K-doped BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.2}$O$_{3-\delta}$ as a promising cathode material for protonic ceramic fuel cells

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Abstract: Slow oxygen reduction reaction (ORR) involving proton transport remains the limiting factor for electrochemical performance of proton-conducting cathodes. To further reduce the operating temperature of protonic ceramic fuel cells (PCFCs), developing triple-conducting cathodes with excellent electrochemical performance is required. In this study, K-doped BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.2}$O$_{3-\delta}$ (BCFZ442) series were developed and used as the cathodes of the PCFCs, and their crystal structure, conductivity, hydration capability, and electrochemical performance were characterized in detail. Among them, Ba$_{0.9}$K$_{0.1}$Co$_{0.4}$Fe$_{0.4}$Zr$_{0.2}$O$_{3-\delta}$ (K10) cathode has the best electrochemical performance, which can be attributed to its high electron (e$^-$)/oxygen ion (O$^{2-}$)/H$^+$ conductivity and proton uptake capacity. At 750 $^\circ$C, the polarization resistance of the K10 cathode is only 0.009 $\Omega \cdot \text{cm}^2$, the peak power density (PPD) of the single cell with the K10 cathode is close to 1 W·cm$^{-2}$, and there is no significant degradation within 150 h. Excellent electrochemical performance and durability make K10 a promising cathode material for the PCFCs. This work can provide a guidance for further improving the proton transport capability of the triple-conducting oxides, which is of great significance for developing the PCFC cathodes with excellent electrochemical performance.

Keywords: proton transport; proton-conducting cathode; protonic ceramic fuel cells (PCFCs); triple-conducting; hydration capability

1 Introduction

As a new generation of energy conversion devices, solid oxide fuel cells (SOFCs) can convert chemical energy in fuels into electricity quietly and efficiently with low emissions, which is of great significance for alleviating the increasingly severe environmental pollution and energy crisis. Recently, the development and research of the SOFCs have attracted much attention. The SOFCs can be classified into oxygen-ion (O$^{2-}$)-conducting solid oxide fuel cells (O-SOFCs) and protonic ceramic fuel cells (PCFCs), according to conducting ions of the electrolyte. Compared to the
traditional O-SOFC, the PCFC has many remarkable advantages. First, energy barrier of proton migration reduces the operating temperature, which coincides with the current development trend of low-temperature SOFCs. Second, the fuel will not be diluted by the generated water during operation, ensuring higher fuel utilization and electrochemical performance. Moreover, the relatively dry atmosphere avoids issues such as Ni oxidation and Ni migration of commonly used Ni-based cermet anodes [1–5].

Nevertheless, sluggish oxygen reduction reaction (ORR) involving the proton transport at the PCFC cathode remains a limiting factor for its electrochemical performance [6,7]. To further reduce the operating temperature of the PCFCs, the development of cathode materials with excellent performance is required. It is well accepted from the working principle of the PCFC cathodes that good proton and electron (e−) transportability is crucial to enhancing the cathode reaction rate. Theoretically, mixed protonic and electronic conductors could extend the active sites across the entire cathode surface. Unfortunately, this type of oxide is rare. Currently, the most popular PCFC cathode materials are hydrated mixed ionic–electronic conducting (MIEC) oxides. According to the proton transport mechanism, proton defects can be generated by hydration reactions, i.e., dissociated water molecules combine with oxygen vacancies (V2O3) and lattice oxygen (O2−) to form two proton defects [8,9]. The MIEC oxides may have appreciable proton conductivity in humid air, which can be attributed to their sufficient oxygen vacancies. As reported by Grimaud et al. [10], the MIEC oxides such as Ba0.5Sr0.5Co0.8Fe0.2O3−δ, PrBaCo2O5+, and Pr2NiO4+δ can absorb the water molecules and form the proton defects in humid atmospheres. Seeking the oxides with the proton transport and hydration properties among the MIEC oxides, i.e., triple-conducting (e−/O2−/H+) oxides, is the current research focus of the PCFC cathodes.

BaCo0.4Fe0.4Zr0.2O3−δ (BCFZ442) is a typical MIEC oxide, and its excellent e−/O2−-conducting properties make it an oxygen-permeable membrane reactor [11,12]. Based on its excellent performance and stability in the membrane reactor environment, BCFZ442 also has the potential to be a promising cathode material for the PCFCs. Shang et al. [13] first demonstrated the application of BCFZ442 as a PCFC cathode, and the single cell with a BCFZ442 cathode showed low electrode polarization resistance, high peak power density (PPD), and high stability. Thermogravimetric analysis demonstrates that BCFZ442 has multiple proton absorption properties and proton defect concentrations [14]. Nevertheless, the extent of the hydration reaction in BCFZ442 is much lower than that in an electrolyte, thus resulting in many unconsumed oxygen vacancies.

To further enhance the proton mobility of BCFZ442, element doping is an effective method. It has been proved that doping high-basicity elements such as Ba and K at the A-site of Sr2Fe1.5Mo0.5O6−δ (SFM) can reduce the proton migration barrier, thereby enhancing the proton transportability [15]. Compared to Ba-doped SFM, K-doped SFM has a lower proton migration barrier and increased proton defect concentration, which can be attributed to the fact that K doping leads to more oxygen vacancies and more negative hydration enthalpy. Moreover, the A-site doping of large heterovalent K+ can alter electronic and structural properties, which is beneficial to bulk conductivity and surface electrocatalytic activity [16]. K-doped SrCo0.9Nb0.1O3−δ also shows improved proton uptake and migration ability over SrCo0.9Nb0.1O3−δ [17], further confirming the feasibility of the K doping strategy. In this work, the proton transport capability of BCFZ442 was optimized by K doping at the A-site for the first time, to the best of our knowledge. The crystal structure, e−/O2−/H+ conductivity, hydration capability, and electrochemical performance of K-doped BCFZ442 were characterized in detail. This work can provide a guidance for further enhancing the proton transport capability of triple-conducting oxides, which is of great significance for developing the PCFC cathodes with excellent performance.

2 Materials and methods

2.1 Material synthesis

Ba1−xKxCo0.4Fe0.4Zr0.2O3−δ (x = 0, 0.05, 0.1, and 0.15) powders were synthesized by the commonly used sol–gel method. In brief, metal-ion nitrates containing Ba(NO3)2 (99.5%, Aladdin), KNO3 (99.99%, Aladdin), Co(NO3)2·6H2O (99.99%, Aladdin), Fe(NO3)3·9H2O (99.99%, Aladdin), and zirconyl nitrate solution (35 wt%, Aldrich) were dissolved in deionized water in a stoichiometric ratio to form a metal ion solution. At the same time, ethylenediaminetetraacetic acid (EDTA; 99.5%, Aladdin) was dissolved in ammonia to form an
is the conductivity of the sample, are the partial 

doctoral degree of metal ions, EDTA, and CA was 1 : 1 : 2. Subsequently, the pH value of the mixed solution was adjusted to ~8 with ammonia, and the mixed solution was continued to be heated and stirred until a transparent gel formed. After degreasing pre-calcination and 2-h calcination at 1000 °C, the Ba1-xKxCo0.4Fe0.6Zr0.2O3-δ (x = 0, 0.05, 0.1, and 0.15) powders were obtained, named K00, K05, K10, and K15, respectively.

2.2 Conductivity and electrical conductivity relaxation (ECR) testing

The conductivities of these four materials were measured by alternating current (AC) impedance spectroscopy. The powders were die-pressed into disks, and then sintered at 1200 °C for 5 h to obtain dense disks. To measure the total conductivity, both sides of the disk were printed with Au paste and connected with two Pt wires. Electrochemical impedance spectroscopy (EIS) was recorded by an electrochemical test system (Interface 5000E, Gamry) at 500–750 °C. To measure the O2− conductivity, a dense yttria-stabilized zirconia (YSZ) sheet was attached to one side of the disk to isolate e−. The junction of the disk and the YSZ sheet was sealed with commercial ceramic glue (Ceramabond, Aremco Products Inc.), as shown in Fig. 1. The other sides of the disk and YSZ sheet were printed by the Au paste and connected with the Pt wires. The EIS was recorded by the electrochemical test system at 600–750 °C. The YSZ sheet had a thickness of ~200 μm, and its impedance was subtracted when calculating the O2− conductivity.

The H+ conductivities of the disk under a wet atmosphere were investigated using a concentration-cell method at 650 °C. Ag paste was printed at the surface of the disk with an active area of 0.2 cm², and the disk was sealed to an Al2O3 tube to form a concentration cell with the configuration of gas (I), Ag|sample|Ag, and gas (II). For a water concentration cell, the observed voltage (Vob) is calculated by Eq. (1) [18]:

\[
V_{ob} = (t_{H^+} + t_{O^2^-}) \frac{RT}{4F} \ln \frac{P_{O_2}^{ii}}{P_{O_2}^{ii}} + t_{H^+} \frac{RT}{2F} \ln \frac{P_{H_2O}^{Hi}}{P_{H_2O}^{Hi}}
\]

(1)

where \( t_{O^2^-} \) and \( t_{H^+} \) are the O2− and H+ transport numbers, respectively; \( P_{O_2}^{ii} \) and \( P_{H_2O}^{Hi} \) are the partial pressures of O2, and \( P_{H_2O}^{Hi} \) and \( P_{H_2O}^{Hi} \) are the partial pressures of H2O; \( R, T, F \), and \( F \) are the ideal gas constant, the thermodynamic temperature, and the Faraday constant, respectively. When \( P_{O_2}^{ii} = P_{O_2}^{ii} \), \( t_{H^+} \) is calculated by Eq. (2). Considering the electrode polarization under testing, the \( t_{H^+} \) is corrected by Eq. (3) [19]:

\[
t_{H^+} = \frac{E_{ob}}{E_{Nernst}}
\]

(2)

\[
t_{H^+} = 1 - \frac{R_{ohm}}{R_{total}} \left( 1 - \frac{E_{ob}}{E_{Nernst}} \right)
\]

(3)

where \( R_{ohm} \) is the resistance of the sample, and \( R_{total} \) is the total resistance composed of \( R_{ohm} \) and the polarization resistance of the Ag electrode; \( E_{ob} \) and \( E_{Nernst} \) are the observed voltage and the theoretical voltage calculated from the Nernst equation, respectively. The H+ conductivity (\( \delta_{H^+} \)) is calculated by Eq. (4):

\[
\delta_{H^+} = t_{H^+} \delta = \frac{t_{H^+} L}{R_{ohm} S}
\]

(4)

where \( \delta \) is the conductivity of the sample, \( L \) is the thickness of the disk, and \( S \) is the active area of the Ag electrode. In the measurement, the gas (I) was humidified 30% O2−70% N2 in water at 73 °C, and the gas (II) was humidified 20% O2−80% N2 at room temperature.

The ECR tests of K00, K05, K10, and K15 were conducted by a standard four-probe method. The cathode powders were die-pressed into green bars, and then sintered at 1200 °C for 5 h to obtain dense bars. Four Pt wires were tightly tied to the bars, and then the Ag paste was used to strengthen the connection between the Pt wires and the bars. The wire-bound bar was fixed on a homemade fixture, and the conductivity was measured by a conductivity meter (DMM7510, Keithley). To obtain the ECR curves of the cathode materials, the oxygen partial pressure around the bar was abruptly changed from 0.21 to 0.1 atm, and the conductivity was recorded as a function of relaxation.
time until it remained constant. According to Fick’s second law, the relative conductivity \( g(t) \) with time \( t \) can be expressed as
\[
g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)}
\]
and then the curves of the samples were fitted by MATLAB software, where \( \sigma(0), \sigma(t), \) and \( \sigma(\infty) \) are the initial, the time-dependent, and the final conductivities, respectively; \( D_{\text{chem}} \) is the chemical diffusion coefficient; \( x, y, \) and \( z \) are half the length, the width, and the height of the bar, respectively; \( \alpha_m, \beta_n, \) and \( \gamma_p \) are the \( m \)th, \( n \)th, and \( p \)th roots, respectively. The parameters \( L_{\alpha}, L_{\beta}, \) and \( L_{\gamma} \) are defined as
\[
\begin{align*}
L_{\alpha} &= x \frac{k_{\text{chem}}}{D_{\text{chem}}} \\
L_{\beta} &= y \frac{k_{\text{chem}}}{D_{\text{chem}}} \\
L_{\gamma} &= z \frac{k_{\text{chem}}}{D_{\text{chem}}}
\end{align*}
\]
where \( k_{\text{chem}} \) is the surface exchange coefficient. \( \alpha_m, \beta_n, \) and \( \gamma_p \) are calculated by Eq. (7):
\[
\begin{align*}
L_{\alpha} &= \alpha_m \tan \alpha_m \\
L_{\beta} &= \beta_n \tan \beta_n \\
L_{\gamma} &= \gamma_p \tan \gamma_p
\end{align*}
\]
To maintain the accuracy of the results, \( m, n, \) and \( p \) were fixed at 10. According to Eqs. (5)–(7), the ECR coefficients (TECs) of these four materials, dense bars coating, and calcining methods. Commercial NiO (99%, J.T. Baker), BZCYYb4411 (Marion Technologies), and graphite (99.5%, Aladdin) powders were thoroughly mixed in a mass ratio of 12 : 8 : 5 by wet ball-milling. The mixed powders were die-pressed after drying, and then pre-sintered at 900 °C for 2 h to obtain a green anode supporter. BZCYYb4411 electrolyte slurry was dip-coated on the surface of the anode supporter; after dying, the supporter was placed in a muffle furnace for high-temperature co-sintering at 1450 °C for 6 h. After the electrolyte layer was densified, the cathode ink containing 50 wt% cathode powders and 50 wt% binder (V-006A, Heraeus) was printed on the surface of the electrolyte, followed by calcining at 1000 °C for 2 h to obtain a single cell. The electrolyte layer had a thickness of ~20 μm, the anode supporter had a thickness of ~800 μm, and the cathode layer had a thickness of ~30 μm and an active area of 0.2 cm².

Before electrochemical performance measurements, the Au paste was applied on the surface of the cathode to act as a current collector, followed by the heat treatment in air at 600 °C for 2 h. Subsequently, the single cell was sealed on the end of an alumina ceramic tube with ceramic glue. During the heating process, the cathode and anode were fed with humidified air (3 mol%) and humidified H₂ (3 mol%), respectively. After an open circuit voltage (OCV) was stabilized, the electrochemical performance testing was started. The EIS and \( I-V \) curves were recorded using the electrochemical test system at 600–750 °C in humid H₂.

2. 4 Other characterizations

To verify the chemical compatibility of the cathode material with the electrolyte, the mixture containing the same mass of K10 and BZCYYb4411 powders was heat-treated in air at 1000 °C for 5 h, and then subjected to X-ray diffractometer (X’Pert Pro-X, PANalytical) analysis with Cu Kα radiation and a silicon strip detector (D/teX, Rigaku). The step scan was operated from 20° to 80° with a scanning speed of 5 (°)·min⁻¹. The chemical stability of the K10 powders in humid air, the phase structures of the synthesized powders, and the surface of the BZCYYb4411 electrolyte was also verified by the X-ray diffractometer. The microstructures of the cross-section of the single cell and the electrolyte surface were characterized by a scanning electron microscope (SEM; Apreo S, Thermo Fisher Scientific). To examine the thermal expansion coefficients (TECs) of these four materials, dense bars.
were prepared (the same way as the samples in the ECR tests). The TECs were measured from room temperature to 1000 °C at a heating rate of 10 °C·min⁻¹ in air by a dilatometer (DIL-402C, Netzsch). To measure the proton uptake capability, the sample was heated from 60 to 800 °C at a rate of 10 °C·min⁻¹ in dry air, and then cooled from 800 to 200 °C at a rate of 10 °C·min⁻¹ in wet air (5 mol% H₂O). During this process, changes in the sample mass were recorded by a thermogravimetric analyzer (TGA; STA 449 C, Netzsch).

3 Results and discussion

The K₀₀, K₀₅, and K₁₀ powders exhibit standard simple perovskite structures without impurity, as shown in Fig. 2(a). However, the second-phase K₂(Fe₂O₄) can also be detected in an X-ray diffraction (XRD) pattern of the K₁₅ sample. It can be seen in Fig. 2(a) that the K doping does not cause a significant shift of the peaks, indicating that the K doping has little effect on the unit-cell parameters. Substitution of smaller Ba²⁺ (1.61 Å) by larger K⁺ (1.64 Å) theoretically increases the lattice constant. In contrast, hetero-valent substitution leads to the formation of more oxygen vacancies, which leads to the shrinking of the lattice. Owing to the low valence state of K⁺, the K doping will cause a decrease in the total valence state of the cations in the perovskite. When the K doping amount exceeds the critical value, impurity phases will be generated to maintain the electrical neutrality of the entire perovskite oxide.

The PCFC cathodes usually face the high-temperature and high-humidity environments when operating. It is necessary to verify the stability of the cathode and its compatibility with the electrolyte. No impurity phase can be found in the XRD patterns of K₁₀–BZCYYb₄₄₁₁-mixed powders after the heat treatment in air for 5 h, as shown in Fig. 2(b), indicating the excellent chemical compatibility between the cathode powder and the electrolyte. The matched TEC between the cathode and the electrolyte is crucial for the long-term stable operation of the single cell. Figure 2(c) shows the thermal expansion behaviors of these four samples. The average TEC value decreases slightly with the increasing K doping amount, which is caused by the decrease in the average valence of the B-site elements [20]. The average TEC values of these four materials are 1.65×10⁻⁵–1.7×10⁻⁵ K⁻¹, indicating the matched TEC with the BZCYYb₄₄₁₁.

Fig. 2  (a) XRD patterns of K₀₀, K₀₅, K₁₀, and K₁₅ powders; (b) chemical compatibility of K₁₀ and BZCYYb₄₄₁₁; (c) TECs of K₀₀, K₀₅, K₁₀, and K₁₅ samples; (d) XRD pattern of K₁₀ powders after heat treatment in 10 mol% H₂O at 800 °C for 10 h.
The structural stability of the K10 sample was evaluated after the heat treatment in humid air (10 mol% H₂O) at 800 °C for 10 h. An XRD pattern without any decomposition sign caused by high-temperature steam confirms that K10 is structurally stable in humid air, as shown in Fig. 2(d). The measurement of e⁻/O²⁻/H⁺ conductivities is necessary for triple-conducting (e⁻/O²⁻/H⁺) cathodes, especially since they contribute significantly to its ORR catalytic activity. The ORR of the PCFC cathode involves e⁻, O₂⁻, and H⁺. The high e⁻/O²⁻/H⁺ conductivities can extend the ORR active sites to the entire cathode surface, which can greatly improve the performance of the cathode. To the best of our knowledge, however, few studies report these three conductivities of the triple-conducting oxides in detail. Figures 3(a) and 3(b) show the total and O²⁻ conductivities of these four samples, respectively. Due to the dominance of e⁻ conductivity, the total conductivities of the samples approximate e⁻ conductivity. Both the e⁻ conductivity and O²⁻ conductivity keep increasing with the increasing K-doping amount at each temperature point. The improvement in O²⁻ conductivity can be attributed to more oxygen vacancies brought by the K doping. The K doping results in a decrease in the total valence state of the cations, and additional oxygen vacancies are created to maintain electrical neutrality. Moreover, K can make the oxygen p-band center closer to the Fermi level, causing a decrease in the oxygen-vacancy formation energy [15,17,21]. More oxygen vacancies can provide more e⁻ to compensate for the holes induced by the K doping, which is beneficial to charge compensation, resulting in the improvement of the e⁻ conductivity [15]. The K10 sample has the highest total conductivity and the O²⁻ conductivity among these four samples. However, they drop sharply for K15, which is mainly affected by the impurities. Although the total conductivity is not outstanding, the high O²⁻ conductivity of K10 is notable. The O²⁻ conductivities of the K10 sample are 3.6×10⁻², 2.2×10⁻², 1.3×10⁻², and 6×10⁻³ S·cm⁻¹ at 750, 700, 650, and 600 °C, respectively. Under the same conditions, the O²⁻ conductivities of the MIEC cathode materials such as La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ (0.01 S·cm⁻¹ at 700 °C) [22], (La₀.₆Sr₀.₄)₀.₉₉CoO₃₋δ (0.01 S·cm⁻¹ at 650 °C) [23], and La₀.₈Sr₀.₂FeO₃₋δ (3.4×10⁻² S·cm⁻¹ at 750 °C) [24] are lower than that of K10. Like the changing trends of the e⁻ and O²⁻ conductivities, the K10 sample has the highest H⁺ conductivity (2.26×10⁻² S·cm⁻¹ at 650 °C) among the four samples, as shown in Fig. 3(c). As stated in Section 1, the proton formation and transport are inseparable from the oxygen vacancies. The K doping promotes the formation of the oxygen vacancies, thereby leading to an increase in the H⁺ conductivity. However, the H⁺ conductivity of the K15 sample is slightly lower than that of K10 due to the presence of the second-phase impurity.
To evaluate the effect of the K doping on oxygen incorporation kinetics, the ECR measurements were performed, and the $k_{\text{chem}}$ and $D_{\text{chem}}$ values were obtained by fitting and simulation calculation, as shown in Fig. 4. Among the four samples, the conductivity of the K10 sample reaches the fastest equilibrium state, i.e., it has the shortest relaxation time when the oxygen partial pressure around the sample is abruptly changed. At 650 °C, the $k_{\text{chem}}$ values are $7.63 \times 10^{-4}$, $9.43 \times 10^{-4}$, $1.19 \times 10^{-3}$, and $4.84 \times 10^{-4}$ cm$^{-1}$ s$^{-1}$, respectively, and the $D_{\text{chem}}$ values are $5.12 \times 10^{-4}$, $5.84 \times 10^{-4}$, $7.26 \times 10^{-4}$, and $4.69 \times 10^{-4}$ cm$^{2}$ s$^{-1}$, respectively, for K00, K05, K10, and K15. In contrast, the K10 sample has the largest $k_{\text{chem}}$ and $D_{\text{chem}}$ values. The A-site doping of large hetero-valent K$^+$ can alter electronic and structural properties, and significantly accelerate the oxygen incorporation kinetics, which is beneficial to the bulk conductivity and surface electrocatalytic activity [16]. With the increasing K doping amounts, the $k_{\text{chem}}$ and $D_{\text{chem}}$ values of the material increase, resulting in a shortening relaxation time. While for the K15 sample, the increase of the relaxation time is likely caused by the second phase.

It is generally accepted that the formation of the proton defects is closely related to the dissociative adsorption of H$_2$O [25,26]. The H$_2$O molecules dissociate into a hydroxide ((OH)$_x$) and proton. The former fills the O$_V$, and the latter forms another hydroxide with O$_6$, as shown in Eq. (8). Figures 5(a)–5(d) show the hydration behaviors of these four materials. As the temperature increases, the O$_6$ are steadily released, and additional V$_O$ are formed, resulting in the weight loss of the samples during the heating phase in dry air. In contrast, the weight of the samples gradually increases during the cooling phase in wet air, which is caused by the combined action of oxygen adsorption and hydration. The weight difference in wet and dry air at the same temperature is attributed to H$_2$O absorption in wet air. The K10 sample has the largest difference, as shown in Fig. 5(e), indicating that the best hydration capability of K10. K10 has the highest oxygen-vacancy concentration, leading to the highest potential for hydroxide defect formation. Moreover, the K doping leads to more negative hydration enthalpy, which is beneficial to increasing the hydration capability and suppressing the proton mobility barrier [15,17,21].

$$\text{H}_2\text{O} + V_O + O_6^x \leftrightarrow 2(\text{OH})_x \quad (8)$$

The electrochemical performance of the K00, K05, K10, and K15 cathodes was subsequently evaluated in the single cells. Figure 6 shows the microstructures of the single cell with the configuration of cathode/BZCYYb4411/Ni–BZCYYb4411. The porous structure of the cathode and anode ensures gas transport, and the electrolyte has intimate contact with the electrodes. After high-temperature sintering, the electrolyte has a thickness of 21 μm and high density. Moreover, the phase of the electrolyte surface has no change, indicating the high chemical stability of BZCYYb4411. The EIS curves of the single cells with the K00, K05, K10, and K15 cathodes are shown in Figs. 7(a)–7(d), respectively, and the specific values can be found in Table 1. With the increasing K-doping amounts, the polarization impedance ($R_p$) values of the single cells show a trend of first decreasing and then increasing at each temperature point. Overall, the single cell with the K10 cathode presents the best electrochemical performance with slightly higher $R_p$ value than that of the single cell with the K05 cathode at only 600 °C, and the $R_p$ values are 0.143, 0.045, 0.018, and 0.009 Ω cm$^{-2}$ at 600, 650, 700, and 750 °C, respectively. These values are much lower than those of the reported PCFC single cells, indicating the excellent performance of the K10 cathode, as shown in Table 2. Each electrochemical process of the single cell contributes to the $R_p$ value, but the impedances of each process overlap each other and are indistinguishable. Distribution of relaxation time (DRT) method can decompose each process by assigning specific fractions in the EIS to the corresponding electrochemical process. Figure 7(e) shows the DRT analysis of the EIS measured at 700 °C, and four
deconvolution peaks can be seen, named P1, P2, P3, and P4 sequentially from high to low frequencies. Each peak in the DRT curve represents a certain reaction step in the electrochemical process of the single cell, and the peak area intuitively reflects the impedance value of the corresponding step. According to the analysis results in Refs. [27–29], P1–P4 correspond to the following reaction steps: diffusion of protons from the anode to the electrolyte (P1); hydrogen adsorption, dissociation, and proton absorption at the anode (P2); oxygen adsorption and dissociation on the cathode surface and electrochemical reduction (P3); and transport of protons in the cathode (P4). According to the DRT analysis, the $R_p$ values corresponding to each peak are shown in Fig. 7(f). The $R_{p3}$ and $R_{p4}$ values show the same changing trend as the total $R_p$ value of the single cell with the increasing K-doping amount, indicating that the K doping affects the proton transport rate and the ORR process of the cathode. The proton transport rate of a triple-conducting cathode is determined by its $\text{H}^+$ conductivity and hydration capability. For the PCFC cathodes, the ORR is not only involved in the transport of $\text{O}_2^-$ and $e^-$ but also the $\text{H}^+$ transport. That is, the ORR catalytic activity of the PCFC cathode is jointly affected by its $e^-/\text{O}_2^-/\text{H}^+$ conductivities. In general, the low $R_p$ values of the K10 cathode could be attributed to its high $e^-/\text{O}_2^-/\text{H}^+$ conductivities and hydration capability.

Fig. 5 Thermogravimetric curves recorded during heating stage in dry air and cooling stage in wet air: (a) K00, (b) K05, (c) K10, and (d) K15; (e) differences in $\text{H}_2\text{O}$ adsorption between heating stage and cooling stage.
Fig. 6 (a) Overall morphology of single cell after reduction; (b) interfacial morphology of cathode and electrolyte; (c) SEM image of cathode; (d) interfacial morphology of anode and electrolyte; (e) SEM image of anode; (f) XRD pattern of electrolyte surface (the inset shows the SEM image of electrolyte surface).

Fig. 7 EIS curves of single cells with (a) K00, (b) K05, (c) K10, and (d) K15 cathodes at various temperatures; (e) DRT analysis of single-cell EIS measured at 700 °C; (f) resistance values of each electrode reaction step for single-cell EIS measured at 700 °C.
The improvement in the electrochemical performance is also reflected in the PPD values of the single cells. The $I-V$ and the corresponding $I-P$ curves of the single cells with different cathodes are shown in Figs. 8(a)–8(d), and the specific PPD values are listed in Table 1. The OCV values of the single cells are lower than the theoretical values due to the humid electrode atmosphere and non-negligible electron leakage of the BZCYYb4411 electrolyte. It can be seen that the PPD of the single cells that the ohmic impedance of the electrolyte accounts for a large proportion of $R_p$, as shown in Figs. 7(a)–7(d). If the thickness of the electrolyte continues to be thinned, it is expected to further reduce the operating temperature of the PCFC, which needs to be further studied. Galvanostatic polarization of the single cell with the K10 cathode was carried out at the applied current density of 400 mA·cm$^{-2}$ and 650 °C, and the cell voltage vs. time curve was recorded, as shown in Fig. 8(e). In this study, the highly stable BZCYYb4411 was used as the electrolyte material for the single cells. Therefore, the stability of the K10 cathode can be intuitively reflected in the single cell. Within 150 h, there is no

| Table 1  Summary of polarization resistances and PPDs for single cells with K00, K05, K10, and K15 cathodes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cathode | Polarization resistance ($\Omega$·cm$^2$) | PPD (W·cm$^{-2}$) |
| | 600 °C | 650 °C | 700 °C | 750 °C | 600 °C | 650 °C | 700 °C | 750 °C |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| K00 | 0.154 | 0.058 | 0.027 | 0.018 | 0.421 | 0.560 | 0.684 | 0.772 |
| K05 | 0.125 | 0.049 | 0.020 | 0.012 | 0.427 | 0.586 | 0.738 | 0.860 |
| K10 | 0.143 | 0.045 | 0.018 | 0.009 | 0.502 | 0.667 | 0.836 | 0.942 |
| K15 | 0.272 | 0.095 | 0.039 | 0.023 | 0.312 | 0.437 | 0.573 | 0.698 |

| Table 2  Comparison of electrochemical performance of PCFC single cells using various cathodes |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cathode | Electrolyte | Temperature (°C) | PPD (W·cm$^{-2}$) | $R_p$ (Ω·cm$^2$) | Ref. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SrEu$_2$Fe$_{1.4}$Co$_{0.6}$O$_3$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (15 μm) | 700 | 0.562 | 0.14 | [30] |
| Ba$_{0.8}$Sr$_{0.2}$Co$_{0.9}$Fe$_{0.1}$O$_3$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (14 μm) | 700 | 0.960 | 0.08 | [31] |
| K$_{0.25}$Sr$_{0.75}$Fe$_{0.8}$O$_{3.5}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (20 μm) | 700 | 0.430 | 0.31 | [21] |
| La$_{0.6}$Co$_{0.3}$Mn$_{0.1}$O$_2$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (15 μm) | 700 | 1.155 | 0.07 | [32] |
| La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$O$_{3.5}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (~13 μm) | 700 | 1.322 | −0.05 | [33] |
| La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$O$_{3.5}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (~13 μm) | 700 | 0.613 | −0.11 | [33] |
| PrBaCo$_{0.6}$O$_{3.4}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (10 μm) | 700 | 0.545 | 0.15 | [34] |
| K$_{0.6}$Sr$_{0.4}$Co$_{0.6}$O$_{3.4}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (20 μm) | 700 | 0.967 | 0.11 | [17] |
| SrCo$_{0.9}$Ni$_{0.1}$O$_2$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (20 μm) | 700 | 0.629 | 0.18 | [17] |
| Nd(Ba$_{0.8}$Sr$_{0.2}$)$_3$Co$_{0.8}$Fe$_{0.2}$O$_{3.8}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (13 μm) | 700 | 0.776 | 0.114 | [29] |
| La$_{0.8}$(Ba$_{0.7}$Sr$_{0.3}$)$_3$Co$_{0.8}$Fe$_{0.2}$O$_{3.8}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (24 μm) | 700 | 0.716 | 0.125 | [35] |
| Nd(Ba$_{0.8}$Sr$_{0.2}$)$_3$Co$_{0.8}$Ni$_{0.1}$O$_{2.8}$ | BaZr$_{0.3}$Ce$_{0.5}$Y$_{0.2}$O$_3$ (~25 μm) | 700 | 0.608 | 0.145 | [36] |
| K10 | BZCYYb4411 (21 μm) | 700 | 0.836 | 0.018 | This work |
| BCFZ442 | BZCYYb4411 (21 μm) | 700 | 0.684 | 0.027 | This work |
significant drop in the cell voltage, indicating the superior stability of the K10 cathode. In summary, K10, with excellent electrochemical performance and durability, is a promising cathode material for the PCFCs.

4 Conclusions

To further improve the proton mobility of BCFZ442 and endow it with more excellent electrochemical performance when used as a PCFC cathode, element doping is an effective method. In this study, K-doped BCFZ442 was synthesized and used as a PCFC cathode. The crystal structures, $\text{e}^-/\text{O}_2^-/\text{H}^+$ conductivities, proton uptake capability, and electrochemical performance were characterized in detail, and the connection between them was established. The K doping is beneficial to improving the oxygen-vacancy concentration, $\text{e}^-/\text{O}_2^-/\text{H}^+$ conductivity, and proton uptake capability, thus leading to the improvement of the electrochemical performance of the K-doped BCFZ442 cathodes. Various properties and electrochemical performance of the K-doped BCFZ442 cathodes reached the best when the K-doping amount was 10 mol%. For the PCFC single cell with the K10 cathode, the $R_p$ and PPD values were 0.009 $\Omega\cdot\text{cm}^2$ and 0.942 W·cm$^{-2}$, respectively, at 750 $^\circ$C, and the cell could operate stably for 150 h. Excellent electrochemical performance and durability make K10 a promising cathode material for the PCFCs. The A-site K doping has been demonstrated to be reliable in the construction and optimization of the PCFC cathodes, which is of great significance for the development of the PCFCs.
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