

Supplementary Materials:

Materials and Methods: The mixed ion conducting ceramic pellets of $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-5}$ containing ~1 wt. % NiO (BCZYYbNiO1) were synthesized by the solid-state reactive sintering (SSRS) method from BaCO_3 (Alfa Aesar, 99.8%), CeO_2 (Alfa Aesar, 99.9%), ZrO_2 (Alfa Aesar, 99.7%), Y_2O_3 (Alfa Aesar, 99.9%), Yb_2O_3 (Alfa Aesar, 99.9%) and NiO (Alfa Aesar, Ni 78.5%) precursor powders. Briefly, stoichiometric amounts of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 , and Yb_2O_3 were weighed and ball milled with isopropyl alcohol solvent (Sigma-Aldrich, 99.5%) and 3 mm diameter spherical yttria-stabilized zirconia (YSZ) grinding media (Union Process). A 1.0 wt. % sintering aid of NiO based on the total weight of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 , and Yb_2O_3 was added into the above powder mixture. The powders were ball-milled for 24 h, and then dried at 80 °C for 48 h. Green pellets were then fabricated by hydraulic compaction under 375 MPa pressure for 2 minutes in a 19 mm diameter circular carbon-aided steel dry-press die. These green pellets were sintered in ambient air at 1350 °C for 24 h to achieve >96% relative density (theoretical density = 6.211 g cm⁻³).²

To produce the control pellet samples, BCZYYb powder was synthesized by the polymeric sol-gel method (BCZYYb-C) from metal nitrate precursors: $\text{Ba}(\text{NO}_3)_2$ (Alfa Aesar, 99+%) , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.5%), $\text{ZrO}(\text{NO}_3)_2$ solution (Sigma-Aldrich, 35 wt. % in dilute nitric acid), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.9%), and $\text{Yb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar, 99.9%, x was determined to be 10.48 by TGA). Sol-gel method was used to assure a microstructurally "fair" comparison to the BCZYYbNiO1 sample as BCZYYb synthesized using oxide precursors without a sintering aid would not sinter at temperatures below 1700 °C (porous BCZYYb synthesized with oxide precursors and no NiO shown in Fig. S5). At these high temperatures, it has been shown that barium volatilization is a problem and leads to BaO formation and decreased proton conductivity.³² Stoichiometric quantities of these metal nitrates were dissolved into de-ionized water to form a clear solution. At the same time, as combined chelating agents, ethylenediaminetetraacetic (EDTA) acid (Alfa Aesar, 99.4%) and citric acid monohydrate (Alfa Aesar, 99+%) were dissolved into an ammonium hydroxide (Alfa Aesar, 28-30% NH_3) aqueous solution while keeping the molar ratio of EDTA acid : citric acid : total ions to be 1 : 1.5 : 1. The metal nitrate solution was slowly added to the chelating solution and the resultant transparent solution was adjusted to pH = 10.0 using ammonium hydroxide or nitric acid. The polymerization was fulfilled by vaporizing excess water at 80 °C with magnetic stirring. The sticky polymerized gel was dried in an oven in ambient air at 150 °C for 48 h to form a black charcoal powder. This black charcoal powder was calcined at 1000 °C for 10 h to produce the BCZYYb sol-gel powder. Green pellets were then fabricated by hydraulic compaction under 375 MPa pressure for 2 minutes in a 19 mm diameter circular carbon-aided steel dry-press die. These green pellets were sintered in ambient air at 1450 °C for 24 h. Both the BCZYYbNiO1 and BCZYYb-C pellets were reduced in 5 vol.% H_2 (balanced with Ar) with a flow rate of 70 standard cubic centimeters per minute (SCCM) at 750 °C for 48 h before physical/electrochemical testing.

The microstructure was characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-7000F) equipped with an energy-dispersive x-ray spectrometer (EDS). FESEM EDS samples were prepared by mounting the samples in epoxy and polishing to 0.05 μm , followed by carbon coating. Grain size measurements were done with multiple FESEM images to achieve statistical reliability (>200 grains sampled). Further microstructure characterization was done using a transmission electron microscope (Philips CM200 TEM with Princeton Gamma-Tech Prism Energy Dispersive X-Ray Spectrometer). TEM preparation was accomplished with a FEI Helios NanoLab 600i DualBeam focused ion beam (FIB) using a standard lift-out method onto a copper half TEM grid.

Magnetometry data was collected using a SQUID MPMS-7 magnetometer (Quantum Design, San Diego, CA, USA). Moment versus field curves were collected at 150 K and 5 K to distinguish between the multiple phases of nickel present in the sample and calculate the amount of reduced Ni^0 metal present in the samples. The percent reduction is the ratio of measured Ni^0 and theoretical Ni^0 . The specific magnetization for Ni^0 at 150 K and 5K was calculated from the NIST 772a then used to determine the actual grams of Ni^0 present in the measured samples. The theoretical grams of reduced Ni^0 was calculated by first approximating the grams of NiO present in the sample from the synthesized weight percent, then assuming 100% of the NiO was reduced to Ni^0 . For conductivity studies, silver paste was applied to each side of the pellets along with a current collector made out of silver mesh and gold wire. After application, they were fired at 800 °C for 5 h to form porous silver electrodes. The conductivities were measured in dry and wet 5 vol.% H_2 (balanced with Ar) at a flow rate of 70 SCCM at different temperatures. The wet gas was prepared by passing through a saturation water bubbler at 25 °C to achieve $p(\text{H}_2\text{O}) \approx 0.03$ atm. Isotope studies were conducted by flowing 5 vol.% H_2 (balanced with Ar) through a water bubbler (25 °C) then, at the same temperature, switching to 5% D_2 gas (balanced with Ar) bubbled through D_2O (25 °C). Final EIS spectra were taken at steady state when the resistance values changed < 2% over 2 h. The measurements were acquired using a Gamry Reference 3000, sweeping from 1 MHz to 0.1 Hz. All measurements were conducted starting at the highest temperature (750 °C) and decremented by 100 °C intervals to a final temperature of 50 °C.

In order to normalize the grain boundary conductivity to take into account different grain sizes (Fig. S5) a specific grain boundary conductivity ($\sigma_{\text{GB,sp}}$) was calculated using the brick layer model shown in eqn (3).²⁴⁻²⁶

$$\sigma_{GB,sp} = \frac{\left(\frac{g}{g+G}\right)L}{R_{GB}A} \quad (3)$$

Where g is the grain boundary thickness (~2 nm, measured via TEM), G is the average grain size (diameter), L is the width of the pellet, R_{GB} is the resistance due to the grain boundary (evaluated from an equivalent circuit fit of the EIS data, e.g. provided in Fig. S6) and A is the surface area of the pellet. Fig. S7 shows a comparison of Nyquist plots for BCZYb-C and BCZYb/Ni in wet 5% H₂ for 100 and 600 °C demonstrating large changes in resistance at lower temperatures.

Gas concentrations for the concentration cell measurements were supplied independently to inside and outside tubes (separated by the sample) in order to create two different atmospheres across the pellet. The outside tube for the reactor was made of transparent quartz to facilitate visual placement of the thermocouple close to the sample and the inside tubes were made of alumina. The inside alumina tubes along with the pellet were sealed using a glass sealant. Temperature measurements were taken with a K-type thermocouple that was placed ~0.5 cm away from the pellet. Pellets were prepared by applying silver paste to each side of the pellets along with a current collector made out of silver mesh and gold wire. After application, they were fired at 800 °C for 5 h to form porous silver electrodes. Both gas streams were prepared by flowing pure H₂ (99.999%) and pure He (99.999%) through individual mass flow controllers, mixed with a total flow rate of 100 SCCM, then run through insulated H₂O bubblers with independent temperature control. After humidification, the gases ran through heated lines to the reactor. Gas composition samples were taken just before entering the reactor and sent through heated lines to an atmospheric sampling mass spectrometer (MKS Cirrus Benchtop Atmospheric RGA System). Error bars reported are calculated from error propagation for uncertainties from thermocouple temperature, mass flow rates, and mass spectrometer.

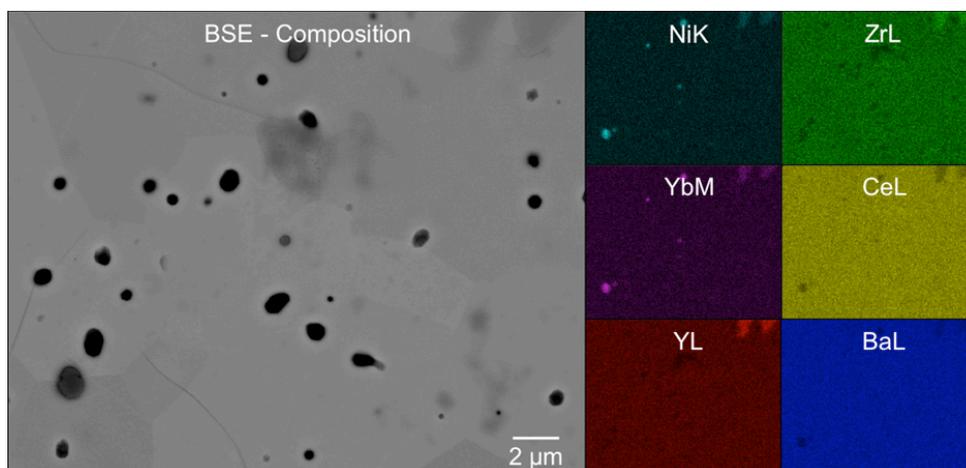


Fig. S1 Energy dispersive x-ray spectroscopy (EDS) map of a polished cross-section of BCZYbNiO₁ pre-reduction. Large image showing compositional backscatter electron image and corresponding elemental maps of Ni, Zr, Yb, Ce, Y, and Ba (and their x-ray peak K, L, or M). The brighter the pixel, the higher the concentration (dark represents depletion).

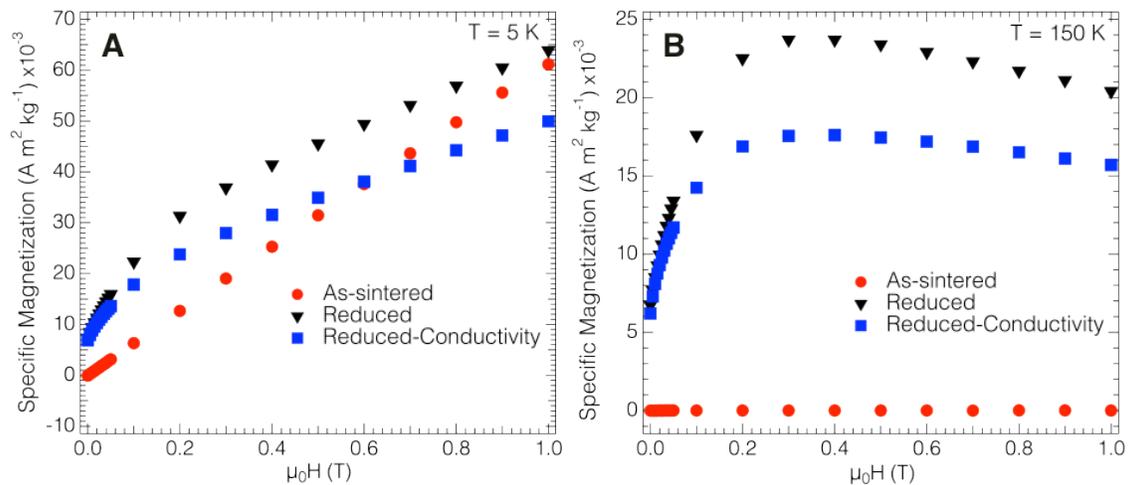


Fig. S2 SQUID magnetometry data for BCZYYbNiO1. (A) Specific magnetization response as a function of field strength for 5 K for an as-sintered pellet, a reduced pellet (5% H₂ bal. Ar for 48 h at 750 °C), and a pellet after long-term conductivity testing (measured in 5% H₂ bal. Ar after reduction for ≈400 h). (B) Same data set for 150 K. The 150 K data set was used for Ni concentration calculations.

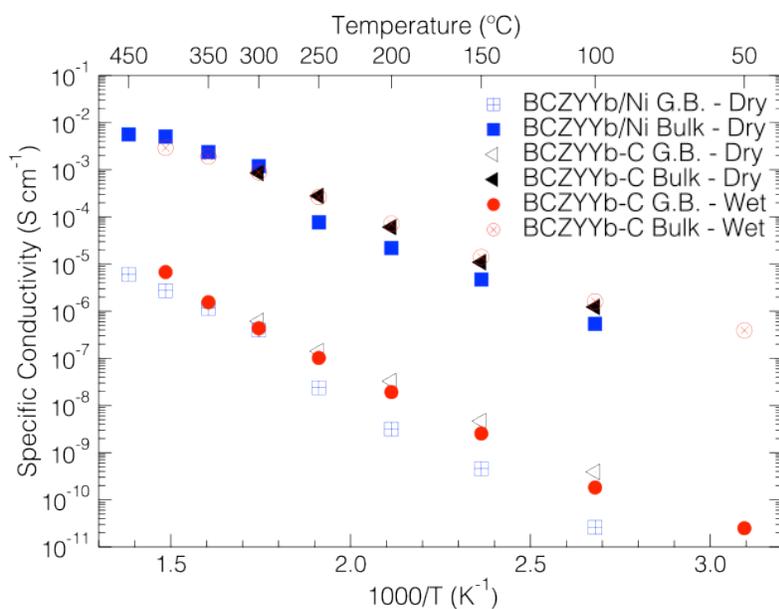


Fig. S3 Specific bulk vs. grain-boundary (G.B.) conductivities determined from electrochemical impedance spectroscopy of BCZYYb/Ni and BCZYYb-C in dry and wet (≈3% H₂O) 5% H₂ (bal. Ar).

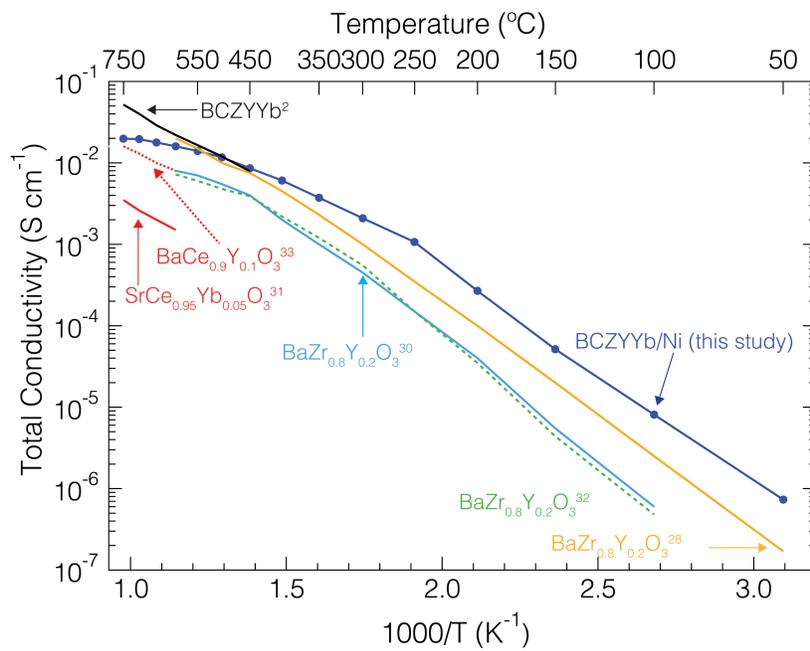


Fig. S4 Comparison of total conductivities for different polycrystalline perovskite proton conductors.

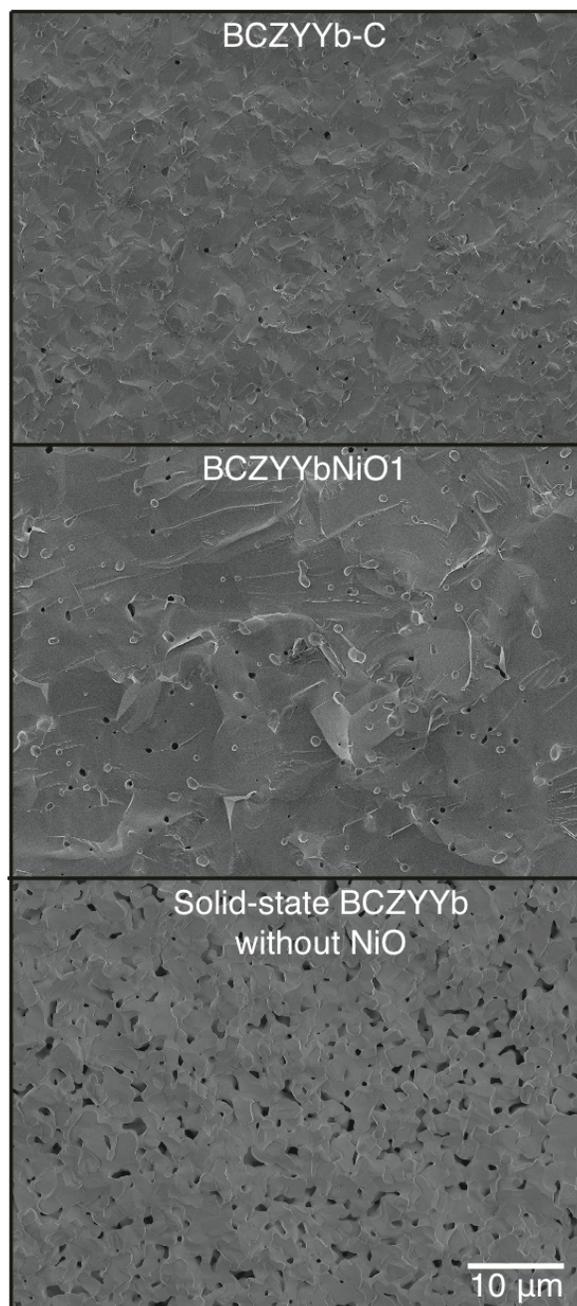


Fig. S5 Secondary electron images of fractured cross-sections of BCZYYb-C (sintered at 1450 °C for 24 h), BCZYYbNiO1 (before reduction – sintered at 1350 °C for 24 h) and a solid- state BCZYYb (sintered at 1500 °C for 24 h) which had no NiO added to the oxide precursors.

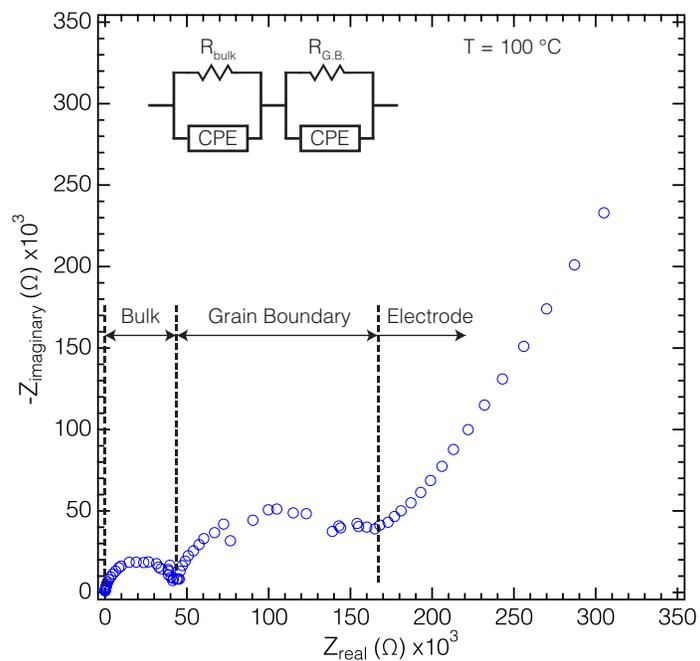


Fig. S6 Example Nyquist plot (real vs. imaginary impedance) of BCZYb-C at 100 °C in dry 5% H₂ (bal. Ar) from 1 MHz to 0.1 Hz demonstrating the equivalent circuit used to model and calculate the bulk and grain boundary (G.B.) resistances.

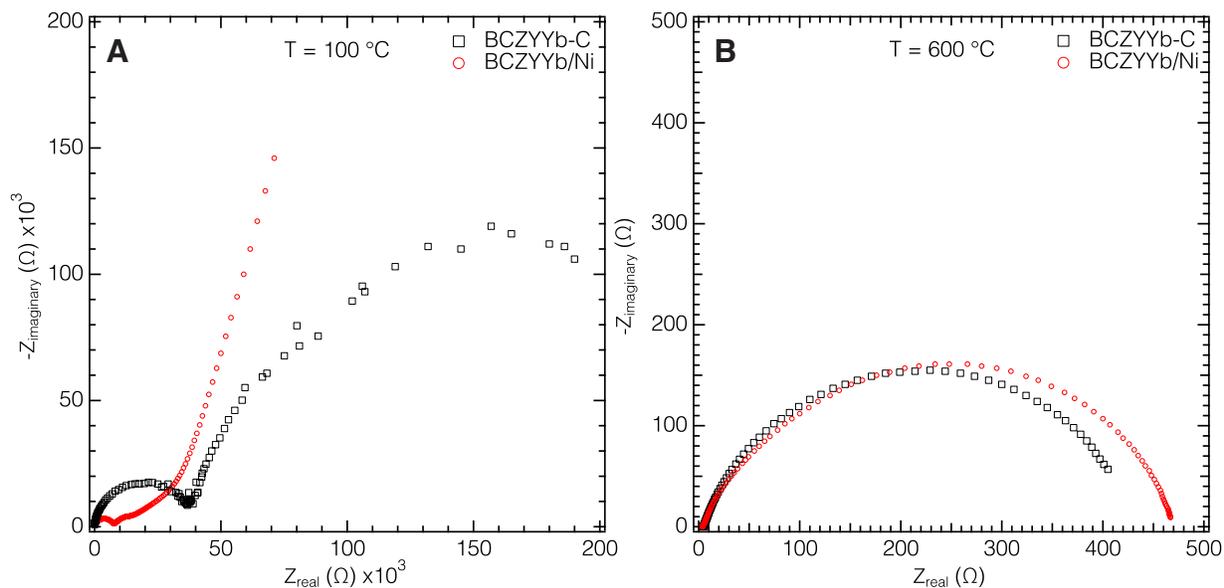


Fig. S7 Comparison of Nyquist plots (real vs. imaginary impedance) for both BCZYb-C and BCZYb/Ni in dry 5% H₂ (bal. Ar) at (A) 100 °C and (B) 600 °C.