Rapid Gas-Phase Synthesis of the Perovskite-Type BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3- δ} Proton-Conducting Nanocrystalline Electrolyte for Intermediate-Temperature Solid Oxide Fuel Cells

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exhibit good crystallinity of the pure orthorhombic perovskite BCZYYb phase. BCZYYb (CA) shows more uniform doping with the element ratio of 1:0.74:0.12:0.08:0.1, which is very close to the theoretical value. The shrinkage and surface SEM (scanning electron microscope) results indicate that the flame-made powders have superior sinterability compared to the sol-gel-made powders because of the smaller primary particle size (~20 nm). Electrochemical impedance spectroscopy tests show that BCZYYb (CA) sintered at 1450 °C has the highest protonic conductivity of 1.31×10^{-2} S cm⁻¹ in wet H₂ when operating at 600 °C and still maintains a high-level conductivity of 1.19×10^{-2} S cm⁻¹ even when the sintering temperature is reduced to 1350 °C, which is mainly attributed to uniform doping and good sinterability. The activation energy for the conductivity of BCZYYb (CA) is also significantly lower than that of conventional electrolytes, which suggests much better conductivity in the intermediate (~600 °C) and even lower operating temperature. The excellent conductivity performance combined with the high-throughput production capability makes the swirling spray flame a promising synthesis method for promoting the BCZYYb electrolytes from lab to industrial-scale solid oxide fuel cells.

KEYWORDS: nanocrystalline BCZYYb proton-conducting electrolyte, spray flame synthesis, sintering behavior, protonic conductivity, intermediate-temperature SOFCs

1. INTRODUCTION

In recent years, solid oxide fuel cells (SOFCs) have attracted great attention for their advantages in the distributed energy conversion, owing to the features of high efficiency, all-solid-state, near-zero pollution, and especially fuel flexibility.¹⁻⁴ However, the high operating temperature of SOFCs around 800 °C is still a major bottleneck that limits the reduction of operation cost and further commercialization, which can be mainly attributed to the temperature dependence of the electrolyte conductivity.⁵ For conventional SOFCs based on oxygen-ion-conductor electrolytes such as yttria-stabilized zirconia (YSZ),⁶ the cell performance drops dramatically as the operating temperature decreases, due to the high activation energy related to the conduction of oxygen ions.⁷ Therefore, an emerging trend in SOFC development is to lower the

operating temperature with higher conductivity electrolytes in the intermediate-temperature range.^{2,8,9}

Answering this need, proton-conducting materials have recently attracted great attention, which exhibit outstanding ionic conductivity in the intermediate-temperature range owing to the lower activation energy of proton diffusion. This type of protonic ceramic is very promising to be used as electrolytes in the next-generation equipment of electro-

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chemical energy conversion and storage.^{6,10,11} Moreover, water is produced at the cathode side in proton-conductor-based SOFCs and thus can be easily removed by the oxygen flow, rather than diluting the fuel stream in current oxygenconductor-based SOFCs, which benefits the water management and further improves the cell efficiency.¹² The most popular proton-conducting oxides are perovskites based on Ba, Ce, and Zr, including yttrium-doped barium zirconate (BZY), yttrium-doped barium cerate (BCY), yttrium- and ceriumdoped barium zirconates (BZCY/BCZY), and yttrium-, ytterbium-, and cerium-doped barium zirconates (BCZYYb). Especially, the multi-element co-doping Ba- $Ce_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) has attracted wide attention for its superior properties, including high conductivity, good thermo-chemical stability, coking resistance, and sulfur tolerance. $^{3,4,7-10,13}$ In addition to perovskites, fluorite-type oxides such as nanocrystalline CeO2, rare-earth doped CeO2, and core-shell structure $CeO_2/CeO_{2-\delta}$ have also been extensively studied.¹⁴⁻¹⁶ However, a rapid, scalable, and costeffective method for synthesizing BCZYYb nanoparticles remains challenging due to the difficulty in uniform co-doping of five different elements.7,10

There are several routes for producing BCZYYb powders. Liu and co-workers were the first to use the most common solid-state reaction (SSR) method to synthesize BCZYYb with stoichiometric amounts of high-purity barium carbonate, zirconium oxide, cerium oxide, ytterbium oxide, and yttrium oxide as raw materials.¹⁷ To achieve uniform doping at the atomic level, SSR usually requires multiple steps of ball-milling combined with high-temperature calcination, making the synthesis process both time- and energy-consuming. Meanwhile, the doping uniformity may still not be satisfactory due to the top-down nature of the synthesis route. Then, the wet chemistry route has been widely used for the preparation of BCZYYb. For instance, Shao et al. utilized a modified sol-gel method to obtain high-quality BCZYYb powders at 1000 °C.^{8,18} Nguyen et al. synthesized fine crystalline BCZYYb by an ammonium carbonate co-precipitation method.¹⁹ The glycine nitrate process (GNP) was also employed to produce BCZYYb powders with smaller sizes and higher purity in reduced time and temperature.^{4,20} However, these approaches are difficult to be scaled up due to the cost and complexity of the multiple-step processes with limited yield and sometimes involving toxic reagents.

On the other hand, spray flame synthesis (SFS), as one of the most efficient gas-phase methods, has shown great potential for rapid and scalable production of co-doping nanoparticles owing to the advantages of being single-step, high-throughput production, and environmentally friendly.²¹⁻²⁶ Known also as flame aerosol technology, SFS typically utilizes economical metallic salts dissolved in a liquid fuel as a precursor solution to generate fine droplets with a mean diameter of several micrometers through an atomizer. Then, the droplets containing the precursor/fuel mixture are ignited by the surrounding flame and undergo evaporation, reaction, nucleation, collision, sintering, and coalescence to form nanoparticles within milliseconds finally.²⁷⁻²⁹ Owing to the bottom-up principle and fast processing time, SFS allows the high-yield synthesis of single- and multi-component metal oxides covering most elements in the periodic table and provides a promising route for flexible doping.

Particularly, for energy, environmental, and catalysis applications where the mass preparation of tailored functional

nanomaterials is urgent,³⁰⁻³² SFS has attracted extensive attention in recent years.³³⁻³⁶ However, the SFS of complex multi-component materials like BCZYYb still remains challenging. It requires a comprehensive understanding and proper matching of precursor preparation, transformation route, and flame organization. To the best of our knowledge, the relevant literature on using spray flame to synthesize BCZYYb electrolytes is limited.

In this study, we demonstrate the rapid and scalable synthesis of BCZYYb electrolyte nanoparticles by SFS using swirling spray flame for the first time. The as-synthesized powders are further sintered into pellets. The ionic conductive performance of BCZYYb pellets is examined under different operating temperatures and atmospheres to study the effect of precursor type and calcination temperature. The flame-made BCZYYb electrolytes exhibit superior properties compared to the sol-gel-made BCZYYb and conventional 8 mol % yttriastabilized zirconia (8YSZ) electrolytes.

2. EXPERIMENTAL METHODS

2.1. Synthesis of BCZYYb Protonic Electrolytes. Figure 1 illustrates the swirling SFS system, including a liquid-precursor



Figure 1. Schematic of the swirling spray flame synthesis system.

feeding unit, a swirling spray flame burner, and a collection unit. The swirling spray flame burner consists of eight tangential slits and a central two-fluid nozzle at the bottom. As seen in the inset graph, fuel $(CH_4, 3 \text{ Lmin}^{-1})$ and oxidant (air, 30 Lmin^{-1}) are individually introduced side-by-side into eight slits. This design ingeniously prevents flame flashback and ensures experimental safety. The tangential slit with a small cross-sectional area (15 mm in length, 1 mm in width) provides a high injection velocity to promote the mixing of fuel and oxidant. Combined with the heat recirculation caused by the strong swirling flow, a rapidly mixed combustion zone is established around the center. The liquid precursor is delivered continuously by an injection pump at a feeding rate of 600 mL h^{-1} then atomized to micron-sized droplets by air (15 Lmin^{-1}) in a twofluid nozzle. The droplets are ignited steadily by the surrounding swirling hot gas and form a spray flame. Here, the swirling flame not only provides a high-temperature environment for the ignition of the spray droplets and especially stabilizes the combustion when the reactor is operated at a high precursor feeding rate for the large-scale synthesis of nanoparticles. Finally, the BCZYYb nanoparticles are generated in the flame and collected by a glass fiber filter above the burner. A photograph of the swirling SFS system and a more intuitive video of the device in operation are displayed in the Supporting Information (Figure S1 and Video S1) for better clarity.

For the preparation of precursor solutions, two different types of barium precursors, barium nitrate and barium acetate, are investigated separately. Stoichiometric amounts (10:7:1:1:1) of barium nitrate [Ba(NO₃)₂, Aladdin, 99.0%] or barium acetate [Ba(CH₃COO)₂, Mreda, 99.0%] together with cerium nitrate hexahydrate $[Ce(NO_3)_3]$. 6H₂O, Mreda, 99.99%], zirconium nitrate pentahydrate [Zr(NO₃)₄. 5H₂O, Mreda, 99.99%], yttrium nitrate hexahydrate [Y(NO₃)₃·6H₂O, Mreda, 99.999%], and ytterbium nitrate pentahydrate $[Yb(NO_3)_3]$. 5H2O, Mreda, 99.99%] are dissolved in a mixed high combustion enthalpy solvent of propionic acid ($C_3H_6O_2$, Macklin, AR \geq 99.5%) and 2-propanol (C_3H_8O , Greagent, AR \geq 99.7%) with a volume ratio of 1:1. For convenience in discussion, the precursor formulation containing barium nitrate is marked as the "N" case and barium acetate is marked as the "CA" case. In order to obtain fine atomization and uniform doping, ammonia water (NH₃·H₂O, Greagent, AR) is added to form a clear solution without visible precipitates. Moreover, affected by the poor solubility of $Ba(NO_3)_{2\prime}$ the "N" case requires more ammonia water than the "CA" case because of its higher NO_3^- concentration and lower pH value.³⁷ In this work, the total metal concentration is 0.4 mol L^{-1} and the corresponding yield of BCZYYb powder is about 38 g h^{-1} at the feeding rate of 600 mL h^{-1} . This yield can be further raised facilely by the increase of both feeding rate and metal concentration.

In addition, the BCZYYb powders named "BCZYYb (sol-gel)" are prepared by the sol-gel method for comparison.^{8,18} Specifically, stoichiometric metal nitrates of $Ba(NO_3)_2$, $Ce(NO_3)_3$, $6H_2O$, $Zr(NO_3)_4$, $5H_2O$, $Y(NO_3)_3$, $6H_2O$, and $Yb(NO_3)_3$, $5H_2O$ are dissolved in deionized water. Then, ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) are added to the mixed solution at a molar ratio of 1:2:1 for EDTA/CA/metal ions. The pH of the solution is adjusted to around 7 by ammonia water. After continuous heating and stirring, a transparent gel is formed and then pretreated at 250 °C for 10 h to obtain the precursors. Finally, the as-synthesized precursors are calcined at 1000 °C for 5 h to achieve the final BCZYYb (sol-gel) powders.

2.2. Material Characterization. The crystal phases of assynthesized nanopowders are analyzed by X-ray diffraction (XRD, SmartLab 9 kW system, Rigaku) with filtered Cu K α radiation (λ = 1.54 Å, 40 kV, 150 mA). Diffraction patterns are obtained from 10° to 90° with a scan speed of 10° min⁻¹ and a resolution of 0.0002° . A transmission electron microscope (TEM, JEM 2010, JEOL Ltd., 120 kV) coupled with an X-ray energy dispersive spectrometry (EDS, B5-U92) is used to characterize the morphology and the elements distribution of samples. Additionally, the crystallinity of the nanoparticles is confirmed by selected area electron diffraction (SAED). The surface microstructures of electrolyte pellets sintered at various temperatures are revealed using a high-resolution SEM (JSM-7401F, JEOL Ltd) operated at 3.0 kV. A gas physisorption and chemisorption analyzer (ASAP 2460, Micromeritics) is used to measure the specific surface area (SSA) of nanoparticles by applying the Brunauer-Emmett-Teller (BET) theory. Assuming all particles to be monodisperse and non-aggregated spheres, the BET-equivalent particle diameter can be calculated as $d_{\text{BET}} = 6/(\rho \cdot \text{SSA})$, where ρ is the density of BCZYYb electrolyte (6.211 g cm⁻³).³

2.3. Cell Fabrication and Electrochemical Tests. The symmetrical cells with the configuration of AglBCZYYblAg are fabricated to investigate the conductivity performance. First, the BCZYYb powders are pressed into a disk shape mold, and then the green electrolyte pellets are sintered in an air atmosphere at four different temperatures (1300, 1350, 1400, and 1450 °C) for 5 h. In the heating stage, the electrolyte pellets are sintered at 5 °C min⁻¹ below 1000 °C and 2 °C min⁻¹ above 1000 °C. In the cooling stage, the electrolyte pellets are sintered at 2 °C min⁻¹ above 1000 °C and natural cooling below 1000 °C. To ensure data comparability, all electrolyte pellets are smoothed to a uniform thickness of 0.4 mm before sintering. Second, the BCZYYb pellets are coated with Ag paste and sintered at 150 °C for 0.5 h to remove the organics to form the Ag electrode. At last, Ag wires are attached to the Ag electrode for ionic conductivity measurements.

Electrochemical impedance spectroscopy (EIS) of the sintered BCZYYb electrolyte pellets is measured under open-circuit conditions in the temperature range of 400–800 °C using a frequency response analyzer (Solartron 1260A) and a potentiostat (Solartron 1287). Measurements are taken at 50 °C intervals under a humidified hydrogen (5 vol % H₂O) atmosphere and the impedance frequency ranges from 1.0 MHz to 0.1 Hz. Particularly, for the EIS measurement under various atmospheres (humidified hydrogen, dry hydrogen, and dry air), a representative intermediate temperature (600 °C) is chosen as the test temperature.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Properties. As shown in Figure 2, the XRD patterns of the "sol-gel", "CA",



Figure 2. XRD patterns of BCZYYb (sol-gel), BCZYYb (CA), and BCZYYb (N).

and "N" samples all exhibit a pure orthorhombic structure of perovskite-type BaCe_{0.8}Zr_{0.2}O₃ (ICSD Database, PDF#70-3670), which is distorted from the ideal cubic structure of BaCeO₃ and belongs to the *Imma* space group.^{8,38} Meanwhile, the slight shift of the diffraction peaks to smaller angles in the XRD patterns suggests the effective substitution of Y for B-site cations in BCZYYb because the dopants force the lattice distortion to accommodate their larger size.³⁹ Compared to the BCZYYb (CA) sample, the crystallinity of BCZYYb (N) is slightly weaker due to the higher water content in the precursor solvent because the higher content of water will significantly reduce the combustion enthalpy of the liquid fuel and the evaporation of water will also absorb more heat, thereby further lowering the synthesis temperature of spray flames. Furthermore, a more significant shift of main diffraction peaks (1 2 1) and (2 0 2) can be observed in BCZYYb (N), as shown in the enlarged XRD patterns of 2theta ranging from 28° to 42° (Figure S2 in the Supporting Information). According to Bragg's law, the larger shift to small diffraction angles indicates that more larger Y³⁺ ions (ionic radius:0.9 Å) are doped into the lattice to replace Zr4+ ions (0.87 Å), resulting in a wider lattice spacing. It is mainly due to the doping deviation caused by the instability of the precursor of BCZYYb (N), as evidenced by the following EDS analysis.

The typical particle morphology, primary size, and electron diffraction of as-synthesized powders are presented in Figure 3. For the BCZYYb (CA) sample, the TEM image (Figure 3a) shows that the electrolyte powders are fairly agglomerated particles, mainly containing small solid spherical primary particles with an average size of 13.6 nm, although a few larger



Figure 3. TEM and SAED images of as-synthesized BCZYYb nanopowders: CA (a-c) and N (d-f).

inhomogeneous particles (such as hollow particle) are also found in the sample (see Figure S3 in the Supporting Information). Under high magnification, the crystal lattice (0.31 nm) belonging to the (1 2 1) plane of orthorhombic BCZYYb can be clearly resolved in Figure 3b. Additionally, by comparing to theoretical *d*-spacing data, more BCZYYb crystal planes of (2 0 2), (2 2 2), (2 4 0), and (4 0 2) are identified in the SAED image (Figure 3c), which well proves the good crystallinity.

As shown in Figure 3d,e, the TEM images of BCZYYb (N) show similar particle morphology to the "CA" sample, except that the average primary particle size (~ 16 nm) is slightly larger. Besides, it is worth noting that more hollow or shell-like particles at much larger sizes (over 100 nm) appear in BCZYYb (N), and the homogeneity of particles deteriorates compared to BZCYYb (CA) (Supporting Information Figure S3). The coexistence of small nanoparticles and large hollow or shell-like particles can be attributed to two formation mechanisms. One is that the metal precursor evaporates at a high temperature and obeys the gas-to-particle route to form small homogeneous nanoparticles. Another one is the dropletto-particle route where the solute precipitates first on the droplet surface during solvent evaporation and then forms an outer shell; the remaining solvent will be trapped and evaporate in this layer; eventually resulting in hollow or shell-like inhomogeneous particles. The higher content of water in precursors will promote the formation of inhomogeneous particles as observed in BZCYYb (N) because the presence of water will lower the droplet temperature and may generate partially hydrolyzed species (metal hydroxides) with a high decomposition point to cause more particles formed from the droplet-to-particle route. The diffraction rings corresponding to the crystal planes (1 0 1), (1 2 1), (1 1 2), (2 0 2), and (2 2 2) of BCZYYb can be resolved in the SAED image (Figure 3f). The small particle size of flame-made samples is very beneficial for further powder sintering to fabricate dense electrolyte pellets.

Furthermore, EDS is used to examine the doping uniformity of "CA" and "N" samples. Figure 4 shows the typical TEM images and the corresponding compositional elements mapping images of BCZYYb (CA) and BCZYYb (N). For the BCZYYb (CA) sample (Figure 4a), the EDS mapping images show that the elements (Ba, Ce, Zr, Y, Yb, and O) are uniformly distributed in the sample. Based on the elemental



Figure 4. Elemental (Ba, Ce, Zr, Y, Yb, and O) mapping images and statistical metal element contents of as-synthesized (a) BCZYYb (CA) and (b) BCZYYb (N) nanopowders.

statistical analysis with several-times averaging, the sampled metal element ratio (Ba:Ce:Zr:Y:Yb) is about (1:0.74:0.12:0.08:0.1), which is very close to the theoretical value (1:0.7:0.1:0.1:0.1). For the BCZYYb (N) sample (Figure 4b), it is seen that the elemental distribution is also uniform from the EDS mapping images, but the sampled metal element ratio (1:0.49:0.12:0.12:0.19) shows a little deviation from the theoretical value. The reason for the larger deviation of BCZYYb (N) may be the larger content of ammonia water in the precursor solution, which leads to the partial hydrolysis of the rare earth nitrate and causes the uneven dispersion of the solute. We will show later that the distortion of the elemental ratio may result in a negative effect on the conductivity of the electrolyte.

3.2. Sinterability of BCZYYb Electrolytes. In this section, we investigate the sintering behavior of as-synthesized BCZYYb powders by shrinkage measurement and surface SEM analysis. Besides, the results are compared to the BCZYYb powders prepared by the sol-gel method.

Figure 5 plots the shrinkage measurement of BCZYYb (CA), BCZYYb (N), and BCZYYb (Sol-gel) with the sintering temperature from 1300 to 1450 °C. Here, the shrinkage is calculated by the equation of $\Delta v/v$, where Δv is the volume change and v is the volume of the electrolyte pellet before sintering. All samples show an increase in the shrinkage with the sintering temperature, and the maximum shrinkage at 1450 °C of BCZYYb (CA), BCZYYb (N), and BCZYYb (sol-gel) is 47.29, 45.98, and 45.92%, respectively. Under all four temperatures, BCZYYb (CA) has the highest shrinkage, BCZYYb (N) is in the middle, and BCZYYb (sol-gel) is the lowest. The difference of shrinkage is particularly significant at a low sintering temperature (1300 °C), as also evident in the SEM images (inset graph of Figure 5). It can be clearly observed that there are many large pores in BCZYYb (sol-gel). This phenomenon is caused by the size difference between flame-made and sol-gel-made samples. BET measurement shows that BCZYYb (sol-gel) has the lowest



Figure 5. Shrinkage of the BCZYYb (CA, N, and sol-gel) pellets sintered from 1300 to 1450 $^\circ$ C for 5 h and SEM images of the BCZYYb (CA, N, and sol-gel) samples sintered at 1300 $^\circ$ C for 5 h (inset).

SSA of 8.73 m² g⁻¹ corresponding to a d_{BET} of 110.7 nm, while the SSA of BCZYYb (N) is higher with an SSA of 20.50 m² g⁻¹ and a d_{BET} of 47.1 nm, and the SSA of BCZYYb (CA) is the highest (SSA = 22.39 m² g⁻¹, d_{BET} = 43.1 nm). The large size of BCZYYb (sol-gel) powders is mainly due to the long-term high-temperature calcination during the preparation process. In contrast, the BCZYYb powders produced by the SFS method have a short high-temperature residence time resulting in smaller size and higher SSA, which significantly promotes the sintering densification process.

Figure 6 shows the surface SEM images of BCZYYb (CA), BCZYYb (N), and BCZYYb (sol-gel) sintered at 1300, 1350,



Figure 6. SEM images of the surface of BCZYYb-sintered pellets [CA (a-d), N (e-h), and sol-gel (i-l)] sintered at 1300, 1350, 1400, and 1450 °C for 5 h, respectively.

1400, and 1450 °C. It can be seen that SEM results are well consistent with the shrinkage tests, again indicating the positive effect of small particle size on the sinterability of BCZYYb. As the sintering temperature increases, the pores gradually disappear and the grain size increases, which improves the proton conductivity. For BCZYYb (CA) and BCZYYb (N), good densification can be achieved at 1400 °C due to the small size of as-synthesized powders, as illustrated in Figure 6c,g. However, for BCZYYb (sol–gel), there are still a few pores observed at 1400 °C (Figure 6k) and the pores disappear when the sintering temperature reaches 1450 °C (Figure 6l). For the lower sintering temperature at 1350 °C, poor sintering with a

large number of visible pores appears in the BCZYYb (solgel) sample (Figure 6j). However, this phenomenon does not appear in BCZYYb (CA) (Figure 6b) and BCZYYb (N) (Figure 6f) until the sintering temperature drops to 1300 °C, as shown in Figure 6a,e because the sintering characteristics of BCZYYb are not only strongly dependent on the sintering temperature but also affected by the particle size. In addition, at lower sintering temperatures (<1450 °C), the influence of particle size difference between flame-made and sol-gel-made BCZYYb powders on sintering becomes particularly significant.

Moreover, the grain size distributions are measured on BCZYYb (CA, N, and sol-gel) sintered at 1300, 1350, 1400, and 1450 °C. As shown in Figure S4 in the Supporting Information, the grain sizes of all samples after hightemperature sintering almost obey a log-normal distribution. With the increase of the sintering temperature, the mean grain size d_{mean} tends to become larger, while the geometric standard deviation $\sigma_{\rm g}$ gradually decreases, which means the grain size distribution becomes more and more concentrated as the grain grows. Compared to the sol-gel-made sample, BCZYYb (CA) and BCZYYb (N) have a faster sintering rate due to smaller particle size, resulting in larger mean grain size. The grain size difference between them reaches a maximum ($\sim 100 \text{ nm}$) at a sintering temperature of 1350 °C and then gradually decreases because the influence of primary particle size on sinterability becomes less dominant at a high sintering temperature (1450 °C). For flame-made samples, the mean grain size of BCZYYb (CA) is slightly larger than that of BCZYYb (N) and the grain size distribution of BCZYYb (CA) is also less dispersive after sintering due to fewer inhomogeneous particles in the sample synthesized from precursors with lower water content.

The shrinkage and surface SEM results indicate that the flame-synthesized BCZYYb nanopowders have good sinterability owing to the small particle size and high SSA. Moreover, a lower sintering temperature can prevent the inevitable loss of the barium element at high temperatures, making it easier to precisely control the cation stoichiometry of BCZYYb perovskite.⁸ Lower sintering temperature also effectively reduces the energy consumption in the scale-up fabrication.

3.3. Electrical Conductivity. Figure 7 shows the EIS of the BCZYYb (CA, N, and sol-gel) samples sintered at 1450 and 1400 °C measured in a humidified hydrogen atmosphere from 400 to 800 °C. The impedance spectra are drawn as Nyquist plots. The ionic conductivity σ of the sample is given by $\sigma = L/RA$, where *L* is the thickness of the sample, *A* is the face area of the electrode (1 cm² for this work), and the ohmic impedance *R* is derived from the intersection of the high-frequency semi-circle with the real *Z'* axis on a complex impedance plane. Table 1 gives a comparison of the ionic conductivity of flame-made BCZYYb (CA), BCZYYb (N), and sol-gel-made BCZYYb (sol-gel) sintered at 1450 and 1400 °C in a wet H₂ atmosphere from 400 to 800 °C, and the corresponding ohmic impedance are listed in Table S1 in the Supporting Information.

For the sample of BCZYYb (CA) sintered at 1450 °C (Figure 7a), the minimum ohmic impedance is 1.86 Ω cm² at an operating temperature of 800 °C corresponding to the highest ionic conductivity of 2.25 × 10⁻² S cm⁻¹. The conductive performance drops with the decrease of the operating temperature and reaches a maximum ohmic impedance of 13.11 Ω cm² at 400 °C, corresponding to a ionic conductivity of 0.32 × 10⁻² S cm⁻¹. The ionic conductivity of the BCZYYb (N and sol-gel) samples is



Figure 7. EIS spectra of BCZYYb [CA (a,b), N (c,d), and sol-gel (e,f)] pellets sintered at 1450 °C (a,c,e) and 1400 °C (b,d,f) in a wet H_2 atmosphere from 400 to 800 °C.

Table 1. Ionic Conductivity of BCZYYb (CA, N, and Sol–Gel) Pellets Sintered at 1450 and 1400 $^{\circ}$ C in a Wet H₂ Atmosphere from 400 to 800 $^{\circ}$ C

	ionic conductivity ($\times 10^{-2}$ S cm ⁻¹)								
sample (in wet H_2)	800 °C	750 °C	700 °C	650 °C	600 °C	550 °C	500 °C	450 °C	400 °C
CA 1450 °C	2.25	1.96	1.78	1.55	1.31	1.03	0.76	0.52	0.32
CA 1400 °C	1.89	1.63	1.46	1.25	1.00	0.74	0.50	0.32	0.19
N 1450 °C	1.82	1.65	1.34	1.02	0.88	0.66	0.50	0.33	0.22
N 1400 °C	1.11	1.00	0.90	0.77	0.62	0.46	0.31	0.21	0.14
sol-gel 1450 °C	1.98	1.71	1.48	1.28	1.01	0.76	0.54	0.36	0.23
sol-gel 1400 °C	0.53	0.46	0.41	0.35	0.28	0.19	0.13	0.08	0.04

slightly lower for the sintering temperature of 1450 °C, as shown in Figure 7c,e. For the BCZYYb (N) nanopowders, although the deviation of the local elemental ratio is significantly larger than that of the BCZYYb (CA) sample, the pellets after sintering at 1450 °C exhibit comparable ionic conductivity (1.82 \times 10⁻² S cm⁻¹ at 800 °C) to BCZYYb (CA). We may speculate that the non-uniform elemental distribution is largely improved by solid-state diffusion during the high-temperature (1450 °C) sintering. For a lower sintering temperature of 1400 °C, the ionic conductivity of BCZYYb (CA) and BCZYYb (N) only show a slight degradation, with the ohmic impedances still below 30 Ω cm² even at an operating temperature of 400 °C. However, the conductivity of the BCZYYb (sol-gel) sample exhibits significant degradation as the sintering temperature drops from 1450 to 1400 °C (Figure 7f). When it operates at 500 °C, the ohmic impedance has already exceeded 30 Ω cm². Moreover, the maximum ionic conductivity is 0.53×10^{-2} S cm⁻¹ at 800 °C, considerably lower than that of BCZYYb (CA) and BCZYYb (N), which are 1.89×10^{-2} and $1.11 \times$ 10^{-2} S cm⁻¹, respectively. The main reason is the poorer densification of BCZYYb (sol-gel) due to larger particle size, which is more significant for lower sintering temperatures. The remaining pores block the pathways for proton migrations and thus reduce the ionic conductivity.

To further compare the electrical property of different samples, we extract the conductivity from the EIS spectra and plot the data in the Arrhenius form from 400 to 800 °C, as shown in Figure 8. The conductivity of conventional 8YSZ is included for comparison.¹⁷ Additionally, EIS measurements are also performed on the flame-made BCZYYb (CA and N) that still maintain good sinterability at 1350 °C and the corresponding EIS spectra and comparison of ohmic impedance and ionic conductivity are displayed in Figure S5 and Table S2 in the Supporting Information. Figure 8 displays that all ionic conductivities increase with an increasing operating temperature, but the activation energies are different. For BCZYYb, the CA sample sintered at 1450 °C exhibits the best ionic conductivity. Notably, even reducing the sintering temperature from 1450 to 1350 °C, the conductivity of BCZYYb (CA) still maintains at a high level owing to the excellent sinterability and uniform elements distribution. As listed at the bottom of Figure 8, the conductivity of BCZYYb (CA, sintered at 1350 °C) operating at an intermediate temperature of 600 °C is 1.19×10^{-2} S cm⁻¹, which is even higher than the conductivity of BCZYYb (N) and BCZYYb (sol-gel) sintered at 1450 °C, which are 0.89×10^{-2} and 1.01 \times 10⁻² S cm⁻¹, respectively. This conductivity value is approximately 4.76 times that of the conventional oxygenion-conductor electrolyte 8YSZ¹⁷ and exceeds the conductivity threshold for the electrolyte to be used in commercial SOFCs.³



Figure 8. Arrhenius plots of ionic conductivity of BCZYYb (CA, N, and sol-gel) sintered at various temperatures, tested in a wet H_2 atmosphere from 400 to 800 °C.

Moreover, the conductivity of BZCYYb (CA) in wet H₂ at 600 °C is comparable to or even better than that of the BCZYYb and BaCe_xZr_yY_zYb_{1-x-y-z}O_{3- δ} series electrolytes prepared by other methods, as summarized in Table S3 in the Supporting Information, indicating that flame-synthesized BCZYYb can be an excellent candidate for the proton-conducting electrolytes applied in intermediate-temperature SOFCs.

Comparing the performance of BCZYYb (CA) and BCZYYb (N), an interesting phenomenon is that the conductivity of BCZYYb (CA) is not sensitive to the sintering temperature, while that of BCZYYb (N) is much more sensitive to the sintering temperature. Take the operating temperature 600 °C as an example, the conductivity of BCZYYb (CA) slightly decreases from 1.31×10^{-2} to $1.19 \times$ 10^{-2} S cm⁻¹ when the sintering temperature decreases from 1450 to 1350 °C, but that of BCZYYb (N) dramatically drops from 0.89×10^{-2} to 0.07×10^{-2} S cm⁻¹. In Section 3.2, it has been shown that the difference in sinterability between BCZYYb (CA) and BCZYYb (N) is quite small because the particle size of the two samples is close. Therefore, the different effect of the sintering temperature may be attributed to the doping uniformity of green powders synthesized by the spray flame. Higher temperature calcination helps nonuniformly distributed elements in BCZYYb (N) to diffuse and re-distribute. This compensation effect becomes much weaker when the sintering temperature decreases, which explains the sensitivity of the BCZYYb (N) sample on the sintering temperature.

From the Arrhenius plots, an apparent activation energy E_a for ionic conduction can be extracted as $\sigma T = A \exp(-E_a/kT)$, where σ is the ionic conductivity, T is the operating temperature, A is the pre-exponential value, and k is the Boltzmann constant. It seems that the Arrhenius plots can be divided into two regimes with different activation energy for all the BCZYYb samples, the low-temperature regime (400–600 °C) with higher activation energies and the high-temperature regime (600–800 °C) with lower activation energies, as also reported in the previous literature.⁴⁰ It can be attributed to the fact that the variation of protonic defects concentration with the temperature regimes. Especially for BaCeO₃-based composi-

tions, the protonic defect concentration drops significantly when the temperature exceeds about 600 °C, while remaining at a relatively stable level below 600 $^{\circ}$ C.¹² Additionally, the dominant competition between proton conduction and oxygen-ion conduction under a wet H₂ atmosphere may also have some influence. The activation energy for BCZYYb (CA) sintered at 1450 °C is only 0.30 and 0.42 eV for the hightemperature and low-temperature regimes, respectively. For the BCZYYb (N) and BCZYYb (sol-gel) samples, the activation energies are slightly larger but still lie in the typical range of proton conduction (~0.3 to 0.6 eV).¹⁸ It should be noted that the activation energies of all flame-made BCZYYb samples are lower than that of BCZYYb prepared by the GNP method (0.78 eV for 400-600 °C, 0.43 eV for 600-800 °C),⁴⁰ some reported traditional electrolyte 8YSZ (~0.94 eV),¹⁷ and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC10, ~0.86 eV),³ which indicates that the SFS method shows great potential for synthesizing a highperformance BCZYYb proton-conducting electrolyte.

Finally, under open-circuit conditions, the influence of the operating atmosphere (wet H_2 , dry H_2 , and dry air) is investigated for different BCZYYb samples (sintered at 1400 °C for 5 h) at an intermediate operating temperature of 600 °C. From the Nyquist plots in Figure 9a, we can see that the



Figure 9. (a) EIS spectra of BCZYYb (CA, N, and sol-gel) pellets sintered at 1400 $^{\circ}$ C tested in wet H₂, dry H₂, and dry air atmospheres under open-circuit conditions, and the corresponding conductive mechanisms (b–d).

ohmic impedance in wet H₂ is always lower than that in dry H₂ and dry air for all the samples, which indicates that the highest conductivity is in wet H₂. For BCZYYb (CA), the ohmic impedance is 8.67 Ω cm² in dry air, 6.35 Ω cm² in dry H₂, and 4.31 Ω cm² in wet H₂, corresponding to the conductivity of 0.50 × 10⁻², 0.68 × 10⁻², and 1.0 × 10⁻² S cm⁻¹, respectively. Due to the less uniform elemental distribution in green nanopowders, the conductivity of BCZYYb (N) is lower than that of BCZYYb (CA), with the value of 0.36 × 10⁻² S cm⁻¹ in dry air, 0.42 × 10⁻² S cm⁻¹ in dry H₂, and 0.62 × 10⁻² S cm⁻¹ in wet H₂. Notably, the highest conductivity for BCZYYb (sol–gel) is 0.28 × 10⁻² S cm⁻¹ in wet H₂, which is even lower than the lowest value of the BCZYYb (CA and N) samples in dry air, demonstrating that poor sinterability has a significant adverse effect on the conductive performance.

As shown in the mechanism diagrams of Figure 9b-d, BCZYYb exhibits three different ionic conducting behaviors under dry air, dry H₂, and wet H₂, respectively, resulting in the conductivity differences presented in Figure 9a. In a dry air atmosphere (Figure 9b), the BCZYYb electrolytes show oxygen-ion conductivity. Oxygen-ion vacancies can react with oxygen to form regular lattice oxygen ions and electron holes to realize oxygen-ion conduction. In a dry H₂ atmosphere (Figure 9c), protons are trapped by lattice oxygen ions and transferred through the form of hydroxyl ions. Under an intermediate temperature of 600 °C in a dry atmosphere, the transference number of protons is larger than that of oxygen ions, as reported in a similar Ba-based proton conductor,³ implying that the proton conduction is dominant here, which is probably why the conductivity measured in dry H₂ is higher than in dry air. Then, if the moisture exists, an extra mechanism of hydration reaction would be introduced (Figure 9d). The vapor-phase water dissociates into a hydroxyl ion and a proton, then combined with a lattice oxygen ion and an oxygen-ion vacancy to generate two protonic defects (hydroxyl ions). This process significantly increases the concentration of protonic defects and eventually leads to higher conductivity.

4. CONCLUSIONS

The perovskite BCZYYb nanoparticles (~20 nm) with the pure orthorhombic structure are successfully synthesized from a self-developed swirling SFS system using two different barium precursors, named as BCZYYb (N) and BCZYYb (CA), respectively. The EDS mapping analysis demonstrates that BCZYYb (CA) has a more uniform metal elements distribution with a ratio of 1:0.74:0.12:0.08:0.1, which is close to the theoretical value. Comparatively, the metal elements ratio in BCZYYb (N) deviates more from the theoretical one. It can be attributed to the larger amount of ammonia water added to the precursor solution, which causes the partial hydrolysis of the rare earth nitrate. In contrast to the BCZYYb powders prepared by the sol-gel method, both flame-made powders show better sinterability because of their smaller particle size. After being sintered to dense pellets, the EIS measurement indicates that BCZYYb (CA) sintered at 1450 $^{\circ}$ C exhibits the highest conductivity in wet H₂, which is 2.25 × 10^{-2} and 1.31×10^{-2} S cm⁻¹ at 800 and 600 °C, respectively. Notably, BCZYYb (CA) still maintains a high-level conductivity even when the sintering temperature is reduced to 1350 °C, which is 1.19×10^{-2} S cm⁻¹ at 600 °C. However, the conductivity of BCZYYb (N) seriously drops, when the sintering temperature decreases. The lower sintering temperature may limit the solid-state diffusion that may promote the possible re-distribution of non-uniformly doped metal atoms in the green nanopowders. The flame-made BCZYYb samples show significantly lower activation energies for ion conduction than some reported conventional electrolytes (8YSZ, GDC10), suggesting the better conductivity performance in the intermediate (~600 °C) and even lower operating temperature.

In summary, the flame-made BCZYYb (CA) powders exhibit superior sinterability and proton conductivity, especially in the intermediate-temperature range. The performance is not sensitive to the sintering temperature, which is beneficial for avoiding barium escape, reducing energy consumption in cell fabrication, and the potential use of metal support to solve the problem of poor mechanical strength. The excellent conductivity performance combined with the high-throughput production capability makes the swirling spray flame a promising synthesis method for promoting the BCZYYb electrolytes used in the nextgeneration intermediate-temperature SOFCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c11492.

Photograph of the swirling spray flame synthesis system; the enlarged XRD patterns of BCZYYb (CA and N) ranging from 28° to 42° , including two main diffraction peaks of (1 2 1) and (2 0 2); TEM images of the distribution of homogeneous and inhomogeneous particles in BCZYYb (CA) and BCZYYb (N); the grain size distributions BCZYYb (CA, N, and sol-gel) sintered at 1300, 1350, 1400, and 1450 °C; the ohmic impedance of BCZYYb (CA, N, and sol-gel) pellets sintered at 1450 and 1400 °C in a wet H₂ atmosphere from 400 to 800 °C; EIS spectra of (a) BCZYYb (CA) and (b) BCZYYb (N) pellets sintered at 1350 °C and measured in a wet H₂ atmosphere from 400 to 800 °C; the ohmic impedance and ionic conductivity of BCZYYb (CA and N) pellets sintered at 1350 °C in a wet H₂ atmosphere from 400 to 800 °C; and summary of the conductivity of the $BaCe_xZr_yY_zYb_{1-x-y-z}O_{3-\delta}$ series electrolytes in a wet H_2 atmosphere at 600 °C (PDF) Video of the swirling spray flame synthesis device in operation (MP4)

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Notes

The authors declare no competing financial interest.

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