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Research Article

Unlocking refractory BaZrO₃-based protonic ceramics via cooperative interfacial low-temperature processing for electrochemical cells

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Abstract

Refractory BaZrO₃-based protonic ceramics offer outstanding chemical stability for protonic ceramic electrochemical cells but require sintering temperatures exceeding 1550 °C because of sluggish cation diffusion, leading to detrimental Ba volatilization, electrode coarsening, and microstructural degradation. Here, we report low-temperature processing of BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY) at only 1350 °C through a cooperative interfacial co-sintering strategy enabled by defect-structure coupling across the electrolyte/support interface. Zinc incorporation increases oxygen-vacancy concentration and is accompanied by enhanced sintering kinetics within the BZY electrolyte, while a Ni-modified BCZYYb support promotes cooperative membrane densification. Electron paramagnetic resonance and X-ray photoelectron spectroscopy confirm enhanced oxygen-vacancy formation, while the reduced thermal budget suppresses Ba evaporation and Ni coarsening, producing a fully dense electrolyte with a proton conductivity of ~0.01 S cm⁻¹ at 550 °C. The resulting cells deliver reversible electrochemical operation with electrolysis current densities reaching -4 A cm⁻² at 1.5 V and exceptional durability, exhibiting an ohmic degradation rate of only 0.012% h⁻¹. This work establishes a defect-chemistry-guided, scalable processing strategy for overcoming diffusion-limited sintering in refractory protonic ceramics and provides a broadly applicable route toward low-temperature manufacturing of advanced solid-state electrochemical devices.

Keywords: *protonic ceramic electrochemical cell, BZY electrolyte, low-temperature sintering, synergistic co-sintering, defect-structure coupling, oxygen vacancies engineering.*

1. Introduction

Protonic ceramic electrochemical cells (PCECs) have emerged as an attractive platform for efficient energy conversion and hydrogen production due to their high energy efficiency and favorable electrode kinetics in the intermediate temperature range (450-600 °C).[1–3] Compared with conventional oxide-ion conducting solid oxide cells, PCECs offer lower operating temperatures and improved thermodynamic efficiency, making them promising candidates for integration with renewable electricity and industrial waste heat.[4,5] However, their large-scale deployment remains heavily bottlenecked by manufacturing challenges, particularly the extreme sintering temperatures required for dense electrolyte fabrication.

Among proton-conducting electrolytes, yttrium-doped barium zirconate (BaZr_{1-x}Y_xO_{3-δ}, BZY) is widely regarded as one of the most chemically stable materials under steam-rich and reducing environments.[6–8] Unlike cerium-rich electrolytes such as BaCeO₃-based systems, which exhibit high conductivity but suffer from chemical instability due to Ce⁴⁺/Ce³⁺ redox activity, BZY offers superior resistance against carbonation and reduction. Nevertheless, BZY is intrinsically refractory due to its high lattice stability and low cation diffusivity. As a result, dense BZY membranes typically require sintering temperatures exceeding 1500-1600 °C.[9,10] Such extreme processing conditions increase fabrication cost, promote Ba volatilization and elemental redistribution, induce Ni coarsening in electrodes, and compromise long-term microstructural stability.[11] Importantly,

insufficient densification at reduced temperatures results in residual porosity and high grain-boundary resistance, severely suppressing proton transport.[12]

To overcome the refractory nature of BZY, various processing strategies have been explored, though each presents important limitations. Field-assisted techniques, such as spark plasma, flash sintering, and microwave-assisted sintering can substantially accelerate densification through externally applied pressure or electromagnetic fields.[13–17] However, these approaches are primarily applicable to bulk ceramics and are difficult to implement for thin electrolyte membranes co-fired on porous electrode substrates because of geometric constraints, thermal nonuniformity, and limited scalability. Alternatively, transition-metal sintering additives such as NiO, ZnO, and CuO are widely employed to reduce apparent sintering temperatures through transient liquid-phase-assisted mass transport.[11,18] While effective in promoting densification, these additives frequently segregate at grain boundaries, forming secondary phases or defect-rich intergranular regions that increase grain-boundary resistance and degrade proton conductivity.[19–21] Consequently, conventional sintering strategies often improve processability at the expense of electrochemical functionality.

Beyond these practical limitations, a more fundamental issue remains unresolved. Solid-state densification of BZY involves thermally activated mass-transport processes that are strongly influenced by point-defect chemistry. Previous studies have shown that oxygen vacancies and dopant-induced defect chemistry can influence atomic transport and densification in BZY-based ceramics.[22–24] However, the influence of defect concentration depends on defect association, local chemistry, and the operative transport pathways.[25,26] Consequently, simply increasing defect concentration does not necessarily enable low-temperature processing while preserving high proton conductivity.

An additional challenge arises from the constrained sintering of supported electrolyte membranes. During co-firing, the porous electrode mechanically restricts the in-plane shrinkage of the electrolyte layer, substantially reducing the effective driving force for densification. Although constrained sintering is well recognized in ceramic processing, its deliberate exploitation through cooperative kinetic matching between electrolyte and substrate has received little attention in protonic ceramic cells. Achieving low-temperature fabrication therefore requires simultaneous engineering intrinsic defect chemistry and interfacial shrinkage behavior, rather than optimizing either component independently.[27,28]

Here, we report a cooperative interfacial processing strategy that simultaneously engineers defects chemistry and constrained co-sintering to overcome the refractory nature of BZY. By incorporating Zn into BZY, oxygen-vacancy concentration is increased simultaneously modifying chemical and electronic environment around Zr. These defect-chemical changes are accompanied by enhanced grain growth and densification and are consistent with the established role of point defects in solid-state mass transport. However, the present measurements do not directly determine oxygen-vacancy mobility or the dominant microscopic diffusion pathway. Simultaneously, partial Ni

incorporation into the BCZYYb fuel-electrode support accelerates substrate shrinkage, establishing kinetically matched co-sintering across the electrolyte-support interface. This cooperative interfacial coupling amplifies the effective driving force for densification, enabling fully dense BZY membranes to be fabricated at an unprecedented temperature of 1350 °C while suppressing Ba volatilization and Ni coarsening. Beyond demonstrating a practical low-temperature processing route, this work establishes a generalizable design principle in which defect chemistry and interfacial mechanics are co-engineered to overcome diffusion-limited processing of refractory protonic ceramics without compromising electrochemical performance.

2. Materials and Methods

2.1 Materials synthesis

BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY), BaZr_{0.76}Y_{0.2}Zn_{0.02}O_{3-δ} (BZYZn02), and BaZr_{0.76}Y_{0.2}Zn_{0.04}O_{3-δ} (BZYZn04) powders were synthesized via a solid-state synthesis route. Stoichiometric amounts of BaCO₃, ZrO₂, ZnO, and Y₂O₃ (≥99.9% purity) were dispersed in isopropanol and ball-milled at 350 rpm for 24 h. The dried mixture was calcined at 1100 °C in air. The calcined powders were re-milled under identical conditions to ensure homogeneity. Phase-pure BZY and BZYZn were obtained after sintering at 1450 °C and 1300 °C, respectively. Electrolyte slurry was prepared by mixing 20 wt% electrolyte powder with 80 wt% organic vehicles consisting of ethyl cellulose (1 wt%), polyvinyl butyral (PVB), polyethylene glycol (PEG 200), α -terpineol, and isopropanol. The mixture was ball-milled at 350 rpm for 24 h. PrNi_{0.7}Co_{0.3}O_{3-δ} (PNC), and NiO-BaCe_{0.7-x}Zr_{0.1}Y_{0.1}Yb_{0.1}Ni_xO_{3-δ} (where x = 0, 0.05, 0.1, and 0.15) were used as air electrode, and fuel electrode materials, respectively. Electrode materials were synthesized via a sol-gel method (see Supporting Information, Section S1).

2.2 Cell fabrication

Electrolyte pellets and fuel electrode support layers were fabricated by uniaxial die pressing (12 mm die) at 200 MPa. Fuel electrodes were mixed with starch (5:1 ratio) as pore former and pre-sintered at 920 °C for 2 h. The fabrication of electrolyte layer onto pre-sintered support substrates was done by following WPS process using as prepared electrolyte slurry. Coated half-cells were pre-sintered at 920 °C for 3 h and subsequently co-sintered at 1350 °C for 10 h. Air electrodes were screen-printed onto densified half-cells in two layers. The first layer was dried at 400 °C for 2 min, followed by application of the second layer and sintering at 1050 °C for 2 h.

2.3 Structural and microstructural characterization

2.3.1 Grain Growth Kinetics

As synthesized electrolyte powders of BZY, BZYZn and BCZYYbNi from SSS process were mixed with 3% PVB solution and grinded for 1 h using mortar and pestle to obtain fine powder. Next, electrolyte pellets were fabricated using uniaxial die pressing and sintered for different times with equal interval i.e., 1 h, 5 h, and 9 h at 1350 °C respectively. Furthermore, BZYZn, and

BCZYYbNi pellets were sintered for 9 h at 1350, 1400, and 1450 °C respectively. Grain growth exponent (n) and activation energy for sintering (Q) were analyzed by using the equation (1):

$$D^n - D_0^n = Kt \quad \& \quad D^n = K_0 \exp\left(\frac{-Q}{RT}\right) t \quad (1)$$

where D_0 and D represents average grain growth at time $t = 0$ and t respectively. K , K_0 , R and T are rate constant, pre-exponential constant, Boltzmann constant, and temperature respectively. The experimentally derived grain-growth activation energies were treated as apparent kinetic parameters for the overall grain-growth process. Equation (5) was subsequently used for a parametric analytical evaluation of the relationships among defect concentration, effectively thermally activated transport, and densification rate, rather than for determination of a specific atomic diffusion coefficient or microscopic diffusion pathway. Microstructural analysis was performed using SEM (TFS Quattro S) equipped with EDS. Grain size was determined using the intercept method in ImageJ. STEM data was acquired using a Cs-corrected TFS Spectra 200 X-CFEG STEM operated at 200kV with a 24.2 mrad convergence semi-angle. STEM-EDS elemental maps were collected and processing using a TFS Super XG2 detector and Velox imaging software.

2.3.2 Pure phase analysis

The investigation of pure phase of as-synthesized electrolyte powders was done by using X-ray diffraction (XRD, Rigaku SmartLab). The 2θ value was set between 20° and 80° with the help of rotating anode source of Cu-K α with the wavelength (λ) of 1.54 Å. Bragg's law was applied for the evaluation of interplanar spacing (d) and lattice parameters (a) using the eq (2) & (3):

$$\theta = \arcsin\left(\frac{\lambda}{2d}\right) \quad \& \quad d = \frac{a}{\sqrt{N}} \quad (2)$$

$$\& \quad N = h^2 + k^2 + l^2 \quad (3)$$

The refinement of obtained XRD spectra was done by using GSAS-II software by following the process of Rietveld refinement.

2.3.3 Oxygen vacancies characterization

The presence of oxygen vacancies fingerprints of as optimized electrolyte powders i.e., BZYZn04, BZY, BCZYYb, & BCZYYbNi10 was done by following EPR and XPS characterization. For EPR, pure phase grinded electrolyte powders were filled about 2.54 cm in a thin-walled quartz EPR sample tube with 4mm diameter obtained from Thermo Fischer Scientific. The power was set to 2.0 mW, microwave attenuation to 20 dB, and 60 s as sweep time in the X-band to enhance the sensitivity for the detection and to avoid the signal saturation. The spectra were recorded at room temperature with a modulation amplitude of 4G along with a microwave frequency of 9.36 GHz. For the calculation of oxygen vacancy concentration, peak area near oxygen vacancy corresponding signal were analyzed by performing double integration intensities. Analysis of presence of oxygen vacancies fraction and Zr-O bond length were investigated by using X-ray photoelectron spectroscopy (PHI Quantera system). TGA characterization was performed by

heating the electrolyte powder from room temperature to 1100 °C in dry air atmosphere (NETZSCH STA 449F3). The heating rate was set to 2 °C min⁻¹ upto 600 °C and further increment in temperature up to 1100 °C with 3 °C min⁻¹. The flow rate of air was set to 100mL min⁻¹. The samples were put into alumina crucible and initially dried at 125 °C for half an hour and further weight change was recorded to investigate the weight loss at higher temperature. Bulk oxygen vacancies present in electrolytes were calculated using the following eq (4):

$$\delta = \frac{\Delta m \times M_s}{m_s \times M_o} \quad (4)$$

where δ is the oxygen vacancies present in the electrolyte, Δm is the change in weight recorded between 300 °C and 600 °C by TGA, M_s is the molar mass of the electrolyte, m_s is the initial weight of the electrolyte at room temperature, and M_o is the molar mass of water, respectively.

2.3.4 Dilatometry analysis

Thermal expansion and shrinkage characterization of powders were recorded by using Linseis DIL dilatometer. Samples were prepared using uniaxial hydraulic press using 10 mm die on applying the pressure of 125 MPa. Fabricated samples were loaded at the center of sample pads of alumina ensuring there was no contact between sample and bottom part of the tube. For dilatometer characterization, dry air (50 sccm) was provided with 500 mN applied force for load controller, and the temperature range was set between room temperature to 1350 °C with the ramping rate of 5 K min⁻¹. The sample was dwelled at 1350 °C for 15 minutes and Linseis software was used for recording the data. The post dwell and rapid cooling process was done with water assistance.

2.3.5 Surface topography mapping

Surface roughness was measured using atomic force microscopy (Park NX10) equipped with SmartScanTM software. The scan rate was set to 1 Hz, and the scanning was done by setting into NCM sweep mode over 20 x 20 μm^2 scan area. Gwyddion software was used for analyzing the root mean square (RMS) roughness of the obtained AFM images. Surface topography depth was measured using a KLA Tencor profilometer with AlphaStep D-500 software. Firstly, the calibration of the lateral and vertical sensors of the profilometer were done by using 900 Å test sample followed by the characterization of fabricated half-cell. For the adhesion strength characterization of air electrode screen-printed on fabricated BZYZn half-cell with increased roughness was done by following ASTM D1002-05 process. Tensile strength testing machine (Mark-10, F505) was used for analyzing the peeling force and shear stress test by applying the break threshold of 100 N at the rate of 30 mm min⁻¹. Shear stress (τ) was calculated using eq (5):

$$\tau = \frac{F_{max}}{A} \quad (5)$$

Where F_{max} is the maximum force registered before failure and A is the overlap area i.e., the area of the glued section of fabricated half-cell.

2.4 Electrochemical measurements

2.4.1 Protonic conductivity

For the protonic conductivity analysis, electrolyte pellets of BZY and BZYZn were sintered at 1350 °C for 10 h. The surface of sintered pellets was cleaned using isopropanol and current collector was applied on both sides' surface using silver mesh. Electrochemical impedance spectroscopy (EIS) and I-V measurements were performed using a Gamry potentiostat over a frequency range of 10^6 - 10^{-2} Hz. Temperature-dependent measurements were conducted between 650 °C and 450 °C in 50 °C intervals, allowing 1 h stabilization at each temperature prior to data acquisition. The heating rate during testing was 3 °C min⁻¹, while controlled ramping and cooling were performed at 1 °C min⁻¹. For symmetric-cell measurements, silver paste and mesh were applied as current collectors. Measurements were first conducted under dry Ar, followed by humidified conditions (3% H₂O) to evaluate protonic conduction. Similarly, the total conductivity of fabricated electrolyte pellets was also measured by applying 3% wet air. The conductivity and activation energy (E_a) of electrolyte pellets were analyzed by using the eq (6) & (7):

$$\sigma = \frac{l}{R.A} \quad (6)$$

$$\& \sigma(T) = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (7)$$

Where l is the thickness of sintered pellet, R is measured ohmic resistance, A is surface area of sintered pellet, σ_0 is pre-exponential factor, k is Boltzman constant and T is temperature.

2.4.2 Full-cell performance

Full cells (active air-electrode area: 0.178 cm²) were assembled using silver mesh current collectors and sealed in a custom alumina fixture using ceramic sealant. Cells were heated to 600 °C at 1 °C min⁻¹ and reduced under H₂/Ar flow (total 20 sccm). The H₂ fraction gradually increased while monitoring the open-circuit voltage (OCV) until stable values above 1.0 V were achieved using VersaSTAT software installed in Princeton Applied Research set up of four probe potentiostat. Fuel-cell mode testing was conducted under H₂ fuel and air oxidant. For electrolysis mode, O₂ was supplied to the air electrode, and steam partial pressure was increased up to 0.2 atm after stabilization of OCV. Electrochemical measurements were performed only after steady-state conditions were reached at each operating point. Faradaic efficiency (FE%) analysis was done by recording the hydrogen production rate ($\eta_{H_2,measured}$) in mol min⁻¹ before and after applying the required current density and following Faraday's law in eq (8):

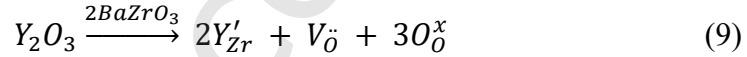
$$FE (\%) = \frac{\eta_{H_2,measured} \times (n.F)}{I} \times 100\% \quad (8)$$

where $n = 2$, Faradaic constant (F) = 96485 C mol⁻¹ and I is the applied current density (A cm⁻²).

3. Results and Discussion

3.1 Defect-chemistry and sintering kinetics

The enhanced sintering activity observed in this work is accompanied by systematic modification of the defect chemistry through aliovalent incorporation, particularly changes in oxygen-vacancy concentration and the local metal-oxygen bond characteristics. In crystalline ceramics, densification during solid-state sintering (SSS) is governed by mass transport of atoms, ions, and charged point defects along specific diffusion pathways.[29] The thermodynamically driving force for sintering originates from the reduction in surface and interfacial free energy, whereas the resulting microstructural evolution depends on the kinetics of the available mass-transport processes. Conventionally, six major transport pathways are considered in solid-state sintering, among which lattice and grain-boundary diffusion can contribute to densification through pore elimination, whereas surface diffusion and vapor transport primarily promote microstructural evolution without directly producing densification (Figure S1). [30, 31] In refractory perovskite oxides, lattice and grain-boundary transport may play important roles in the densification process, while the concentrations and distributions of point defects, including oxygen vacancies, can influence the defect chemistry and transport characteristics of the material. Thus, these established sintering concepts are used as a theoretical framework for interpreting the experimentally observed densification behavior. For the BZY-based system, acceptor doping with Y^{3+} on Zr^{4+} sites generate oxygen vacancies according to Kröger-Vink notation, eq (9):



This reaction indicates that acceptor substitution produces oxygen vacancies for charge compensation, which are well known to enhance proton incorporation under humid conditions. To

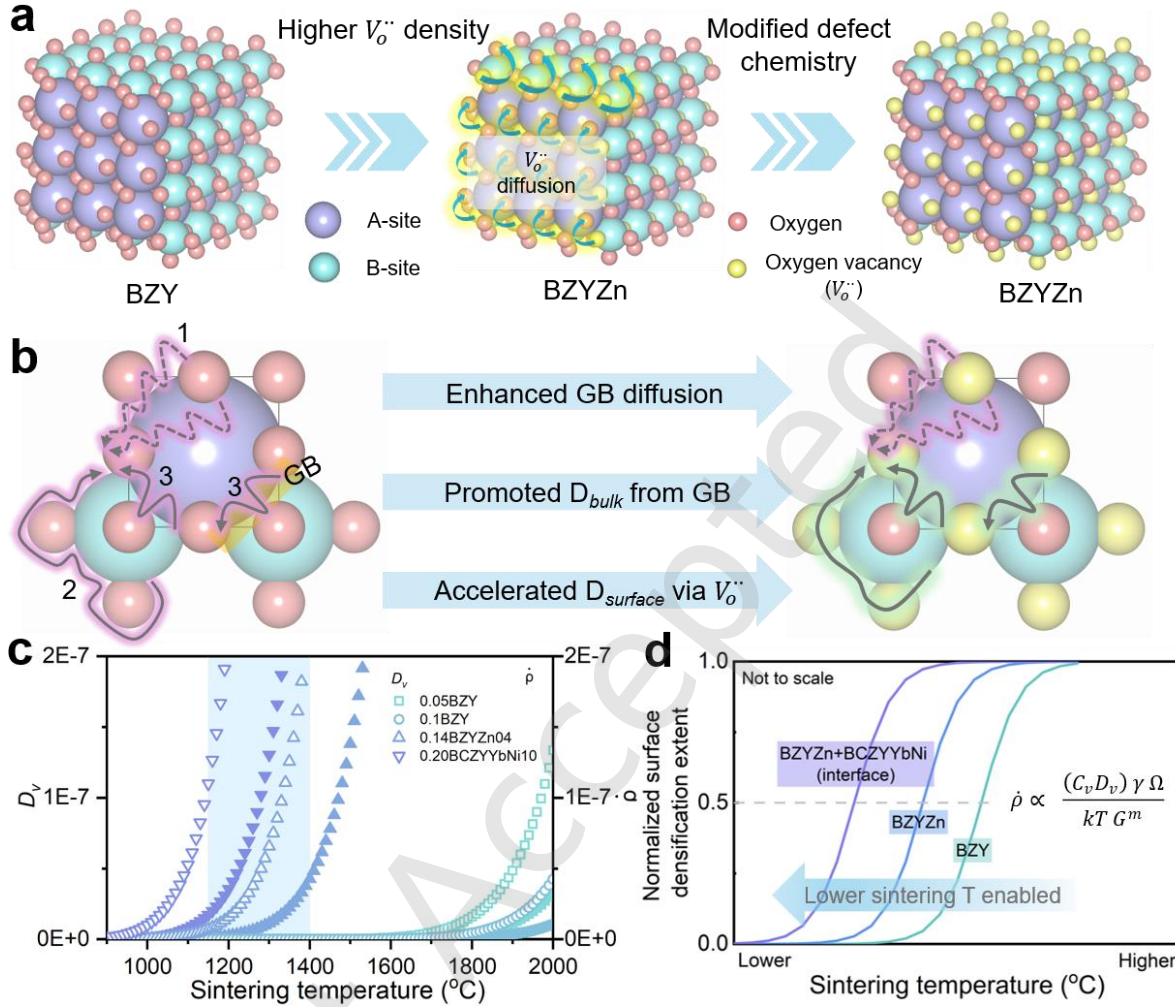
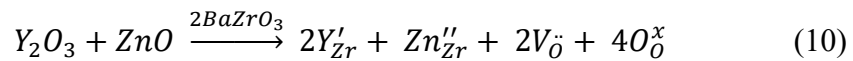


Figure 1. (a) Atomistic schematic comparing pristine BZY and Zn-modified BZY (BZYZn). Zn incorporation increases the oxygen vacancies ($V_o^{\bullet\bullet}$) concentration and may influence vacancy-mediated transport. (b) Proposed possible solid-state mass-transport pathways in BZYZn. Step 1 represents surface diffusion; Step 2 represents bulk diffusion originating from surface; and Step 3 represents grain-boundary diffusion together with bulk diffusion originating from the grain boundary (GB). The illustrated pathways represent possible solid-state mass transport processes and are not intended to identify the dominant microscopic diffusion pathway. (c) Analytical evaluation of the temperature-dependent vacancy diffusivity (D_v) and densification rate ($\dot{\rho}$) within the proposed sintering framework, highlighting the earlier onset of densification and accelerated sintering enabled by Zn doping. (d) Conceptual densification curves showing that vacancy-enabled transport shifts densification to lower temperature in Zn-modified BZY systems.

further increase the extrinsic vacancy fraction, a +2-valence dopant (Zn^{2+}) was introduced into the B-site of the perovskite lattice. The corresponding defect reaction can be expressed as eq (10):



Compared to conventional BZY, Zn incorporation increases the oxygen-vacancy density and modifies local bonding environments, that might contribute to the enhancement of defects-

mediated transport (Figure 1a). Oxygen vacancies are thermodynamically favored at grain boundaries due to lower formation energies, resulting in vacancy accumulation at these interfaces. According to vacancy-mediated diffusion theory, atomic flux proceeds in the opposite direction of vacancy flux; thus, within a vacancy-mediated diffusion framework, vacancy redistribution may facilitate atomic mass transport during sintering, which contributes directly to neck growth and pore elimination during sintering (Figure 1b). The densification kinetics can be quantitatively described using Coble's model for diffusion-controlled sintering, eq (11):

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{H_1 D \Omega \phi^{(m-1)/2}}{G^m k T} \left(\frac{\alpha \gamma_{sv}}{r} \right) \quad (11)$$

where D represents the effective diffusion coefficient (lattice or grain-boundary), r is particle or grain size, T is absolute temperature, and the remaining parameters account for geometry and stage of sintering.[30] Since diffusion in crystalline oxides is vacancy mediated, the atomic diffusion coefficient (D_a) can be expressed as eq (12):

$$D_a = C_v D_v \quad (12)$$

where C_v is the fraction of vacancy sites and D_v is the vacancy diffusion coefficient. Combining this relation with Coble's expression yields eq (13):

$$\dot{\rho} \propto \frac{C_v D_v \gamma \Omega}{k T G^m} \quad (13)$$

where $\dot{\rho}$ is the densification rate. Within this analytical framework, an increase in the concentration of mobile defects can increase the effective diffusion coefficient and consequently influence the calculated densification rate. [31,32] This relationship is used here as a theoretical framework and does not establish experimentally that oxygen-vacancy mobility increases upon Zn incorporation. In BZY, the activation energy for lattice diffusion is exceptionally high (~3.7-4.5 eV), which explains the refractory nature of BZY and the requirement for temperatures above 1500 °C for full densification (Figure S2). Simply increasing Y content modestly increases vacancy concentration but may also elevate activation energy due to defect association and lattice distortion. In contrast, aliovalent incorporation of Zn in BZY and Ni in the BCZYYb is associated with a lower apparent activation energy for the overall grain-growth process. The evaluation of apparent activation energy required for sintering (Q) in the case of newly developed electrolytes were done by applying grain growth kinetics equations.[33,34] Electrolyte pellets were sintered by varying the time as well as sintering temperature (Figure S3a & S3b). Both BZYZn04 and BCZYYbNi10 exhibited the enhanced grain-growth kinetics at 1350 °C, as the obtained slope from $\ln(D)$ versus $\ln(t)$ plot provided the exponent (n) of value approx. to 2 (Figure S3c).[35,36] The value is reported here as a kinetic descriptor of the observed grain-growth behavior and is not used to assign a specific atomic diffusion pathway. The apparent activation energy derived from grain-growth kinetics for BZYZn04 was ~3.1 eV while BCZYYbNi10 showed a further reduction which was ~2.5 eV (Figure S3d). These values are regarded as effective kinetic parameters describing the overall thermally activated grain-growth behavior under the investigated conditions and are not

assigned to a specific oxygen-vacancy migration, lattice-diffusion, or grain-boundary diffusion process.[37] Together with the enhanced grain growth, these results demonstrate modification of the overall sintering kinetics in the aliovalently modified compositions.

Analytical evaluation using eq. (13) (Figure 1c) was performed to illustrate the underlying relationships among vacancy concentration, thermally activated mass transport, and densification within the proposed solid-state sintering framework. Within the model, increasing the vacancy fraction from ~ 0.05 to ≥ 0.2 and together with variation in the effective activation-energy parameter over the investigated range, results in an increase in the calculated effective transport coefficient and densification rate, particularly at elevated temperatures. The analysis therefore illustrates the coupling between defect concentration and thermally activated transport and provides an analytical basis for understanding their combined influence on densification at reduced temperatures, without assigning the observed sintering behavior to a specific microscopic diffusion pathways. Importantly, in practical PCEC architectures the electrolyte is fabricated as a thin membrane on a porous support. Achieving dense half-cells at reduced temperature therefore requires synchronized sintering behavior between electrolyte and electrode. By introducing aliovalent Ni dopants into the BCZYYb support, the sintering activity of the porous layer is also enhanced, minimizing differential shrinkage and promoting interfacial compatibility. This cooperative defect engineering in both layers establishes a synergistic BZYZn/ BCZYYbNi co-sintering mechanism (Figure 1d), further lowering the effective densification temperature while preserving structural integrity.

3.2 Enhanced oxygen vacancy concentration with sintering activity

To investigate defect-chemistry assisted sintering enhancement while preserving protonic transport, 4% ZnO was incorporated into BZY (BZYZn04) and 10% NiO was intrinsically doped into BCZYYb (BCZYYbNi10). The dopant concentrations were selected within the reported aliovalent solubility limits and as optimized in this work to maintain phase stability, proton conductivity, and chemical robustness under harsh operating conditions as provided in (Table S1).[38–40] X-ray diffraction analysis confirmed the formation of single-phase perovskite structures after synthesis (Figure 2a).[41–43] Compared with BCZYYb, BCZYYbNi10 exhibited a systematic peak shift in diffraction patterns, indicating lattice expansion (Figure S4).[44,45] Further, Rietveld refinement for each electrolyte was performed to identify the phase formation (Figure 2b & S4). The weak secondary reflections were assigned to trace BaCO_3 , a common secondary phase in Ba-containing proton-conducting perovskites. Residual BaCO_3 may originate from incomplete solid-state reaction of the Ba precursor or from recarbonation of Ba-rich surface species during cooling and exposure to atmospheric CO_2 . Because similar reflections were observed in both undoped and doped samples, their formation cannot be specifically attributed to dopant incorporation. The trace-phase contents obtained from Rietveld refinement are considered semiquantitative because of the weak diffraction intensities and relatively high phase-specific Bragg residuals. Therefore, the predominantly single-phase perovskite compositions, containing only minor or trace BaCO_3 , were considered sufficiently phase-pure for the subsequent physicochemical and electrochemical measurements (Table S2). The presence and evolution of

oxygen vacancies were investigated using electron paramagnetic resonance (EPR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Comparison of EPR analysis was done for pure

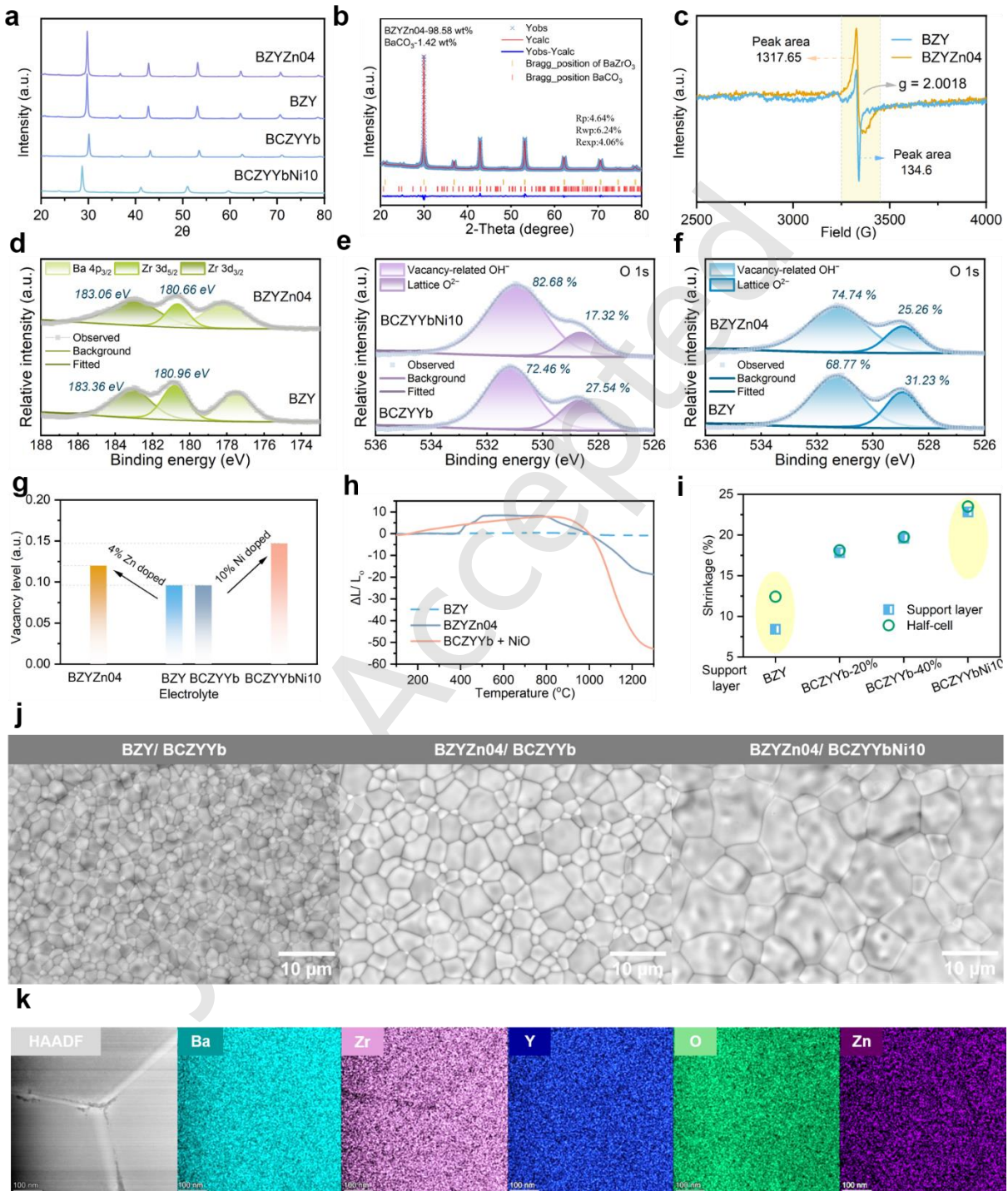


Figure 2. (a) X-ray diffraction patterns of BCZYbNi10, BCZYb, BZY and BZYZn04, confirming preservation of the single-phase perovskite structure after dopant incorporation. (b) Rietveld refinement of BZYZn04 (c) Electron paramagnetic resonance (EPR) spectra comparing BZY and BZYZn04, revealing enhanced defect-related signals

consistent with increased oxygen-vacancy concentration. (d) X-ray photoelectron spectroscopy (XPS) core-level spectra in the Zr 3d/Ba 4p region for BZY and BZYZn, showing a binding-energy shift associated with modified local bonding environment upon Zn doping. (e,f) Deconvoluted O 1s XPS spectra for (e) BZY versus BZYZn and (f) BCZYYb versus BCZYYbNi, indicating increased contributions from vacancy-related oxygen species in doped compositions. (g) Quantitative comparison of relative oxygen-vacancy concentration for all compositions, highlighting defect enrichment in Zn- and Ni-modified systems. (h) Dilatometry curves of electrolyte powders and NiO, demonstrating earlier onset and enhanced shrinkage for defect-engineered materials. (i) Comparison of shrinkage behavior in support layers and corresponding half-cells, showing significantly enhanced densification, with the largest shrinkage observed for BCZYYbNi-based systems. (j) Surface microstructures of half-cells sintered at 1450 °C, illustrating grain growth enhancement when transitioning from BZY to BZYZn04 electrolytes and from BCZYYb to BCZYYbNi10-based support layers. (k) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of BZYZn, along with corresponding STEM elemental dispersive X-ray spectroscopy (STEM-EDS) elemental maps (Ba, Zr, Y, O, and Zn), showing homogeneous elemental distribution near grain-boundaries (inset 100nm).

phase obtained BZYZn04 and BZY (Figure 2c) as well as BCZYYb and BCZYYbNi10 (Figure S5). In the case of BCZYYbNi10 high peak intensity was observed due to Ni incorporation. However, BZY and BZYZn04, both electrolytes exhibited higher peak around $g = 2.002$ that corresponds to oxygen vacancies signals (Figure 2c). BZYZn04 in pure phase indicated higher peak area of 1317.65 compared to BZY with 134.6 (Figure S6). XPS analysis revealed an approximately 0.3 eV shift toward lower binding energy for the Zr - O-related signal in Zn-doped BZY compared with undoped BZY, indicating a modification of the local chemical and electronic environment surrounding Zr upon Zn incorporation (Figure 2d). This shift may be associated with changes in local charge distribution, coordination, and/or defect-related chemical environments within the BZY lattice.[46] Zinc incorporation increases oxygen-vacancy concentration and is associated with enhanced sintering behavior within the BZY electrolyte, while a Ni-modified BCZYYb support provides shrinkage-matched sintering kinetics that cooperatively promote membrane densification. Quantitative spectral analysis indicated that oxygen-vacancy concentration increased by approximately 10% in BZYZn and 14% in BCZYYbNi10 relative to their undoped counterparts (Figure 2e & 2f). Next, the purity of crystal and sensitivity toward EPR signals due to high temperature sintering was investigated in the case of BZYZn04 by varying the temperature from 1300 °C to 1450 °C with an equal interval. XRD characterization of obtained pellets showed the presence of impurities at increased temperature above 1400 °C (Figure S7a) as reported in literature. Bragg's law equation is useful in analyzing the lattice parameters.[47] The parameters calculated for obtained XRD spectra exhibited a decreasing trend in lattice parameters on increasing the pellets sintering temperature (Figure S7b). EPR characterization of sintered pellets at different temperatures showed the subtraction of multiple peaks near the main region in the case of BZY (Figure S8a). On increasing the temperature from 1300 to 1450 °C while BZYZn04 demonstrated faint responses aligning with XRD results due to the formation of Y_2O_3 (Figure S8b). This suggested that there might be contraction in the lattice as Y_2O_3 was found at higher temperatures due to evaporation of Ba. These results suggest that lowering the sintering temperature is also required to preserve the purity and electrochemical performance of the electrolyte. According to Kröger-Vink notation, aliovalent doping should enhance oxygen non-

stoichiometry parameter under idealized charge-compensation conditions (Supplementary S1b). Thus, further bulk oxygen vacancy characterization was performed using thermogravimetric analysis (TGA) and recorded the weight change between room temperature to 1100 °C (Figure S9a). The weight loss analysis between 300 °C to 600 °C revealed that BZY and BCZYYb have same concentration as 0.096 while BZYZn04 and BCZYYbNi10 exhibited increased concentration of about 0.12 and 0.14 respectively (Figure 2g). These results confirm that aliovalent doping effectively enhances extrinsic vacancy concentration while maintaining phase integrity.[44] Sintering behavior was evaluated using dilatometry measurements. The increased vacancy concentration may contribute to enhanced mass transport during solid-state sintering. Both BZYZn04 and BCZYYbNi10 exhibited significantly higher shrinkage compared with undoped BZY, with accelerated densification initiating near 1000 °C (Figure 2h). In contrast, negligible shrinkage was observed for BZY within this temperature regime. The fuel electrodes were also compared based on their dilatometry characterization, NiO-BCZYYbNi10 exhibited improved sinterability compared to NiO-BZY and NiO-BCZYYb (Figure S9b). Furthermore, noticeable expansion in the modified BZY compositions and the synthesized fuel electrodes, including the BZY-based fuel electrode containing 60% NiO, over the temperature range of 200 to 800 °C was observed. This behavior can be explained as the presence of transition metal species and Ce-containing components which can influence the thermal and chemical expansion of the materials.[48,49] Furthermore, under oxidizing conditions, the electrolyte compositions exhibited measurable weight loss, as confirmed by TGA analysis. The shrinkage evolution is consistent with the analytical relationship between vacancy concentration, diffusion coefficient, and densification rate described previously. Half-cell architectures were fabricated using the wet powder spraying (WPS) process to evaluate substrate-electrolyte co-sintering behavior.[50] Shrinkage measurements at 1450 °C revealed that modifying the fuel electrode composition significantly influenced densification kinetics. Relative to BZY-based electrodes, BCZYYb-based supports increased shrinkage by approximately 89.4%, on intrinsic Ni doping (Figure 2i). Notably, externally increasing NiO content upto 80% in BCZYYb-20% alone produced only moderate sintering enhancement, indicating that intrinsic lattice doping plays a more dominant role than extrinsic additive loading. This behavior may be associated with changes in defect chemistry and the resulting sintering kinetics.

Scanning electron microscopy characterization confirmed that Zn-doped electrolytes produced larger grain sizes compared with undoped BZY. When combined with Ni-doped BCZYYb supports, pronounced grain growth was observed at the electrolyte surface, supporting the existence of cooperative densification across the BZYZn04/BCZYYbNi10 interface (Figure 2j). The observed Zr-O bond binding energy shift indicates modification of the local chemical environment upon Zn incorporation, which may influence defect interactions. Scanning transmission electron microscopy energy dispersive X-ray spectroscopy (STEM-EDS) mapping of BZYZn04 revealed a uniform distribution of elements at grain boundaries, without detectable intergranular secondary phase formation, supporting that half-cell densification followed a solid-state sintering mechanism (Figure 2k).

3.3 Dense Zn-modified BZY microstructure for high proton conductivity at 1350 °C

The influence of composition and temperature on microstructural evolution was systematically investigated by varying defect concentrations in both electrolyte and substrate layer on using Zn as 2% (BZYZn02) and 4% (BZYZn04) and Ni as 0% (BCZYYb), 5% (BCZYYbNi05), 10% (BCZYYbNi10) and 15% (BCZYYbNi15) respectively. The densification of the electrolyte layer was found to depend strongly on the shrinkage behavior of the porous support (Figure 3a). Introducing Zn content promoted grain growth within the electrolyte while increasing Ni content into the BCZYYb substrate successfully eliminated residual electrolyte porosity and enabled thin dense membrane formation of 15 μm at 1350 °C (Figure 3b). The undesirable nickel coarsening in the support layer was observed on excessive use of Ni; thus 10% Ni doping was identified as the optimal composition (Figure S10a). Lower sintering temperatures also reduced warping and nickel particle growth and minimal elemental segregation, improving overall structural quality (Figure S10b & S10c). SEM analysis revealed that the matched shrinkage kinetics between electrolyte and substrate minimizes differential densification stress, suppresses microcrack formation and enables uniform grain growth across the fabricated electrolyte layer using WPS process (Figure 3c). This behavior was further confirmed by analyzing the shrinkage behavior of sintered supports layers and half cells demonstrating the increase in the defect concentrations was accompanied by enhanced densification (Figure 3d). The resulting electrolyte microstructure exhibited an average grain size of approximately 4 μm , comparable to values typically achieved only at substantially higher sintering temperatures (Figure 3e).[8,51–53] High-resolution SEM combined with EDS mapping further confirmed the absence of significant detectable elemental segregation at grain boundaries for optimized half cell structure (Figure S11). The formation of dense microstructures at reduced temperatures is consistent with enhanced overall mass-transport and sintering kinetics associated with Zn modification. During sintering, vacancy flux is driven from regions of high chemical potential (convex surfaces) toward regions of lower potential near pore surfaces, while atomic species diffuse in the opposite direction, promoting pore annihilation and grain coalescence (Figure 3f). The modified Zr-O bonding environment induced by Zn incorporation may influence the kinetic barriers associated with mass transport during sintering, that might facilitate atomic migration at lower thermal budgets. In addition, the presence of Zn may contribute to transient interfacial diffusion behavior during the intermediate sintering stage.[54] Although no stable secondary liquid phase was detected, local compositional perturbations associated with Zn substitution may promote short-range mass transport, assisting densification without forming persistent grain-boundary blocking phases. As sintering progress through the intermediate and final stages, multiple solid-state mass-transport pathways, including lattice and grain-boundary transport, may contribute to pore elimination and microstructural evolution. The present measurements, however, do not independently determine their relative contributions. Thus, enhanced densification is interpreted as being associated with modified defect chemistry and overall mass-transport kinetics of dense protonic ceramic membranes at 1350 °C while maintaining structural uniformity.

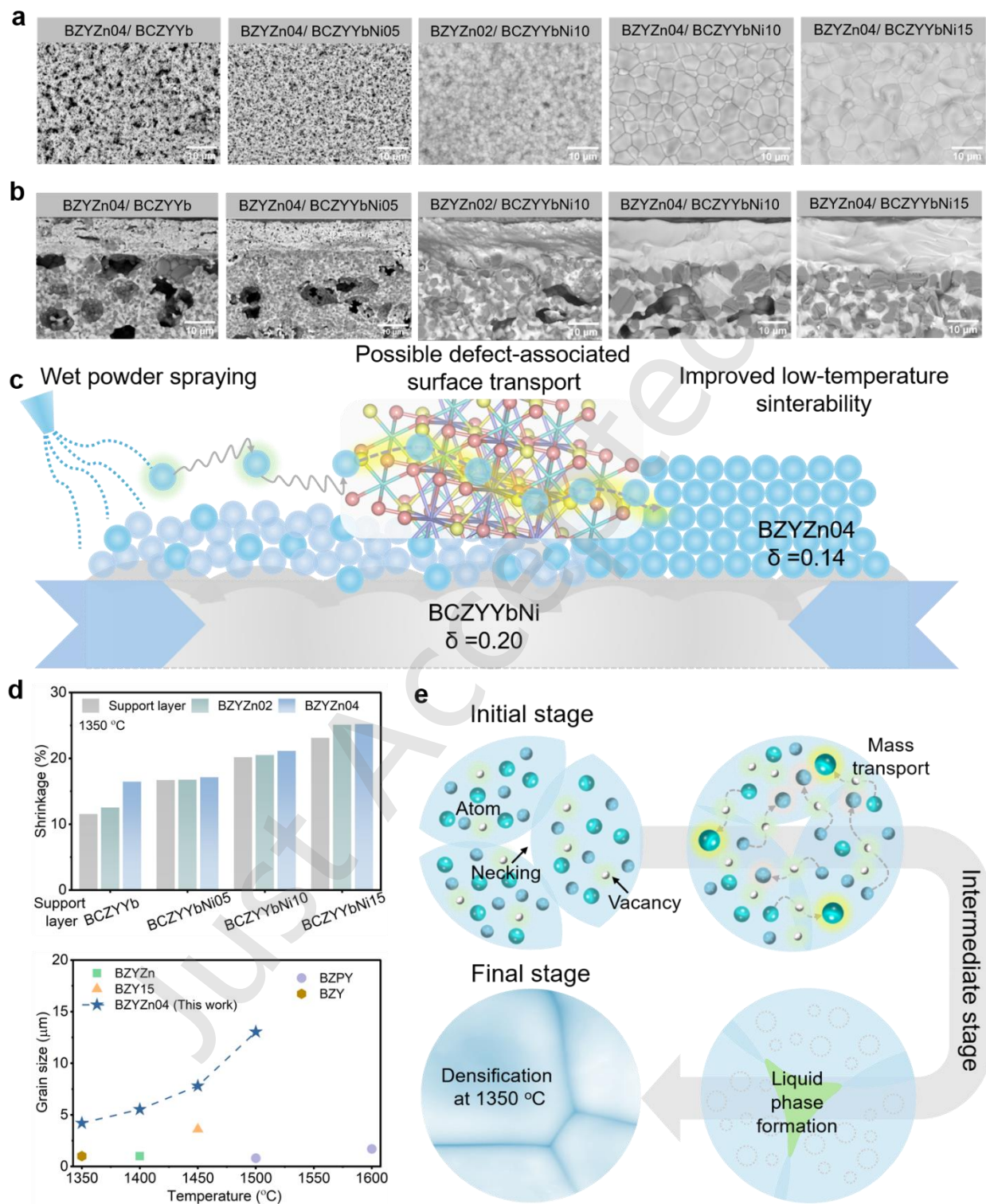


Figure 3. (a) Surface SEM micrographs of BZYZn/BCZYYbNi half-cells sintered at 1350 °C (left to right) on increasing dopant concentrations, showing progressive densification at reduced temperatures. Scale bars, 10 μm. (b) cross-section images to the relative of (a). (c) Schematic illustration of the BZYZn/BCZYYbNi heterointerface, highlighting the oxygen-vacancy-rich BCZYYbNi10 support ($\delta \approx 0.14$) and BZYZn electrolyte layer ($\delta \approx 0.12$),

which together promote interfacial mass transport and cooperative densification. (d) Linear shrinkage of the BZYZn-BCZYYbNi structure on increasing Zn as well as Ni content in electrolyte and support layer respectively. (e) Grain size as a function of sintering temperature, benchmarking BZYZn against representative BZY-based electrolytes reported in the literature. [8,51,55–57] (f) Schematic of the intermediate-stage sintering mechanism, conceptual representation of defect-associated neck formation, subsequent mass transport, and possible transient liquid-phase contribution, leading to dense microstructures at reduced temperature.

3.4 Boosted protonic conductivity by BZY structure

After confirming that BZYZn04 yields dense half-cells at 1350 °C, we evaluated electrochemical properties by fabricating electrolyte pellets. Firstly, EIS characterization was done from 650 °C to 450 °C in wet atmosphere using the fabricated pellets of BZY at different sintering temperature to investigate the effect of variance in temperature on protonic conductivity. The results showed that BZY conductivity plummeted on decreasing the sintering temperature (Figure 4a). In contrast, Zn modified BZY pellets exhibited higher ionic conductivity than pristine BZY sintered at 1350 °C and analyzed under identical conditions. Further, the activation energy (E_a) analysis for proton conduction were evaluated as 0.633 eV and 0.520 eV for BZY and BZYZn04, respectively, which shows the decrement in E_a for BZYZn04 compared to BZY. The process was investigated in detail by performing DRT analysis using DRTtools. On the logarithmic frequency axis, peak area reflects resistance contribution, and peak position reflects time constants.[58,59] Using EIS recorded at 600 °C for BZY and BZYZn04 (Figure 4b) with circuit fitting, analysis was performed over 10MHz to 1mHz. The obtained result demonstrated that BZYZn04 has reduced high-frequency peaks versus BZY, indicating lower intrinsic protonic resistivity (Figure 4c). Similar phenomenon was observed in BZY depicted that the decrease in protonic conductivity of pellets sintered at 1350 °C was due to increase in internal resistance (Figure S11a). At lower frequencies, BZYZn04 showed several peaks and increased peak height, while BZY exhibited broad without peak height separation with related frequencies showed the sluggish kinetics near grain boundaries. Nevertheless, the higher total protonic conductivity of BZYZn04 is consistent with contributions from both modified bulk transport characteristics and the optimized microstructure. However, the present measurements do not quantitatively separate the respective contributions of defect chemistry and microstructural/ grain boundary effects. Furthermore, the primary charge carrier for conductivity was examined thoroughly by collecting EIS spectrum in dry Ar atmosphere and 3% wet Ar atmosphere. The Arrhenius plot for protonic conductivity showed a significant increase in wet Ar atmosphere (Figure S11b).

We also compared our achieved proton conductivity with literature reports for BZY-based electrolytes (Table S2) at 600 °C (Figure 4d). Many studies have shown sintering of BZY also decreases conductivity strongly with reduced sintering temperature, which was also confirmed in our study. In contrast, the newly synthesized BZYZn04 electrolyte achieved $\sim 0.013 \text{ S cm}^{-1}$ at 600 °C, despite sintering at 1350 °C.[10,22,26,60–72] Thus, the increased oxygen-vacancy related signals and modified Zr-O chemical environment observed by EPR and XPS demonstrate changes in defect chemistry upon Zn incorporation. These changes occur concurrently with enhanced grain growth and higher protonic conductivity in BZYZn04. These observations suggest that defect-

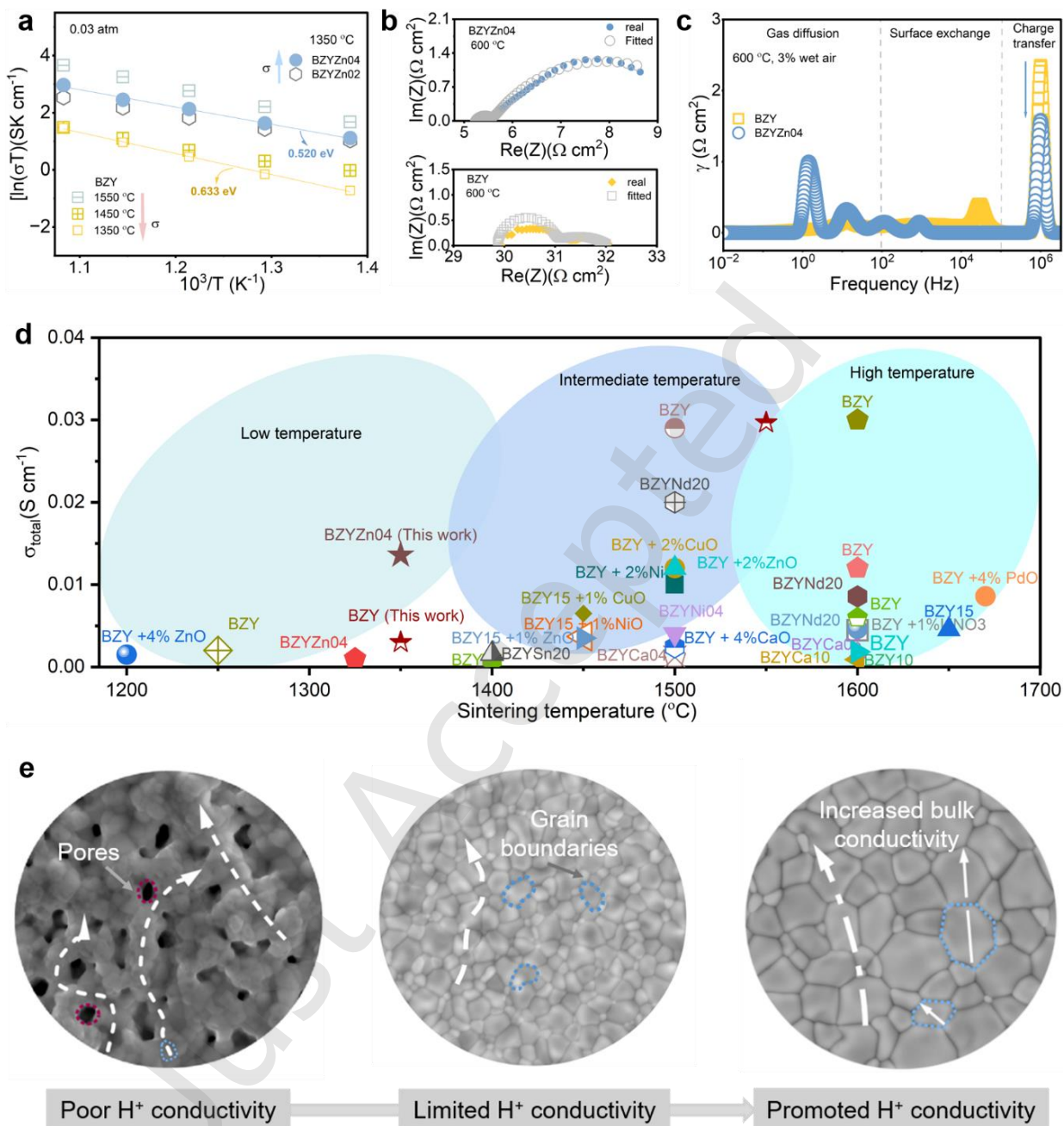


Figure 4. Low-temperature sintering enabled by Zn modification preserves high proton conductivity by reducing transport barriers in BZY electrolytes. (a) Arrhenius plots of total conductivity for comparison of BZY and BZYZn measured under 0.03 atm humidified atmosphere. (b) Distribution of relaxation times (DRT) analysis resolving key resistive contributions, including gas diffusion, surface exchange, and charge-transfer processes, with BZYZn exhibiting reduced polarization intensity relative to BZY. (c) Benchmark of total conductivity at 600 °C versus sintering temperature for reported BZY-based electrolytes, showing that this work achieves competitive conductivity at substantially lower sintering temperatures.[10,20,22,26,60–72] (d) Schematic illustration of microstructure-transport relationships, showing that reduced porosity, improved grain-boundary connectivity, and enhanced bulk pathways in the dense electrolyte collectively facilitate proton transport.

chemical modification may contribute to the ionic transport behavior, while the accompanying microstructural evolution and reduced grain-boundary resistance may also contribute to the enhanced overall conductivity. Therefore, the conductivity behavior is interpreted in terms of the combined influence of defect-chemical and microstructural changes. Dense microstructure and controlled grain growth are electrolytes near the 1600 °C range to reach a protonic conductivity of 0.01 S cm^{-1} . The decrease in total ionic conductivity at lower sintering temperature is crucial as residual porosity causes very poor proton conduction, which is a major scalability barrier for PCECs (Figure 4d) even when electrolyte has higher hydration kinetics.[43] Further, small grains ($\sim 1 \text{ }\mu\text{m}$) increase grain boundary resistivity due to the presence of large number of grain boundaries that limits the protonic conductivity of electrolyte. The increased grain growth reduces the number of grain boundaries and consequently decreases the contribution of grain-boundary resistance to the total ionic conductivity. Thus grain-growth is beneficial for effective proton transport and may contribute to the higher ionic conductivity observed for BZYZn04 and BZY system sintered at 1350 °C. Concurrently, aliovalent doping at the B-site modifies the defect chemistry, which may also influence proton incorporation and transport. Therefore, the enhanced protonic conductivity of BZYZn04 is interpreted as reflecting the combined influence of defect-chemical modification and microstructural evolution, demonstrating a favorable balance between enhanced densification kinetics and ionic conduction. Our study also stands out in terms of increase in protonic conductivity despite doping while literature has reported that the sintering was enhanced whereas protonic conductivity decreased upon aliovalent doping in the BZY system. To our knowledge, even with sintering aids, Ce-free BZY systems have rarely achieved such high protonic conductivity at 1350 °C. This work therefore suggests that strategic defect chemistry engineering combined with SSS, while avoiding secondary phases can enable both scalable fabrication and high ionic conductivity.

3.5 Full-cell electrochemical performance

The electrochemical functionality of the dense Zn-modified BZY electrolyte was further evaluated through full-cell testing in both fuel-cell (FC) and electrolysis-cell (EC) operating modes using a screen-printed $\text{PrNi}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ (PNC) cathode, which was previously demonstrated as an effective mixed ionic-electronic conductor.[73] After reduction at 600 °C, the cell exhibited an open-circuit voltage of approximately 1.0 V, confirming gas-tight electrolyte integrity and indicating that Zn incorporation did not compromise membrane selectivity. Full-cell polarization characteristics were measured across the intermediate temperature range of 450-600 °C. In FC mode, the cell delivered peak power densities of approximately 0.77, 0.52, 0.32, and 0.19 W cm^{-2} at 600, 550, 500, and 450°C, respectively (Figure 5a), accompanied by corresponding area-specific ohmic resistances of 0.12, 0.21, 0.33, and $0.48 \text{ }\Omega \text{ cm}^2$ (Figure S12a). The relatively low ohmic resistance values reflect the combined effects of high proton conductivity and dense microstructural formation. In EC operation, the cell demonstrated efficient hydrogen evolution behavior under 20% steam humidity with an oxygen flow rate of 30 sccm at the air electrode. At an applied voltage of 1.5 V, current densities reached approximately -4 A cm^{-2} at 600 °C (Figure 5b). Stepwise voltage polarization

tests further revealed stable electrochemical conversion behavior, with current densities of -1.70, -1.07, -0.59, and -0.16 A cm⁻² at 1.3 V under decreasing temperature conditions and the EIS spectrum was also recorded and fitted using equivalent circuit model (Figure S12b). The performance level at 1.2 V (approximately -1.0 A cm⁻² under 0.2 atm steam pressure) satisfies preliminary benchmarks for next-generation protonic ceramic electrochemical systems.[74] Further, BZY based full cells were also fabricated at 1450 °C, and electrochemical performance in FC mode were performed between 600 °C and 450 °C (Figure S13a). BZY-based cell delivered ~0.5 W cm⁻² at 600 °C, ~40% lower value than BZYZnO4. The decrease in BZY performance was observed due to higher ohmic resistance as compared to BZYZnO4 (Figure S13b). This explains that BZYZnO4 exhibits higher ionic conductivity as compared to BZY as observed in Figure 4a. The ohmic resistance obtained for BZY full cells are 0.24, 0.32, 0.42, and 0.58 at 600, 550, 500, and 450 °C, respectively (Figure S13c).

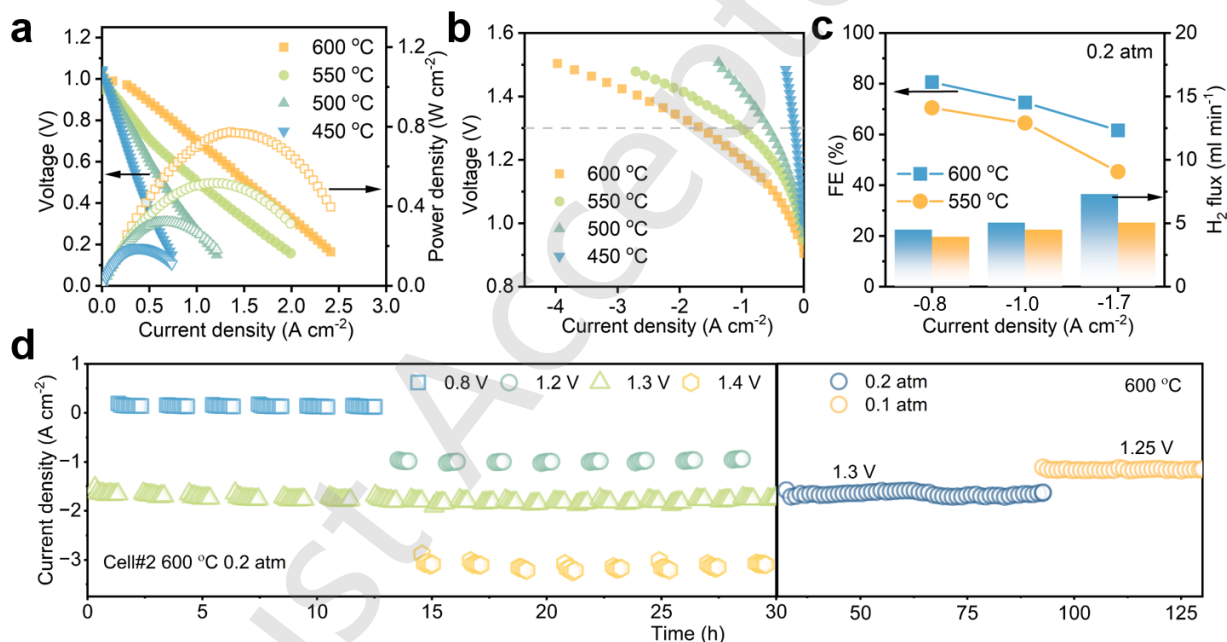


Figure 5. The BZYZnO4-based cell delivers strong reversible performance and stable operation at intermediate temperatures. (a) I-V-P curve measured in fuel-cell mode from 450 to 600 °C, showing improved output at higher temperature. (b) Polarization characteristics in electrolysis mode over the same temperature range. (c) Faradaic efficiency and H₂ flux as a function of current density at 550 and 600 °C under 0.2 atm. (d) Stability at 600 °C. Left, current-density response during stepped-voltage operation (0.8, 1.2, 1.3 and 1.4 V) under 0.2 atm. Right, extended operation at fixed bias under 0.2 and 0.1 atm, showing stable current output over prolonged testing.

Electrochemical conversion of BZYZnO4 cell in EC mode was further analyzed by applying the current densities of -0.8, -1.0, and -1.7 A cm⁻², at both 600 °C (Figure S14a) and 550 °C. Faradaic efficiency measurements yielded electrochemical conversion efficiencies of 80.67%, 72.59%, and 61.6% at 600 °C and 70.5%, 64.5%, and 45.3% at 550 °C for -0.8, -1.0, and -1.7 A cm⁻², respectively (Figure 5c). The gradual decrease in Faradaic efficiency at higher current density is attributed to increased polarization losses and non-ideal electrochemical pathways under high current loading.[75]. Reversible operation was evaluated by alternating the cell voltage between

FC and EC operating regimes with the steam pressure of 0.2 atm on air electrode side. The device responded rapidly to operating mode switching while maintaining a current density of approximately -1.7 A cm^{-2} at 1.3 V, demonstrating good electrochemical stability. Long-term durability testing under cycling polarization conditions further confirmed operational robustness.

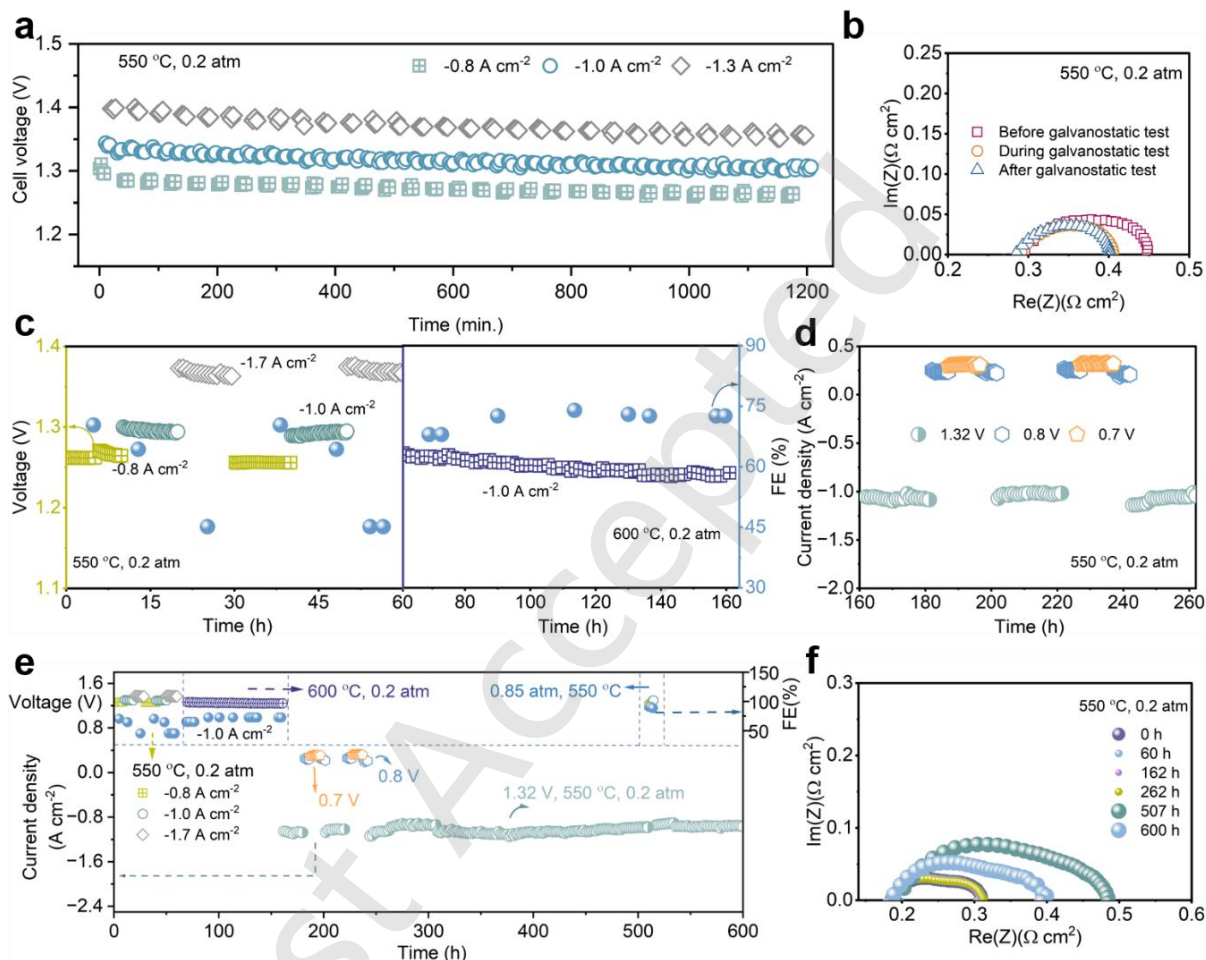


Figure 6. The BZYZn-based cells exhibit stable reversible operation and robust electrolysis durability at 550°C . (a) Cell voltage response during repeated current-density switching between -0.8 , -1.0 and -1.3 A cm^{-2} at 550°C under 0.2 atm steam, demonstrating stable electrochemical operation. (b) Nyquist plots collected before, during and after the galvanostatic test, showing minimal change in impedance. (c), (d) Initial 260 h stability corresponding to (e) Long-term galvanostatic cycling between 550°C and 600°C under 0.2 atm steam on applying the current density of -0.8 , -1.0 and -1.7 A cm^{-2} respectively, followed by potentiostatic stability between 1.32, 0.8 and 0.7 V at 550°C , showing only minimal current decay over extended operation, with a degradation rate of $0.012\% \text{ h}^{-1}$. (f) EIS spectrum collected during corresponding to (c).

The cell maintained a current density near -1.7 A cm^{-2} during 100 h of testing with negligible performance decay (Figure 5d). The collected EIS spectrum during extended stability testing revealed an increase in ohmic resistance on decreasing the steam pressure from 0.2 atm to 0.1 atm (Figure S14b). Extended stability evaluation at 550°C showed similarly stable behavior. Under dynamic galvanostatic operation, the cell maintained consistent voltage response under applied current densities between -0.8 , -1.0 and -1.3 A cm^{-2} (Figure 6a). It was observed that the collected

voltage responses decreased slightly at higher current densities, while it remained relatively stable at lower current densities values which also suggests that the cell's performance should be higher at thermoneutral voltages and current densities. EIS characterization during galvanostatic operation showed that ohmic resistance of the cell remained relatively stable, suggesting the gas tightness and robustness of the fabricated electrolyte layer (Figure 6b). The cell underwent thermal cycling between 550 and 600 °C during galvanostatic stability and reserving the performance up to 100 h as first 60 h were performed at 550 °C and later increased to 600 °C (Figure 6c). At 600 °C, EIS spectra were recorded and showed minimal increment in polarization resistance that could be attributed to the decrement of cell voltage on applying fixed current density of -1.0 A cm^{-2} . Extended reversible operation stability of the cell was further performed on decreasing the temperature to 550 °C by alternating the applied voltage between 1.32, 0.8 and 0.7 V for 100 h (Figure 6d). The cell responded accordingly to applied voltage. Further the cell showed relatively stable performance under potentiostatic operation achieving same performance as galvanostatic condition for over 400 h corresponding to a degradation rate of approximately $0.012\% \text{ h}^{-1}$ (Figure 6e). During the long-term stability test, short-term galvanostatic performance was further analyzed on increasing the steam concentration from 0.2 atm to 0.85 atm for 9 h. The obtained FE% during galvanostatic results revealed that the cell achieved from 65% to 88% on increasing the steam pressure from 0.2 atm to 0.85 atm due to decrease in polarization resistance (Figure S15b). The EIS spectra collected over 600 h indicated that the cell was stable during EC performance while the polarization resistance increased during reversible operation (Figure 6f). The minimal change in resistance indicates excellent structural and interfacial stability of the defect-engineered electrolyte architecture. The minimal evolution of ohmic resistance during extended operation indicates strong structural and interfacial robustness of the cooperative effects of vacancy-mediated sintering, chemically stable perovskite framework formation, and dense microstructural. These developments collectively contribute to maintaining high electrochemical conversion efficiency under intermediate-temperature operating conditions.

3.6. Thermo-mechano-chemical stability

Operational durability under repeated thermal perturbation is critical for practical PCECs, particularly as operating temperatures are progressively reduced. The BZYZn-based full cell was therefore subjected to accelerated thermal cycling between 600 °C and room temperature, including a prolonged 5 h dwell at room temperature under each cycle (Figure 7a). The open-circuit voltage (OCV) was continuously monitored during controlled cooling ($1 \text{ }^{\circ}\text{C min}^{-1}$) and reheating ($1.1 \text{ }^{\circ}\text{C min}^{-1}$) (Figure S16). The reversible OCV response over more than five severe cycles indicates that the electrolyte layer remains gas-tight and electrochemically functional despite repeated thermo-mechanical stress. Thermal cycling operation was performed to analyze the mechanically resilient electrolyte/electrode interfaces and the absence of progressive microcracking. To quantitatively evaluate structural stability, EIS was performed at 600 °C and 550 °C after each thermal cycle (Figure S17) and I-V curves were recorded simultaneously after long-term stability in FC mode (Figure S18). The degradation in performance can be attributed to

the increment in ohmic resistance. The ohmic resistance (R_o) was increased compared to initial performance and further increased by approximately 10% during the initial 24 h but subsequently stabilized over the next 100 h at 550 °C, suggesting minor early-stage interfacial relaxation followed by stable operation (Figure 7b). Similar operation was performed in EC mode by thermal cycling between 600 °C to 500 °C for 4 cycles. The cell exhibited slight increment in performance at both temperature (Figure S19a and S19b). EIS characterization at 600 °C revealed that R_o decreased at high temperature while polarization resistance (R_p) remained stable. This demonstrates the high stability of Zn-modified BZY electrolyte based full-cells (Figure S19c). At 500 °C both ohmic and polarization loss remained stable, that indicates the further enhancement in the performance of the cell would increase the stability of PCECs at lower temperature (Figure 19d). Post-test cross-sectional SEM analysis confirms strong interfacial bonding between the

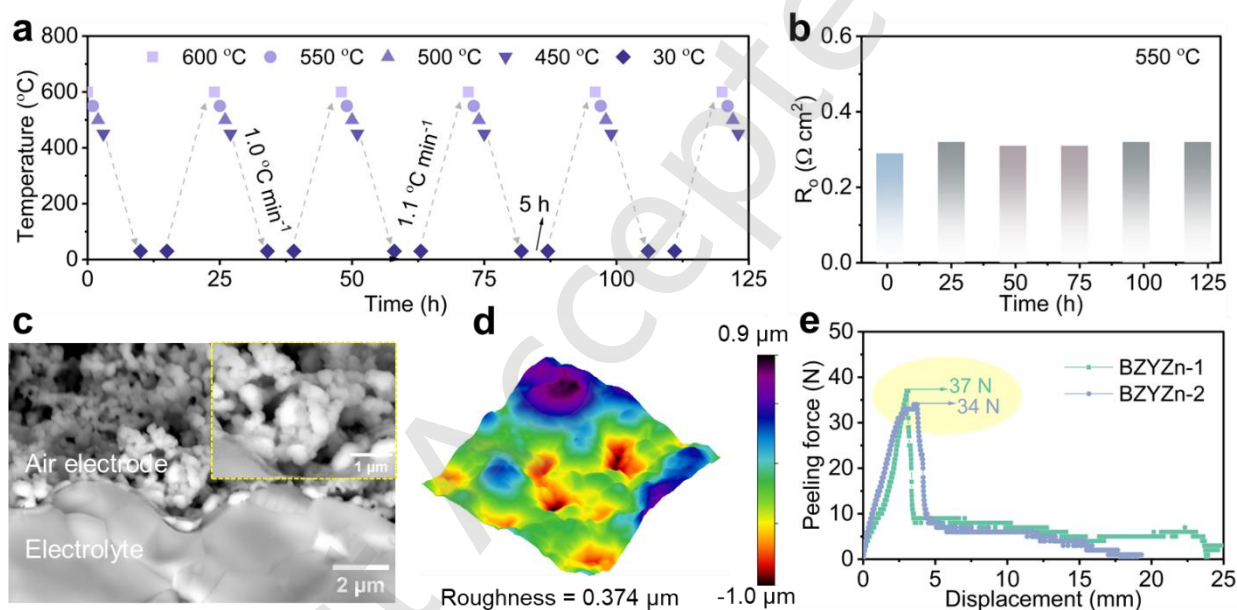


Figure 7. BZYZn-based cells exhibit robust thermal cycling stability and strong electrode/electrolyte interfacial adhesion. (a) Thermal-cycling protocol used to evaluate cell durability, involving repeated heating and cooling between room temperature and 600 °C. (b) Ohmic resistance R_o measured during thermal cycling at 550 °C, showing minimal variation over 125 h. (c) Cross-sectional SEM image of the air-electrode/electrolyte interface after testing, with inset showing the porous electrode microstructure. Scale bars, 2 μm and 1 μm (inset). (d) Representative surface topography map of the BZYZn half-cell electrolyte. (e) Peel-test curves for two BZYZn samples, showing peak peeling forces of 37 and 34 N, respectively, indicating strong interfacial adhesion.

electrolyte and electrodes (Figure 7c, S20, S21). Thermal cycling endurance in multilayer ceramic architectures is primarily governed by microstructural integrity and interfacial adhesion, as mismatch in thermal expansion coefficients can induce stress accumulation leading to delamination or cracking. Atomic force microscopy (AFM) analysis reveals that the BZYZn electrolyte exhibits a controlled surface topography characterized by distributed peaks and valleys (Figure 7d). Compared to undoped BZY ($\sim 0.6 \mu\text{m}$) (Figure S22a), the BZYZn half-cell displays a reduced but more uniformly distributed roughness ($\sim 0.39 \mu\text{m}$), consistent with refined grain size and homogeneous densification. The presence of micro-scale valleys ($\sim 3 \mu\text{m}$ depth, profilometry;

Figure S22b) facilitates mechanical interlocking between electrode and electrolyte layers while maintaining a pinhole-free dense structure. The mechanical robustness of the interface was further confirmed by shear strength testing following standard ASTM D1002-05 procedure,[76] yielding adhesion forces of 30-40 N (Figure 7e), with the average shear stress of 47.73 N cm^{-2} comparable to previously reported strongly bonded perovskite interfaces.[77] Collectively, the dense microstructure, mechanically interlocked electrode/electrolyte architecture suppress stress localization during thermal cycling, and chemically stable interfaces enabling stable electrochemical operation under severe thermo-mechanical conditions.

3.7 Cooperative defect-driven sintering paradigm

The present work establishes a defect-structure-coupled processing paradigm for refractory protonic ceramics, in which aliovalent modification of defect chemistry is combined with synchronized shrinkage across the multilayer architecture. Unlike conventional additive-assisted approaches that introduce transient liquid phases or extrinsic sintering promoters, the present strategy combines controlled modification of oxygen-vacancy-related defect chemistry with compatible shrinkage behavior between the electrolyte and support layers. This cooperative coupling enables effective densification at reduced thermal budgets without introducing secondary phases or compromising electrochemical functionality. At the core of this strategy lies the concurrent modification of vacancy population, accompanied by the mechanically compatible co-evolution of electrolyte and electrode microstructures. By minimizing differential densification stress and avoiding grain-boundary blocking phenomena, the approach stabilizes dense microstructures while preserving proton-conducting pathways. The mechanism therefore integrates defect chemistry, mass-transport kinetics, and interfacial mechanics into a unified sintering framework. Importantly, this design principle is not confined to Zn-modified BZY systems. Refractory protonic ceramic may benefit from defect-mediated kinetic acceleration provided that dopant selection maintains structural stability and chemical compatibility. More broadly, the results demonstrate that coupling defect-chemical modification with cooperative interfacial shrinkage control provides a promising processing strategy for reducing the fabrication temperature offering a scalable route toward high-performance ceramic electrochemical devices.

4. Conclusion

In summary, we establish a defect-structure-coupled co-sintering strategy that enables dense fabrication of BZY-based protonic ceramic electrolytes at 1350°C without reliance on liquid-phase sintering additives. Through aliovalent Zn incorporation, oxygen-vacancy related defect chemistry is modified, accompanied by enhanced grain growth and overall sintering kinetics while maintaining structural stability and proton conducting functionality. Concurrent kinetic matching between electrolyte and supporting electrode layers suppresses differential densification stress, minimizing elemental interdiffusion, Ni coarsening, and structural warping during co-firing. The resulting architecture exhibits high electrochemical performance in both fuel-cell and electrolysis modes, together with robust thermo-mechano-chemical stability under prolonged operation and

repeated thermal cycling. Importantly, the cooperative coupling of defect-chemical modification and interfacial shrinkage matching processes provides a generalizable framework for processing diffusion-limited refractory protonic ceramics under reduced thermal budgets. The present results therefore establish a relationship among aliovalent defect modification, enhanced sintering behavior, and favorable protonic conductivity, while the specific microscopic diffusion pathways responsible for the enhanced sintering remain to be determined. This work highlights the potential of defect-chemistry and interfacial engineering as a scalable route for manufacturing high-performance protonic ceramic electrochemical devices, offering a pathway toward lower-temperature fabrication without compromising structural integrity or electrochemical functionality.

Author Contributions

H.D. conceived and supervised the project. A.K. performed the electrochemical experiments and conducted the primary data analysis with support from S.Z. L.Y. and C.D. contributed to the analysis and interpretation of the electrochemical data. N.M.R. and J.W.P. performed the EPR measurements and analysis. M.V.W. and S.S. conducted the S/TEM characterization and analysis. S.K., I.T.B., and Y.G. assisted with experimental data collection. A.K. and S.Z. prepared the initial manuscript draft. All authors discussed the results, contributed to manuscript revision, and approved the final version. A.K. and S.Z. contributed equally to this work.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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