

Supporting Information

Failure of Protonic Ceramic Fuel Cells (PCFCs) Under Gaseous Cr and CO₂ Exposure and the Introduction of Protective Barrier Layer for Mitigation

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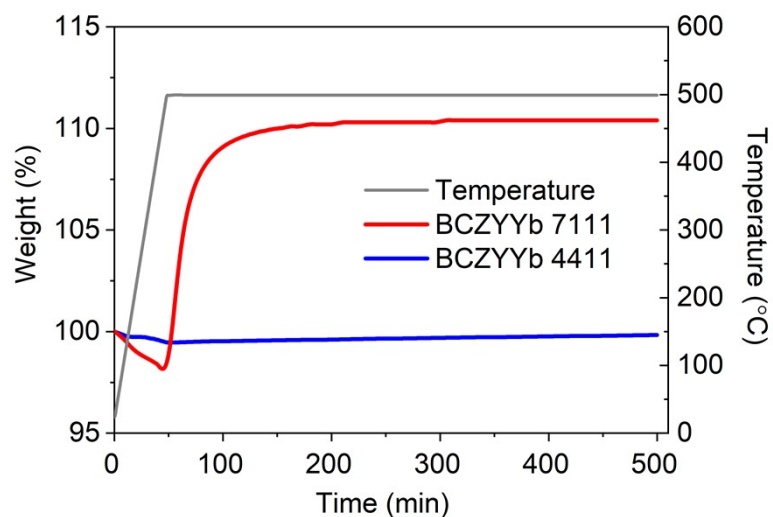


Fig. S1. Stability of BCZYYb electrolytes under CO₂ environment. (a) Thermogravimetric profile of BCZYYb 7111 and 4411 electrolyte upon exposure to 60% CO₂ (balanced with N₂) at 500°C for 8 h.

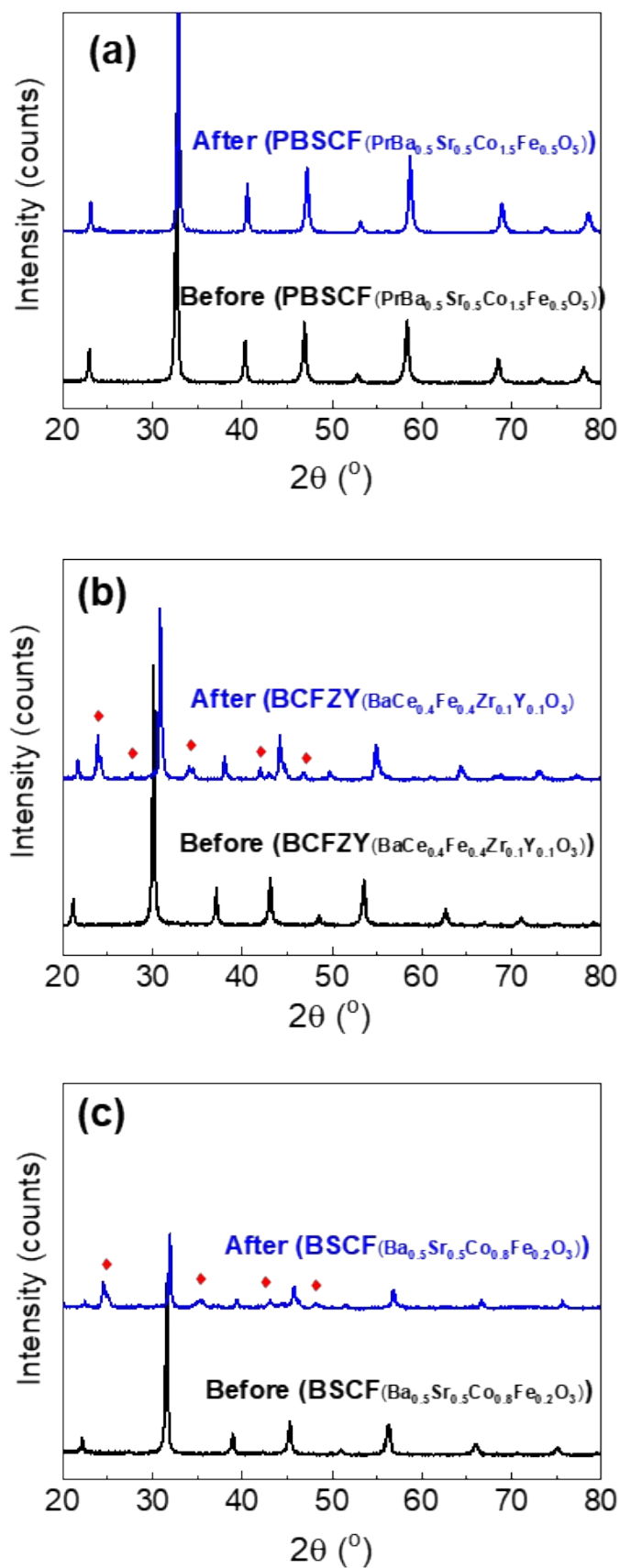


Fig. S2. Stability of cathode materials under high humidity environment. XRD patterns of air electrode materials before and after exposure to 30% humidified air at 550°C for 300 h. (a) PBSCF (b) BCFZY (c) BSCF. Red diamonds represent newly formed phases.

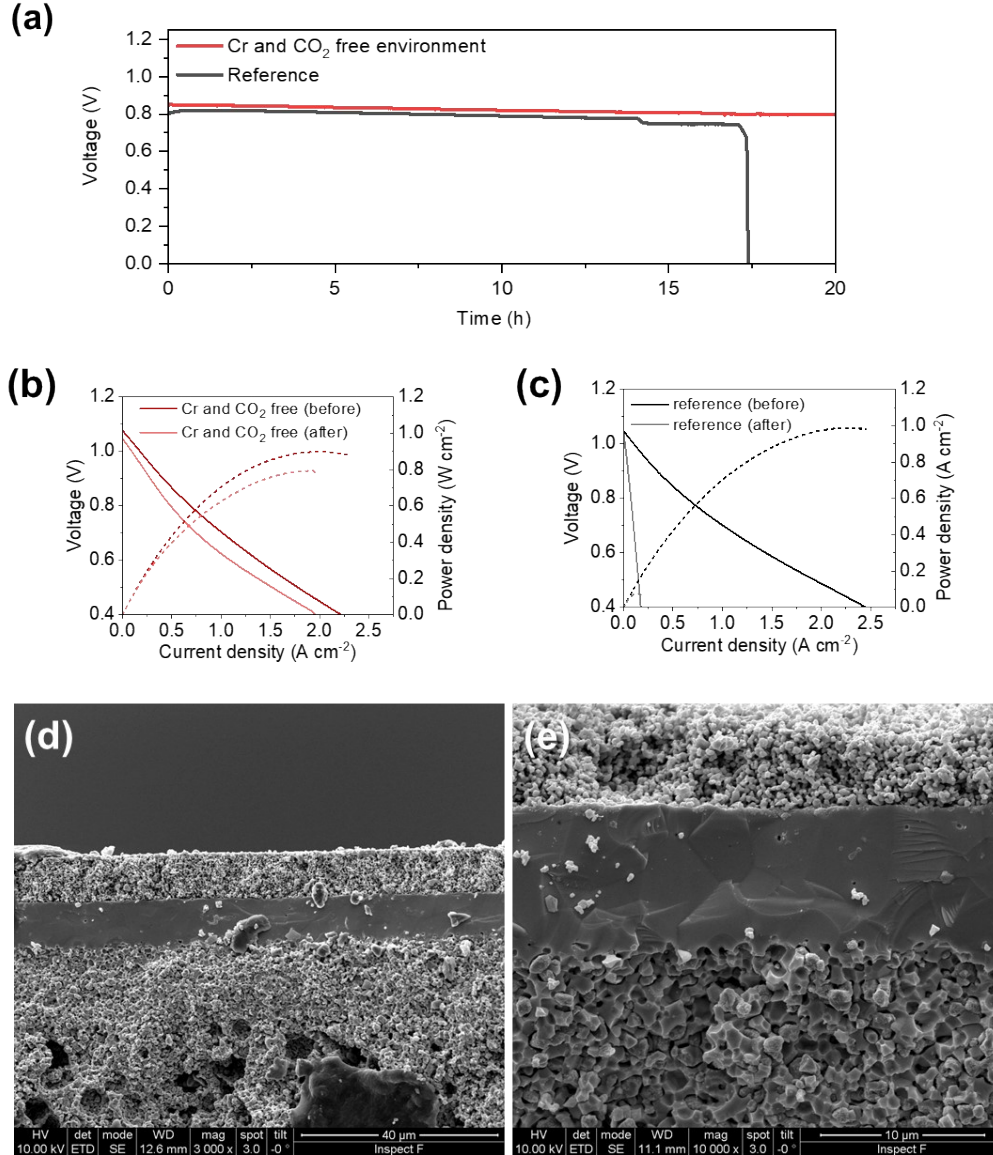


Fig. S3. Comparison of PCFCs tested under realistic and cleaner operating conditions. (a) Galvanostatic tests of the cells under realistic and cleaner operation conditions at 600 °C and a current density of 0.5 A cm⁻². I-V-P curves of the cell at 600°C with 3% humidified H₂ and air injected into the fuel electrode and air electrode, respectively, for the cell operated at (b) Cr and CO₂-free, cleaner, operating condition, and (c) realistic operating condition. (d, e) Cross-sectional SEM images of the PCFC tested under cleaner operating condition.

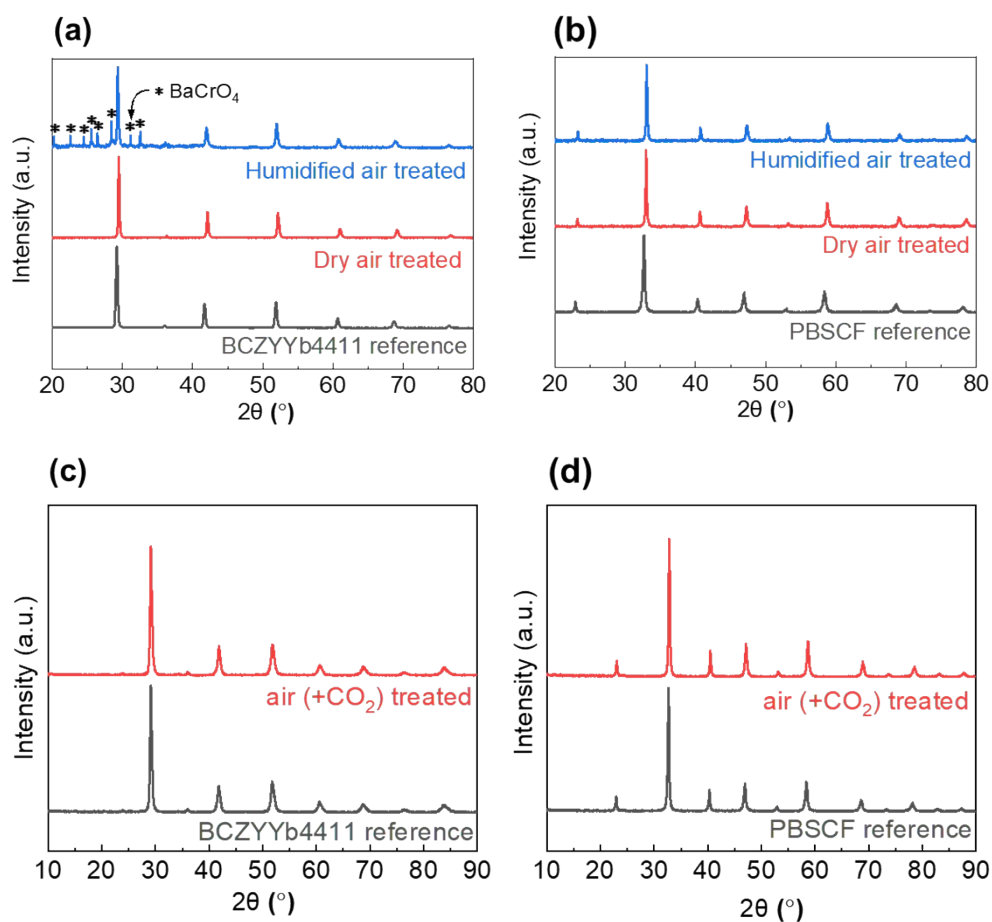


Fig. S4. Stability of air electrode and electrolyte materials under Cr and CO₂ exposure. XRD patterns of (a) BCZYYb4411 and (b) PBSCF pellets before (grey) and after exposure to dry (red) and 3% humidified air (blue) at 600 °C for 24 h with Cr₂O₃ pellet in proximity. XRD patterns of (c) BCZYYb4411 and (d) PBSCF powders before (grey) and after exposure to atmospheric air containing CO₂ (red) at 600 °C for 24 h. The reference position for BaCrO₄ is extracted from PDF#00-035-0642.

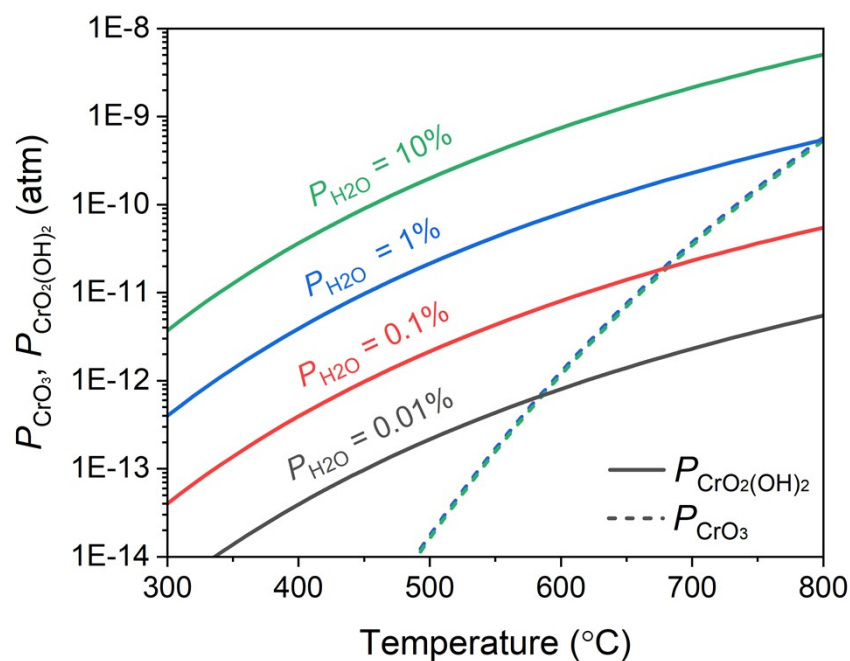


Figure S5. Equilibrium vapor pressure of gaseous Cr species simulating the air electrode environment. Thermodynamic equilibrium pressures of gaseous Cr species $CrO_2(OH)_2$ (solid) and CrO_3 (dash) at different partial pressure of water (black for 0.01%, red for 0.1%, blue for 1%, and green for 10%). Calculated by Gibbs free energy minimization method using HSC 10 Chemistry.

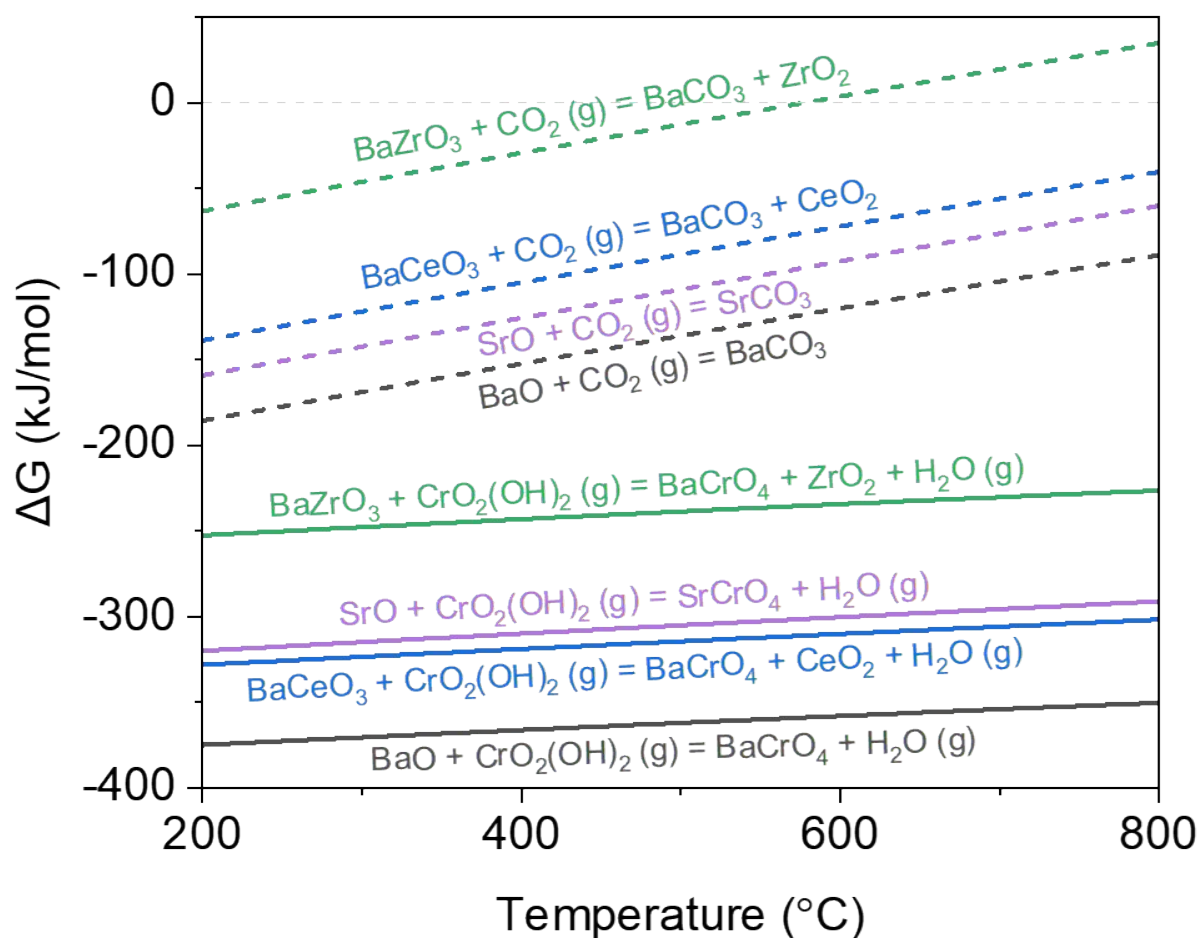


Figure S6. Gibbs free energy of chromate and carbonate formation from different Ba oxides and Sr oxide. Gibbs free energy for chromate (solid lines) and carbonate (dashed lines) formation from BaO (dark grey), BaCeO₃ (blue), BaZrO₃ (green), and SrO (purple) is depicted. Data sourced from HSC 10 Chemistry.

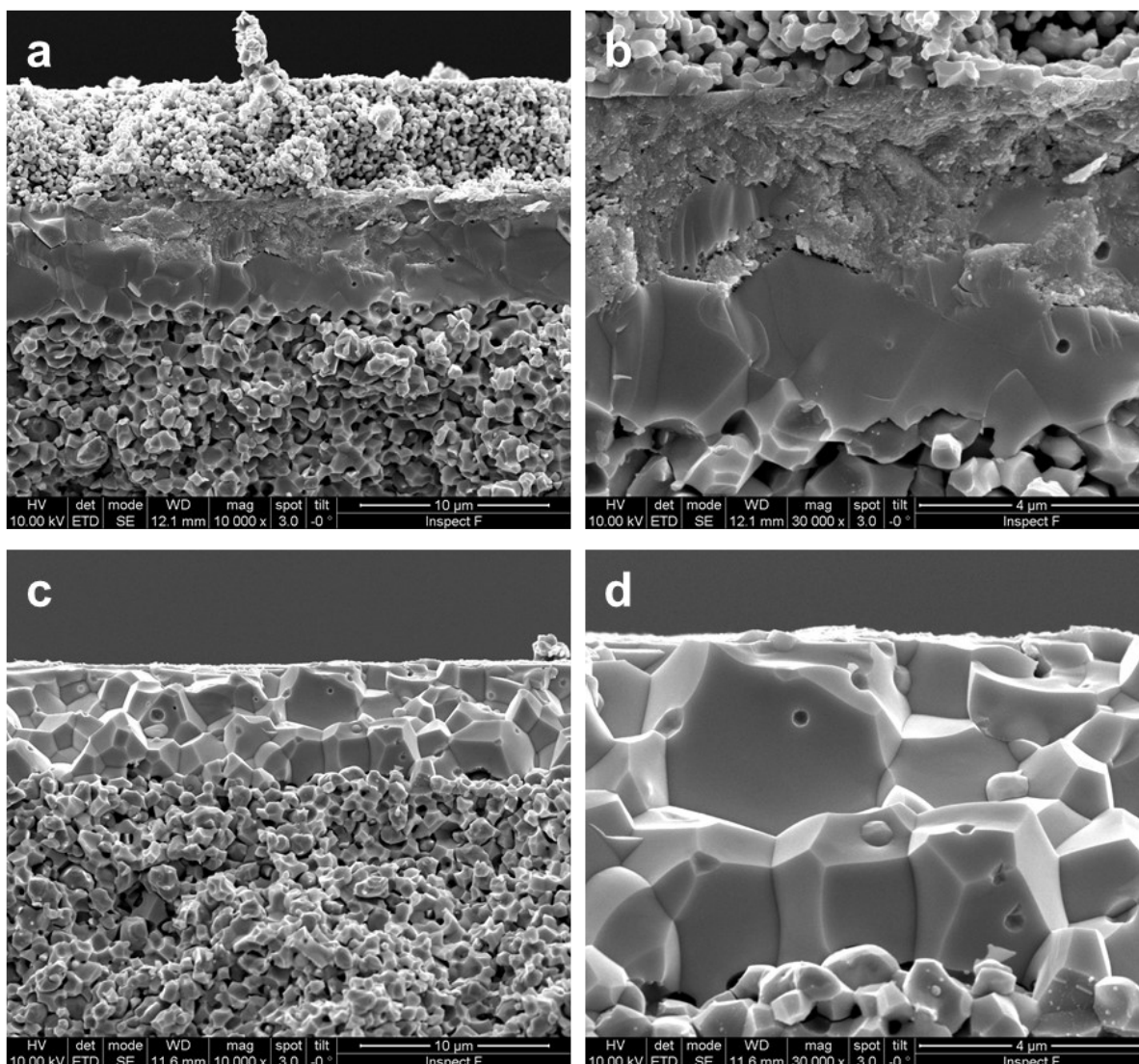


Fig. S7. Cross-sectional SEM images of PCFCs after ~ 20 h long-term test. Cross-sectional view of the PCFC at the (a, b) air electrode covered region, and (c, d) electrolyte without a covered air electrode following galvanostatic testing at 600 °C with a current density of 0.5 A cm⁻² under fuel cell operation condition. Fuel electrode layer, electrolyte, and air electrode from bottom to top.

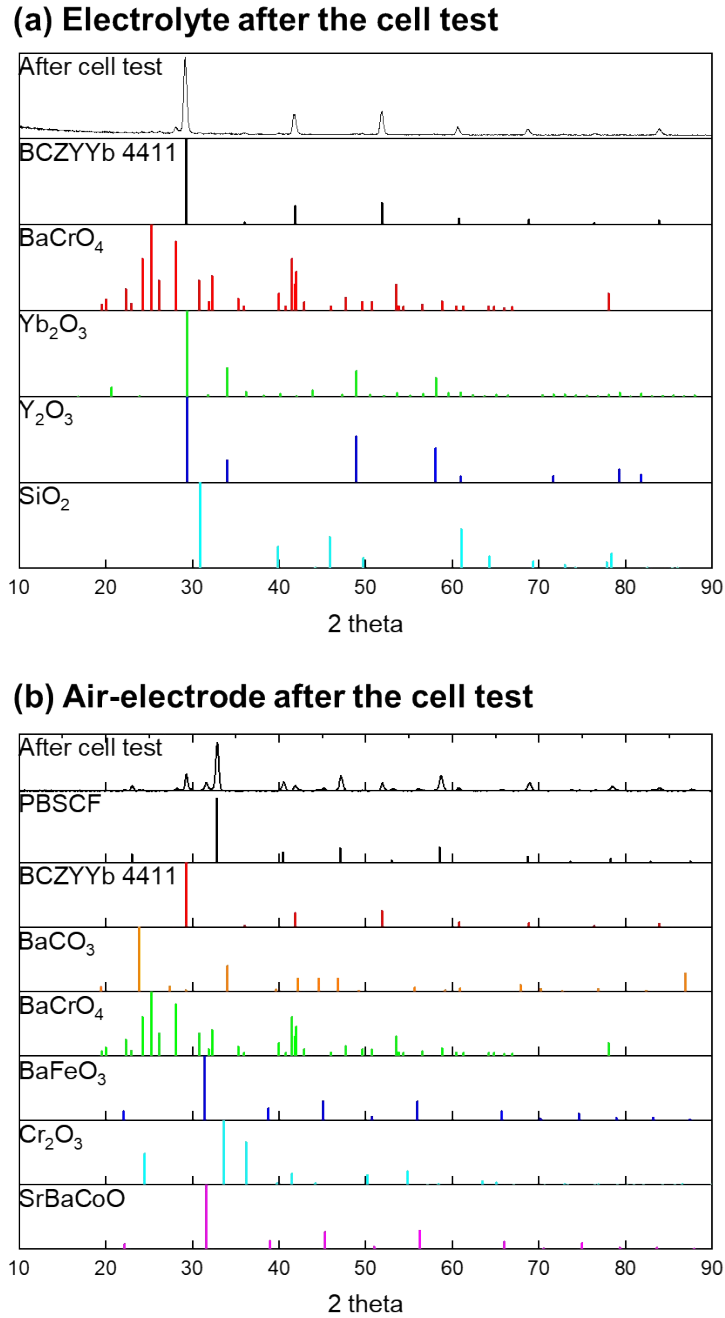


Fig. S8. Detailed XRD analyses of the electrolyte and air-electrode after the cell degradation. XRD were conducted on surface of (a) electrolyte, and (b) air electrode. Reference XRD peaks are based on the following PDF cards: BaCrO₄ from PDF#00-035-0642; Yb₂O₃ from PDF#01-077-0458; Y₂O₃ from PDF#98-010-9481; SiO₂ from PDF#01-082-0513; BaFeO₃ from PDF#01-075-0426; Cr₂O₃ from PDF#98-017-3470; Sr_{0.5}Ba_{0.5}CoO_{2.5} from PDF#98-016-3670; BaCO₃ from PDF#00-001-0506. BCZYYb 4411 reference peaks are extracted from raw powder XRD.

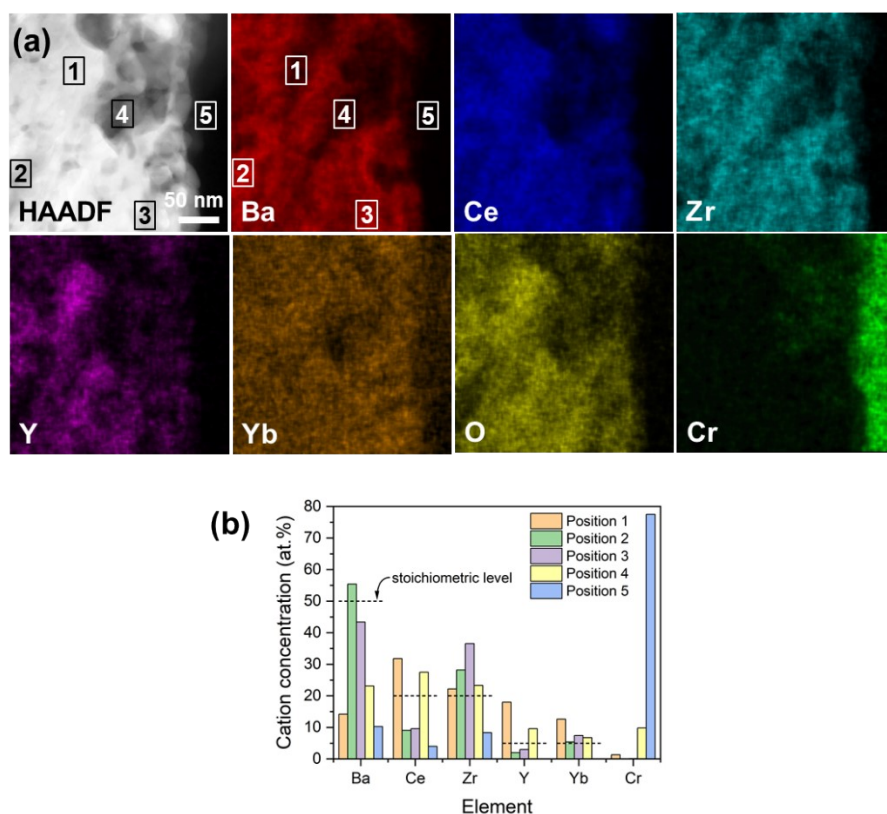


Fig. S9. Detailed investigation of the degradation at the electrolyte after the 20 h cell test. (a) HAADF-STEM image and EDS mapping images of the constituent elements. Quantitative element mapping (Qmap) was applied for Yb and Cr. (b) Cation compositions derived from the EDS analysis in (a) at different positions.

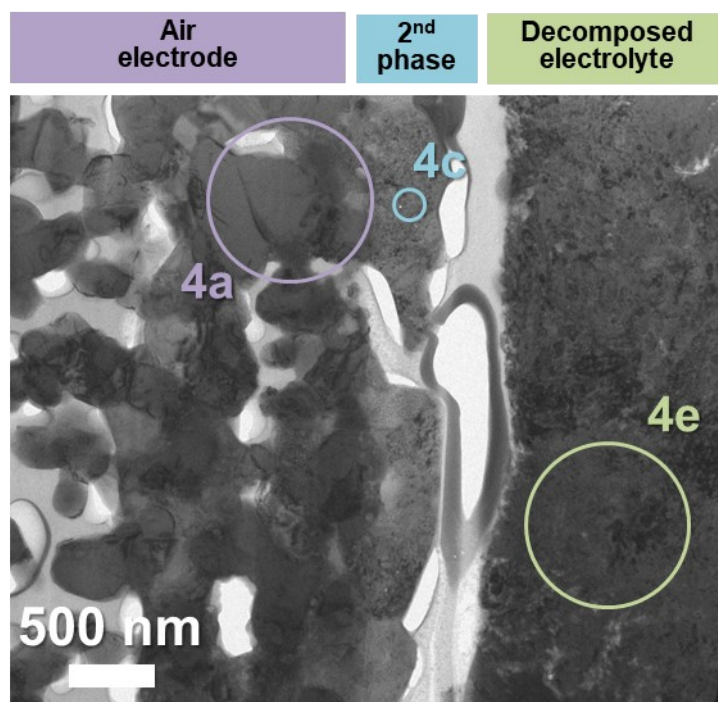


Fig. S10. (a) TEM image of the degraded cell used for SAED measurements. The circles indicate regions used for SAED measurements for Figure 4a, 4c, and 4e.

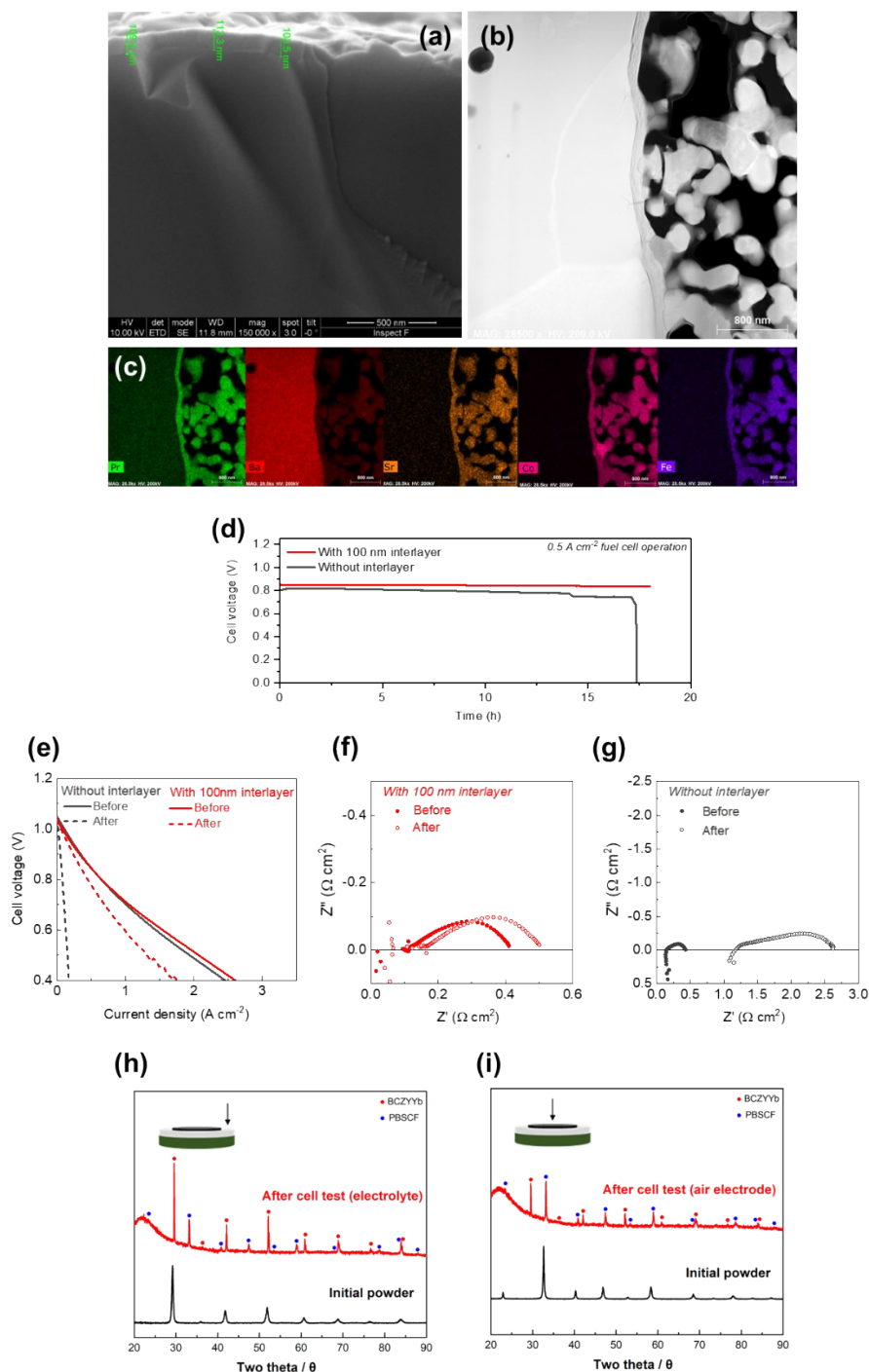


Fig. S11. Morphology of 100 nm thick PBSCF interlayer and the effect on the stability. (a) SEM image (b) STEM-HAADF and (c) STEM-EDS measurements for the cell with 100 nm thick PBSCF interlayer prepared with pulsed laser deposition. (d) Galvanostatic test at 600 °C and a current density of 0.5 A cm⁻² under fuel cell operation of the reference cell without dense PBSCF interlayer (shown in Fig. 1), and the cell with 100 nm dense interlayer. (e) I-V characteristics of the corresponding cells before and after galvanostatic test. (f, g) Nyquist plots of impedance spectra of the corresponding cells before and after galvanostatic test. X-ray diffraction patterns of (h) BCZYYb4411 electrolyte after the cell test with corresponding initial powder, and (i) PBSCF air electrode after the cell test with corresponding initial powder.

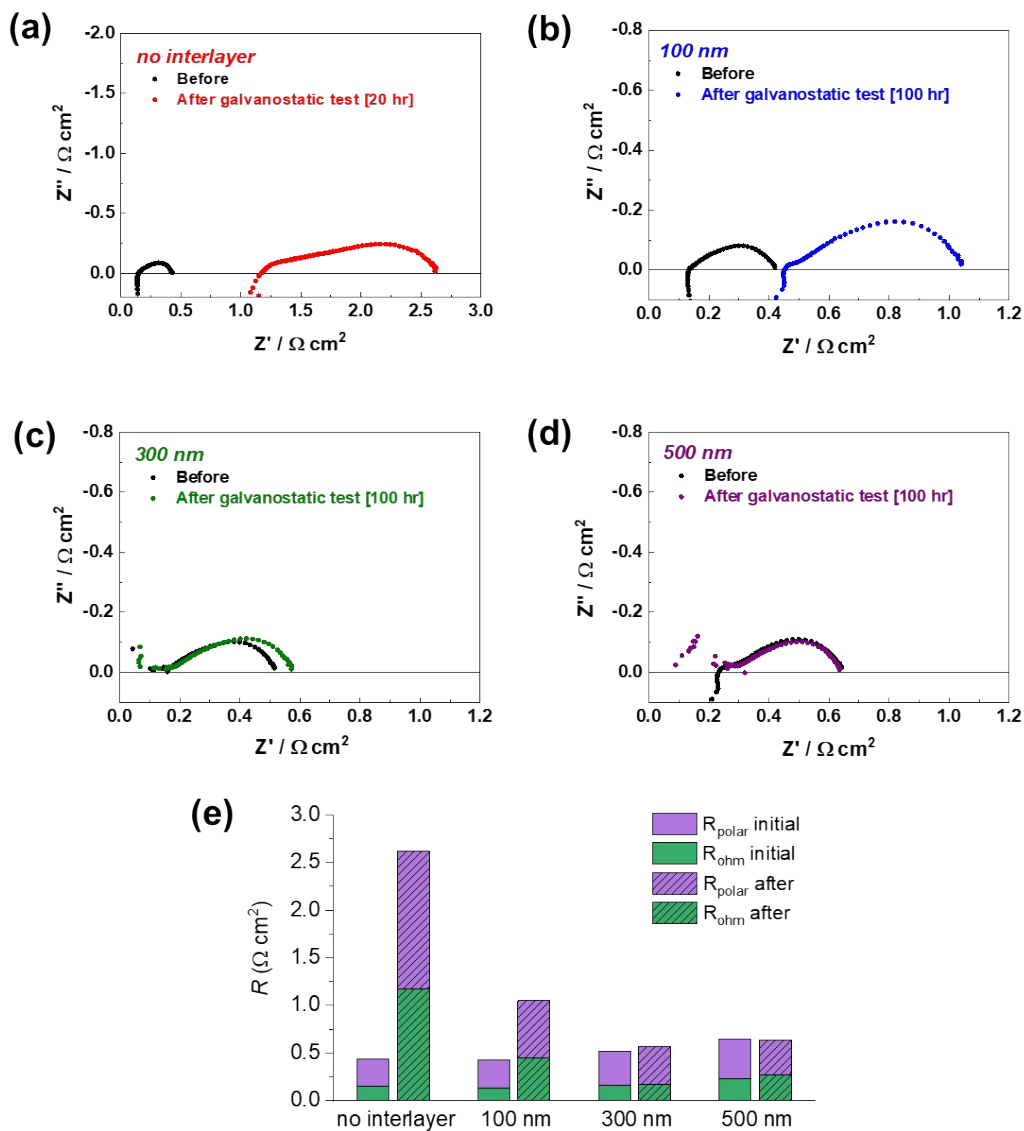


Fig. S12. Electrochemical impedance analyses of the PCFCs before and after the long-term tests. (a–d) Nyquist plots of impedance spectra of the PCFC without a PBSCF interlayer and cells with dense PBSCF interlayer with thicknesses of 100 nm, 300 nm, and 500 nm before and after the long-term tests at open circuit voltage. (e) Comparison of the impedance before and after the long-term test

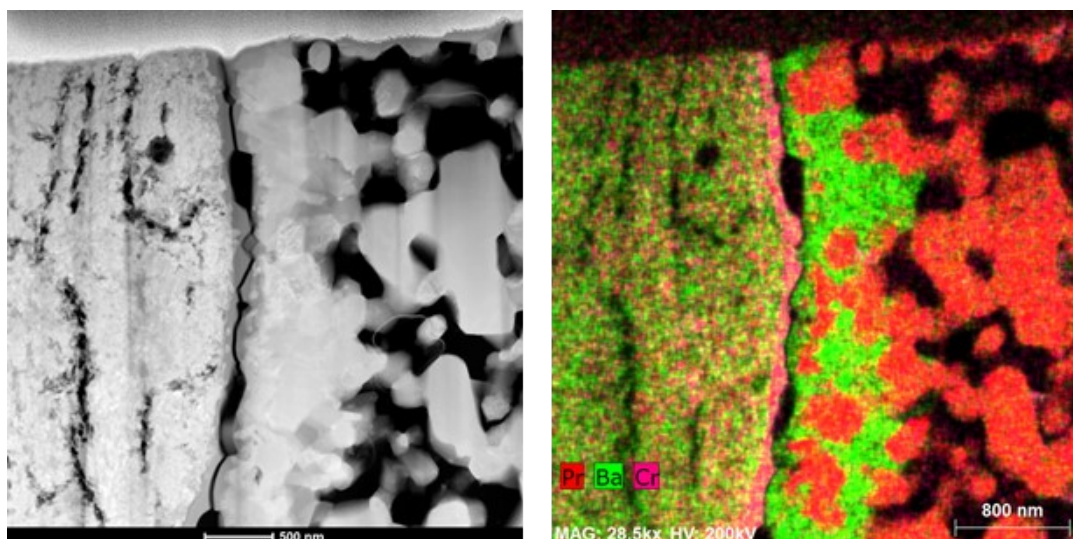


Fig. S13. Characterization of the failed cell with a 100 nm interlayer after ~100 h operation. HAADF-STEM image alongside EDS mapping image of the constituent elements Ba, Cr, and Pr from the cell tested for ~100 h with a 100 nm interlayer.