from the image, the Co 2p spectrum consists of two prominent intensity peaks. The peak at low binding energy is confirmed as the Co 2p_{3/2} fraction, while the high binding energy fraction is Co 2p_{1/2} [41]. The Gaussian method was used to fit the XPS survey curve, and the different characteristic peaks that were obtained after fitting represent the different valence states of cobalt. The Co 2p spectrum shows a doublet, a low-energy band (Co 2p_{3/2}) at around 779.81 eV and a high-energy band (Co 2p_{1/2}) at around 794.99 eV. The energy difference between Co 2p_{3/2} and Co 2p_{1/2} is approximately 15.00 eV. In addition, the satellite peak is found around 788.01 eV, indicating that Co²⁺ ions are present in cobalt-containing oxide materials [42]. The XPS binding energies of Fe 2p_{3/2} are between 706.00 and 720.02 eV, as shown in Figure 4b. Fe 2p_{3/2} can be further split into four bands, the binding energy from low to high corresponds to Fe²⁺, Fe³⁺, Fe⁴⁺ and satellite peaks, respectively.

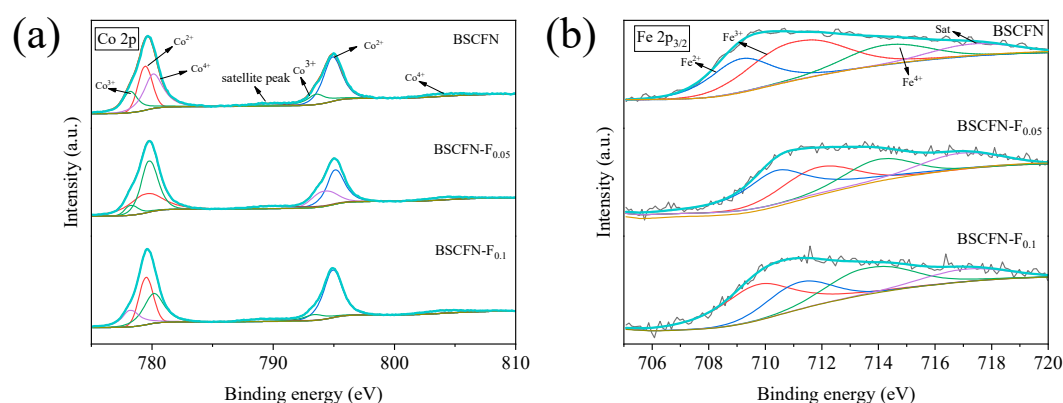


Figure 4. XPS spectra of (a) Co 2p and (b) Fe 2p for BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1}.

Binding energy is the energy required for orbital electrons to escape from atoms. The easier the process of electron detachment, the lower its binding energy is. Co⁴⁺ ions have a more significantly positive charge and lower electron cloud density than Co³⁺ and Co²⁺ ions, so Co⁴⁺ ions should have far greater 2p electron binding energy. Similarly, the binding energy of Fe⁴⁺ is also higher than Fe³⁺ and Fe²⁺. Counter to that trend, the trivalent cobalt ion is more unstable than the divalent cobalt ion, and its binding energy is also naturally smaller than that of the divalent cobalt ion [43]. Therefore, the characteristic peaks at 778.15/793.55 eV, 778.22/794.12 eV and 778.15/793.38 eV can be attributed to Co³⁺ ions, the peaks at 780.10/803.50 eV, 779.73/804.06 eV and 780.15/803.96 eV can be attributed to Co⁴⁺ ions and the peaks at 779.43/794.9 eV, 779.43/795.06 eV and 779.51/794.89 eV can be assigned to Co²⁺ ions. The multivalent states of Co and Fe lead to them mainly existing on the surface in the form of oxides, which plays an essential role in ORR. At the same time, the content of Fe ions on the surface of BSCFN is very low; therefore, Co ions play a vital role in the oxygen reaction processes of the oxygen electrode.

According to the charge compensation mechanism, the doping of fluorine ions can inevitably affect the valence state of the B-site ions. The results of Gaussian fitting of the curve of Co 2p are shown in Table 3, and it can be seen that the valence state of surface Co ions changes with the amount of doped fluorine ions. Among them, when the doping ratio of fluorine ions reaches 0.05, the average valence of Co ions in BSCFN increases from 2.81 to 2.93, indicating that fluorine ions have been mainly doped in oxygen vacancies and interstitial vacancies in BSCFN at this time. When the doping ratio is 0.10, the average valence state of Co ions is reduced to 2.80. At this time, fluorine ions have replaced oxygen ions, resulting in a decrease in B-site ions' valence states. These valence state changes show that the introduction of fluorine ions can generate oxygen vacancies [44]. According to the XPS fitting results, the valence states of B-site transition metal ions on the surface of the samples can be estimated. The average valence states of B-site transition metal ions in the bulk phase of samples were determined by titration method. As can be seen from Figure 5,

the average valence states of cations for B-site transition metals cobalt and iron in BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1} samples were 2.61, 2.72 and 2.66, respectively. The results showed a trend of first increasing and then decreasing, which was consistent with the XPS fitting results and proved the reliability of the experimental results.

Table 3. The Gaussian fitting results of BSCFN and BSCFN-F_x (x = 0.05, 0.1) of XPS spectra for Co 2p.

Samples	Co ²⁺		Co ³⁺		Co ⁴⁺	
	B.E/eV	Area/%	B.E/eV	Area/%	B.E/eV	Area/%
BSCFN	779.43/804.06	47.90	778.15/793.38	23.50	780.10/803.50	28.60
BSCFN-F _{0.05}	779.43/795.06	44.40	778.22/794.12	17.30	779.73/804.06	38.30
BSCFN-F _{0.1}	779.51/794.89	53.20	778.15/793.55	13.20	780.15/803.96	33.60

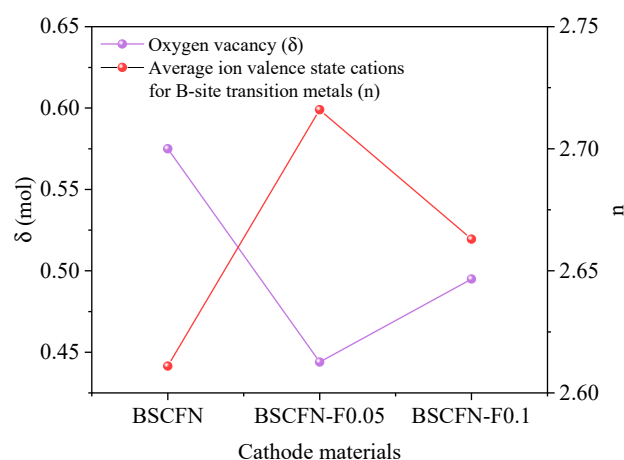


Figure 5. Oxygen vacancy concentration and average valence states of cations for B-site transition metals cobalt and iron of BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1}.

The cathodic reaction kinetics of the samples can be investigated in depth using the O 1s XPS spectra in Figure 6. The O 1s spectra of the BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1} samples all contain four overlapping bands, corresponding to (in order of binding energy from low to high) lattice oxygen O^{2−} (O_α) at ~529.31 eV, active oxygen O₂^{2−} or O[−] (O_β) at ~530.72 eV, hydroxyl or surface adsorbed oxygen -OH or O₂ (O_γ) at ~531.38 eV, caused by the surface defect, and chemisorbed or physisorbed molecules such as water or carbonate (H₂O or CO₃^{2−}) (O_ε) at ~532.39 eV [45,46]. The results after peak fitting of the XPS pattern of O 2p are shown in Table 4. It is obvious that, with the incorporation of fluorine ions, both O_β and O_γ increase by varying degrees. Primarily, the proportion of O_γ increased from 20.40 in BSCFN to 29.60 in BSCFN-F_{0.1}, which means that more surface defects, such as oxygen vacancies, are generated in the BSCFN-F_{0.1} sample. Active oxygen (O_β) has high mobility and is a highly active species during chemical reactions. Therefore, the enhancement of O_β in BSCFN-F_{0.1} plays a vital role in ORR catalytic activity [46]. In addition, the lattice oxygen of BSCFN-F_{0.1} (area ratio of O_α = 15.70%) is lower than that of BSCFN (area ratio of O_α = 45.00%). It is demonstrated that, as the number of fluorine ions increases further, they occupy lattice oxygen sites in the BSCFN structure, which is consistent with the previous conclusion.

Table 4. The Gaussian fitting results of BSCFN and BSCFN-F_x (x = 0.05, 0.1) of XPS spectra for O 1s.

Samples	O _α		O _β		O _γ		O _ε	
	B.E/eV	Area/%	B.E/eV	Area/%	B.E/eV	Area/%	B.E/eV	Area/%
BSCFN	529.3	21.50	530.7	18.10	531.38	20.40	532.39	40.00
BSCFN-F _{0.05}	529	23.10	530.69	23.90	531.21	21.60	531.8	31.40
BSCFN-F _{0.1}	528.86	15.70	530.52	30.50	531.12	29.60	531.81	34.20

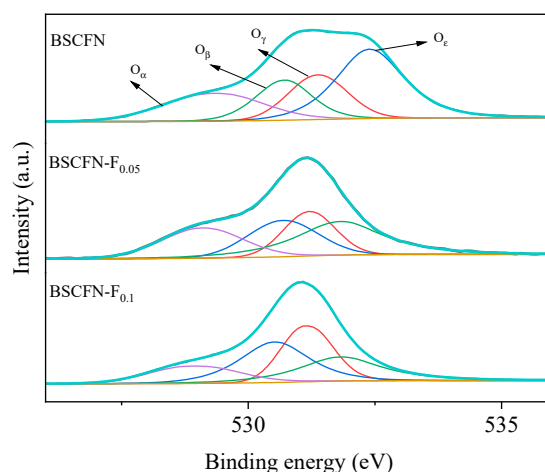


Figure 6. XPS spectra of O 1s signal for BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1} powers.

The electrical conductivity of the BSCFN and BSCFN-F_x ($x = 0.05, 0.10$) in the range of 300–900 °C was evaluated by the four-probe test method. As shown in Figure 7a, all samples show the same trend of change. With the increase in temperature, they show semiconductor conduction behaviour; that is, the electrical conductivity always shows an upward trend. In the test temperature range, the highest electrical conductivities of BSCFN, BSCFN-F_{0.05} and BSCFN-F_{0.1} oxides were 14.78, 16.67 and 8.74 S cm^{−1}, respectively, at 900 °C. According to the charge compensation mechanism, fluorine ion doping will change the valence state of the B-site, and the change of the B-site valence state depends on the doping position of the fluorine ion. When the mole number of the fluorine ion doping ratio reaches 0.05, fluorine ions occupy oxygen vacancies and interstitial sites, resulting in an increase in the valence state of the Co ions [34], resulting in more charge carriers being generated, as well as enhanced electrical conductivity. The difference is that, when the doping ratio reaches 0.1, fluorine ions begin to occupy the positions of oxygen ions, which in turn leads to a lower valence state of Co ions and a larger radius, thereby reducing the number of carriers.

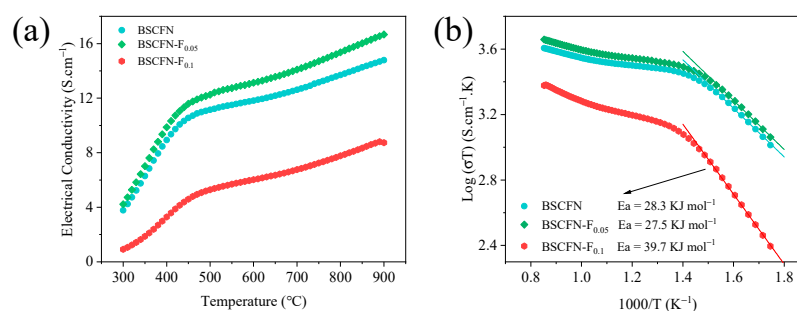


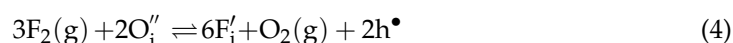
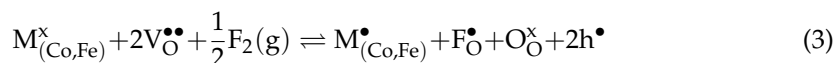
Figure 7. (a) Electrical conductivities and (b) Arrhenius plots of BSCFN and BSCFN-F_x ($x = 0.05, 0.1$) cathode materials at 300–900 °C in air.

The electron conduction mechanism of the perovskite material below 450 °C is the jump of p-type small polarons, which is related to the change of valence of trivalent and quadrivalent Co and Fe ions. In this case, charge transfer is controlled by temperature, which can be explained by the small polaron conduction equation:

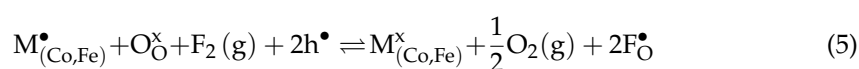
$$\sigma = \frac{A}{T} \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

A represents the material related constant containing carrier concentration phase, T is the absolute temperature, E_a is the activation energy and k is the Boltzmann's constant. Figure 7b shows the relationship between Log (σT) and 1/T. In the range of 300–450 °C, the

activation energy of the sample is related to the valence states of Co and Fe ions. When the fluorine ion doping rate is 0.05, it is conducive to electron conduction, high conductivity, low activation energy, high electron hole concentration and high concentration of B-site tetravalent ions, that is, fluorine ions occupy the oxygen vacancy and oxygen interstitial site. It can be expressed by a quasi-chemical equation:



On the contrary, when the doping ratio reaches 0.1, it is not conducive to electron conduction, and the concentration of B-site tetravalent ions is low, that is, fluorine ions replace oxygen ions.



$M_{(\text{Co,Fe})}^x$ represents the B-site metal elements Fe and Co in low valence state, $V_{\text{O}}^{\bullet\bullet}$ is the oxygen vacancy, $M_{(\text{Co,Fe})}^{\bullet}$ represents the B-site metal elements Fe and Co in high valence state, O_{O}^x is oxygen ion, $F_{\text{O}}^{\bullet}$ is lattice fluorine occupying oxygen site, $h^{\bullet}$ represents the electron hole [47], $O_i^{\prime\prime}$ is oxygen interstitial site and $F_i^{\prime}$ represents F on interstitial sites.

2.3. Cell Performance and Durability

EIS can directly assess the ORR activity of the BSCFN and BSCFN- F_x ($x = 0.05, 0.1$) electrodes in a humid air atmosphere. The tested cell configuration was a BZCYYb-supported symmetric cell. The electrolyte layer thickness of three cells was around 0.5 mm, and the electrode layer thickness of all the cells is around 17 μm . Based on the EIS of all electrode materials, we can find that the BSCFN- $F_{0.1}$ electrode exhibited the best performance at all temperatures (Figure 8a). For example, an ASR value of 0.11 $\Omega \text{ cm}^2$ at 650 $^{\circ}\text{C}$ was achieved, much lower than that of BSCFN, and lower than some other high-performance Co-containing cathode materials. Figure 8a shows the Arrhenius plots of the ASR values of BSCFN- F_x on symmetric cells at different temperatures. The cathodic activation energies (E_a) of BSCFN, BSCFN- $F_{0.05}$ and BSCFN- $F_{0.1}$ are 104.0, 102.8 and 104.6 kJ mol^{-1} , respectively.

Figure 8b shows the EIS diagrams of the three components at 600 $^{\circ}\text{C}$, which intuitively reflects the greatly improved electrochemical performance with the introduction of fluorine, by which the ASR value of BSCFN- $F_{0.1}$ is only half that of BSCFN (0.23 vs. 0.44 $\Omega \text{ cm}^2$). The data table obtained by fitting the BSCFN and BSCFN- F_x ($x = 0.05, 0.1$) EIS values is listed in Table 5, which shows the fitted plot for system analysis. The value of the total area specific resistance (ASR) comes from the sum of R_{E1} and R_{E2} . R_{E1} and R_{E2} represent the charge transfer process and the oxygen surface process, respectively [48]. This is based on capacitance and relaxation frequency calculations of the charge transfer process:

$$C = \frac{(RQ)^{1/n}}{R} \quad (6)$$

$$f = \frac{(RQ)^{-1/n}}{2\pi} \quad (7)$$

The capacitance and relaxation frequencies at high frequency are calculated by the above formulas (Table 6). The capacitance and relaxation frequencies of all three samples are in the range of 10–100 mF cm^{-2} and 10–1000 Hz, both of which are within the characteristic range of electron transfer. This also confirms that the high frequency end is the electron transfer resistance of the oxygen reduction process. The experimental data are in accordance with the fitting results. R_{E1} and R_{E2} were significantly reduced in BSCFN- $F_{0.1}$, and the

cathode exhibits fantastic ORR activity, indicating that the introduction of fluorine ions promotes electron transfer and electrode surface ion diffusion.

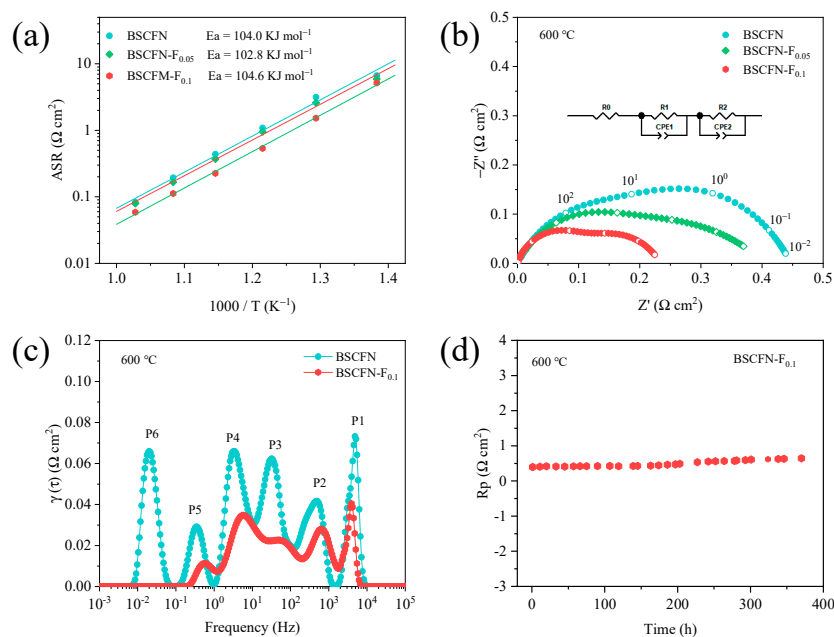


Figure 8. (a) Arrhenius plots of ASR values of BSCFN and BSCFN-F_x (x = 0.05, 0.1) electrodes. (b) EIS Nyquist plots and (c) corresponding DRT analysis of BSCFN and BSCFN-F_x (x = 0.05, 0.1) at 600 °C. The test frequency has been marked in the graph and the unit is Hz. (d) Stability of the BSCFN-F_{0.1} electrode based on the configuration of symmetric cell.

Table 5. Results from fitting the BSCFN and BSCFN-F_x (x = 0.05, 0.1) EIS data.

	R_{ohm} $\Omega\ cm^2$	R_{E1} $\Omega\ cm^2$	CPE1-T	CPE1-P	R_{E2} $\Omega\ cm^2$	CPE2-T	CPE2-P	ASR $\Omega\ cm^2$
BSCFN	2.40	0.26	0.10	0.62	0.45	0.57	0.60	0.71
BSCFN-F _{0.05}	3.04	0.28	0.12	0.61	0.37	0.42	0.43	0.64
BSCFN-F _{0.1}	2.84	0.17	0.13	0.71	0.21	0.74	0.58	0.38

Table 6. The capacitance and relaxation frequencies of the charge transfer process for the three samples.

	C1 (mF cm ⁻²)	f1 (Hz)
BSCFN	11.00	57.37
BSCFN-F _{0.05}	13.68	41.58
BSCFN-F _{0.1}	27.24	34.39

To attain a profound understanding of the cathodic ORR process, we used the distribution of relaxation time (DRT) technique to process and analyse the obtained EIS data [49]. Figure 8c shows the DRT curves corresponding to the EIS of BSCFN and BSCFN-F_{0.1} at 600 °C. High frequency peak (P1) at the frequency range of 10³–10⁴ Hz is related to proton diffuse process. It is assigned to the transfer of protons through the electrolyte and electrode interface. The intensity of P1 decreased significantly, indicating that the proton conductivity in the electrode of BSCFN-F_{0.1} increased significantly. Proton conduction in perovskite oxides is mainly through hydroxide defects, which are produced by dissociation and adsorption of water in oxygen vacancies [50]. The P2 and P3 in the frequency range 10¹–10³ Hz were identified as charge transfer processes, including oxygen ion transfer at the cathode/electrolyte interface and electron transfer during oxygen reduction, which was caused by the use of wet air in the proton-conducting symmetric cell test. Water in

the air would be adsorbed in the oxygen vacancy of the electrode, thus inhibiting the charge transfer of oxygen ions [51]. P4 in the frequency range 10^0 – 10^1 Hz was the cathode oxygen surface reaction process. It is the main speed control step in the reaction process. For the low frequency peak (P5), the gas diffusion process in the porous anode does not play a key role in electrode performance. We can know that the peaks of each frequency segment have been reduced by a great degree, indicating that the corresponding process has been optimised. In addition, the performance of the electrode on the proton conductor mainly depends on the ORR activity and the proton conductivity of the electrode. The performance of the BSCFN- $F_{0.1}$ electrode is better than that of BSCFN, which is mainly due to the increase in proton conductivity in the electrode. Figure 8d presents the stability results for the symmetrical cell with the BSCFN- $F_{0.1}$ electrode at 600 °C in an air atmosphere with 3% humidity. It can be seen that the symmetrical cell remained stable for nearly 400 h. These facts show that the doping of fluorine ions in BSCFN is suitable for the development of intermediate- and low-temperature SOFC cathode materials.

In order to more comprehensively estimate the ORR catalytic activity of BSCFN and BSCFN- F_x ($x = 0.05, 0.1$) cathodes on single cells, we prepared single cells with the configuration of NiO-BZCYYb|BZCYYb|cathodes and accomplished I–V tests on the single cells. The cathode and electrolyte layers' thickness of these three cells were around 18 and 20 μm , respectively. Figure 9a–c shows the I–V–P curves of a single PCFC with BSCFN or BSCFN- F_x ($x = 0.05, 0.1$) cathode at 450–700 °C. The obtained OCV values are in perfect agreement with the theoretical Nernst voltage (1.01 V at 600 °C), which indicates that the sealed cells are acceptable. In the range of 450–700 °C, with 50 °C steps, the single cell made with the BSCFN- $F_{0.1}$ cathode exhibited the best electrochemical properties, and its maximum power densities were 335, 430, 527, 633, 720 and 840 mW cm^{-2} , respectively. This is higher than many other halogen-doped cathodes (Table 7). Figure 9d compares the peak power densities of PCFCs when different components are used as cathodes. It shows that, in the test temperature range, the performances of BSCFN- F_x ($x = 0.05$ and 0.1) were better than that of BSCFN at each temperature, especially in the case of BSCFN- $F_{0.1}$; there is a particularly obvious improvement within the low temperature environment, where the peak power density reached 335 mW cm^{-2} at 450 °C, 145% higher than for BSCFN. To accurately measure the cell stability, a new single cell with a silver mesh brush on the cathode surface (in the same batch as the single cell performance test) was tested with an OCV value of 1.013 V at 600 °C. As shown in Figure 10a, the BSCFN- $F_{0.1}$ cathode shows high durability of ~120 h at a current density of 0.16 A cm^{-2} . A cross-sectional image of the fuel cell after the test, observed by SEM, is shown in Figure 10b. The micrograph demonstrates that the porous electrodes adhered closely to the compact electrolyte. No obvious microcracks or delamination were found. The joints of each component are in good contact and have good structural stability. It also can be seen from the Figure 10b that the electrolyte is dense, while the cathode and anode are loose and porous. The porous microstructure of the fuel electrode facilitates hydrogen and oxygen transport and electrochemical reactions, resulting in lower electrode polarisation resistance and higher power density.

Table 7. The peak power densities of PCFCs with single-phase cobalt-containing cathodes at 600 °C as reported in the literature.

Cathode	Electrolyte	PPD (mW cm^{-2})	References
$\text{BaFe}_{0.6}\text{Co}_{0.3}\text{Ce}_{0.1}\text{O}_{2.95-\delta}\text{Cl}_{0.05}$	BZCYYb	593	[52]
$\text{BaCe}_{0.4}\text{Fe}_{0.4}\text{Co}_{0.2}\text{O}_{3-\delta}$	BZCYYb	237	[53]
$\text{La}_{1.6}\text{Sr}_{0.4}\text{Cu}_{0.6}\text{Ni}_{0.4}\text{O}_{4+\delta}$	BZCYYb	272	[29]
$\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5.84-\delta}\text{F}_{0.16}$	BZCYYb	510	[54]
$\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.7}\text{Fe}_{0.3})_{0.6875}\text{W}_{0.3125}\text{O}_{3-\delta}$	BZCYYb	582	[55]
BSCFN- $F_{0.1}$	BZCYYb	633	This work

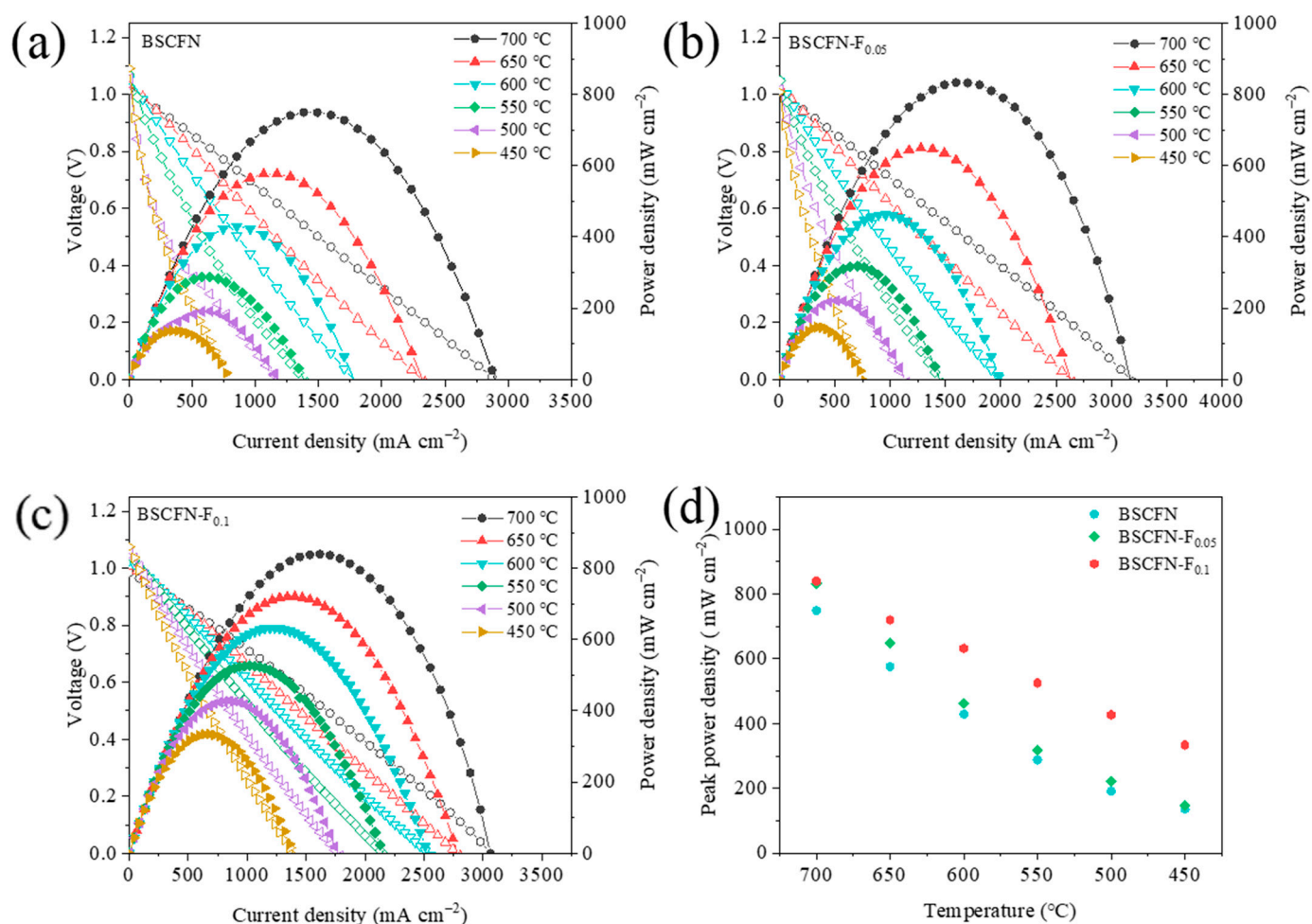


Figure 9. I–V and I–P curves of single cells with (a) BSCFN, (b) BSCFN-F_{0.05} and (c) BSCFN-F_{0.1} cathodes at 450–700 °C. (d) PPD comparison chart for BSCFN and BSCFN-F_x ($x = 0.05, 0.1$).

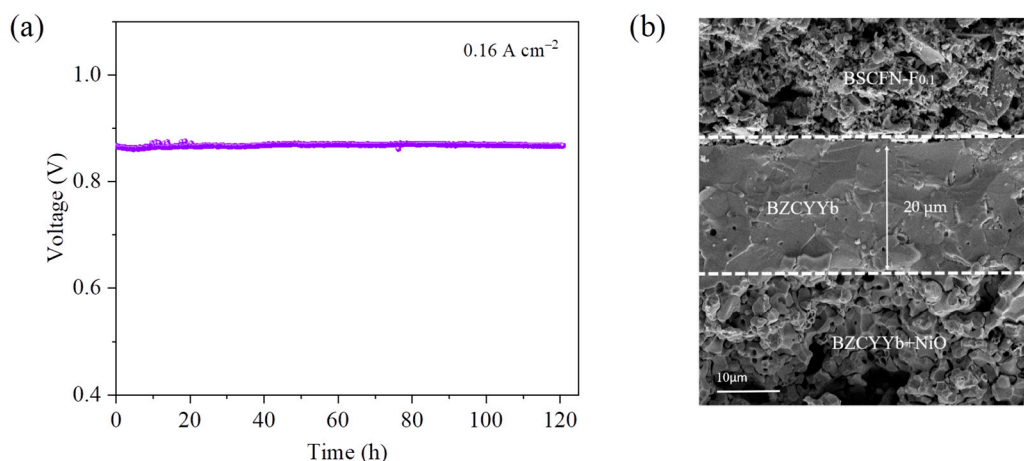


Figure 10. (a) Single-cell stability test results for the fuel cell with BSCFN-F_{0.1} cathode at 600 °C and (b) the cross-sectional SEM image of this cell after the stability test.

3. Experimental

3.1. Materials Preparation

BSCFN and BSCFN-F_x ($x = 0.05, 0.1$) were fabricated via the solid-phase method by dissolving BaCO₃, SrCO₃, CoO₄, Fe₃O₄, Nb₂O₅ and SrF₂ within a ball mill in a certain proportion, with ethanol as a solvent. The mixture was ball-milled for 24 h and placed in

a Petri dish to dry. The resultant dried solids were ground into a powder and heated at 900 °C for 10 h. The cathode powder was put into a mould, pressed into a disc shape and then calcined at 1100 °C for a further 10 h. These tablets were then ground into a powder to obtain the BSCFN cathode material.

BZCYYb was synthesised by a traditional sol-gel process [56,57]. $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were mixed in deionised water and stirred until transparent. Certain proportions of ethylenediaminetetraacetic acid (EDTA), citric acid (CA) and ammonia (n metal ions: n EDTA: n CA: n ammonia solution = 1:1:2:10) were introduced to the nitrate solution as a complex agent. The solution was heated and stirred to form a gel, followed by heating at 250 °C for 6 h to acquire the BZCYYb precursor, and then the BZCYYb precursor was calcined at 1000 °C for 5 h to obtain the BZCYYb electrolyte material.

3.2. Cell Fabrication and Test

Symmetrical cells with BSCFN (or BSCFN- F_x) | BZCYYb | BSCFN (or BSCFN- F_x) configurations were assembled for electrochemical impedance spectroscopy (EIS) measurements. A weighed amount of the prepared BZCYYb powder was formed into a dense BZCYYb electrolyte pellet via the dry pressing method; the radius of each pellet was about 7.5 mm. The pressed electrolyte pellets were calcined at 1450 °C for 5 h. The electrode slurry was prepared by ball-milling after mixing the electrode powder and dispersant; a spray gun was used to uniformly spray the porous cathode slurry onto both sides of the BZCYYb electrolyte pellets, which were then placed on a zirconia plate and calcined in air at 800 °C for 2 h to obtain the symmetrical cells. In this paper, the polarization impedance of the test electrode is measured using a Princeton impedance analyser, and the measurement frequency is 1 MHz–0.01 Hz. To test the single cell performance, anode-supported PCFCs with BSCFN (or BSCFN- F_x) | BZCYYb | NiO-BZCYYb configuration were fabricated using the dry pressing method reported previously [58]. The NiO-BZCYYb anode was composed of nickel oxide powder and BZCYYb powder in a weight ratio of 70:30 mixed with a pore-forming agent, binding agent and ethanol. Half-cells were obtained by calcining the bilayer pellets at 1450 °C for 10 h. The area of the cathode is $\sim 0.48 \text{ cm}^2$. For the cell performance test, wet H_2 (3% H_2O) and air were used as the fuel and the oxidant, respectively. Their flow rates were 80 and 120 mL min^{-1} , respectively. The current-voltage data of the single cells were collected using a Keithley 2440 digital sourcemeter.

3.3. Characterisations

A German Bruker D8 Advance X-ray diffractometer (German Bruker brand) was used to identify the crystal structures of materials. The phase composition of the sample was measured by XRD and quantitative analysis of the phase content was obtained by Rietveld full spectrum refinement. The morphology of the PCFC was surveyed using a field emission scanning electron microscope (FE-SEM Quanta-2000, Hitachi Corporation of Japan). The morphology, structure and elemental distribution of the cathode powder was examined by HR-TEM, HAADF-STEM and EDS mapping using an FEI Titan G2 80-200 (FEI Corporation of the United States). The element valence and binding energy information of samples were obtained from XPS measurements using Al K rays (1486.60 eV) on a Thermo ESCALAB 250 instrument (Thermo manufacturer in the United States).

The electrical conductivity of the electrode was measured in ambient air by means of a four-probe test. The electrode material was first prepared into a bar, and calcined at 1100 °C for 5 h. A Keithley 2420 sourcemeter (American Tektronix company) was used to record the voltage when a constant current was passed through the electrode. The titration test began by placing 0.1 g of the powder under test in an iodine bottle, and excess KI powder was added to cover the powder under test. Then, 2 mL solution of 6 mol L^{-1} HCl was added and placed in a dark place for about 0.5 h. After the powder was dissolved, 30 mL deionized water was added to dilute the solution. Finally, 0.01 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_3$ solution was used for titration, and an appropriate amount of starch solution was added as an indicator near the end of titration.

4. Conclusions

In conclusion, we have identified fluorine ion-doped BSCFN with a cubic perovskite structure as a promising perovskite cathode material. BSCFN-F_{0.1} has a higher concentration of oxygen vacancies at operating temperature, which accelerates the reaction kinetics of oxygen incorporation and the oxygen ion diffusion rate, making the BSCFN-F_{0.1} cathode perform better than BSCFN. The performance of the PCFCs with the structure of Ni-BCZYYb|BCZYYb|BSCFN (or BSCFN-F_x) further reflects the application prospects of the BSCFN-F_{0.1} cathode material, with an open circuit potential of 1.03 V and a peak power density of 632.11 mW cm² at 600 °C. In addition, the symmetric cell fabricated with BSCFN-F_{0.1} as the electrode maintained a stable performance for nearly 400 h at 600 °C in an air atmosphere. Above all, fluorine ions doping strategies can be used to explore high-performance PCFC cathode materials.

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