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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

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Revitalizing interface in protonic ceramic cells by acid etch

Wenjuan Bian^{1,2,†}, Wei Wu^{1,†,*}, Baoming Wang³, Wei Tang^{1,2}, Meng Zhou², Congrui Jin⁴,
Hanping Ding¹, Weiwei Fan⁵, Yanhao Dong^{5,*}, Ju Li^{3,5,*}, Dong Ding^{1,*}

¹*Energy and Environmental Science and Technology, Idaho National Laboratory, Idaho Falls, ID 83415, USA*

²*Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, USA*

³*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

⁴*Department of Civil and Environmental Engineering, University of Nebraska–Lincoln, Lincoln, NE 68583, USA*

⁵*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

†: Equal contribution.

* Corresponding authors. Emails: wei.wu@inl.gov (W.W.), dongyh@mit.edu (Y.D.), liju@mit.edu (J.L.), dong.ding@inl.gov (D.D.).

Abstract

Protonic ceramic electrochemical cells hold the promise to be operated below 600 °C^{1,2}. Although the high proton conductivity of the bulk electrolyte has been demonstrated, it cannot be fully utilized in electrochemical full cells due to unknown causes³. Here we showed that it all comes from poor contacts between the low-temperature processed oxygen electrode-electrolyte interface. We demonstrated that a simple acid treatment can effectively rejuvenate the high-temperature annealed electrolyte surface, resulting in reactive bonding between the oxygen electrode and the electrolyte and improved electrochemical performance and stability. This enables exceptional protonic ceramic fuel-cell performance down to 350 °C, with peak power densities of 1.6 W cm⁻² at 600 °C, 650 mW cm⁻² at 450 °C, and 300 mW cm⁻² at 350 °C, as well as stable electrolysis operations with current densities above 3.9 A cm⁻² at 1.4 V and 600 °C. Our work highlights the critical role of interfacial engineering in ceramic electrochemical devices and offers new understanding and practices towards sustainable energy infrastructure.

Introduction

Protonic ceramic fuel/electrolysis cells (PCFCs/PCECs) are promising intermediate-temperature (400-600 °C) electrochemical cells for reversible conversions between chemical and electrical energy with high efficiency and zero emissions¹⁻⁴. One of their key components is the perovskite-structure oxide electrolyte (e.g., BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} abbreviated as BZCYYb and BaZr_{0.8}Y_{0.2}O_{3-δ} abbreviated as BZY), whose high bulk proton conductivity allows for lower temperatures operations than that for oxygen ion conductor-based solid oxide fuel/electrolysis cells (SOFCs/SOECs) because of smaller activation energy⁵⁻⁷. Nevertheless, there are still electrolyte-related challenges that limit PCFC/PCEC applications, including: First, while the sintered bulk electrolyte shows high proton conductivity (e.g., >10 mS cm⁻¹ at 500 °C), the ohmic resistance in electrochemical cells is larger than the theoretical value estimated from bulk ionic conductivity alone, with an “unidentified origin”. The inconsistency was proposed to come from poor contacts between oxygen electrode and electrolyte³. Second, the oxygen electrode-electrolyte

interface is mechanically weak, which causes delamination and other forms of degradation, especially under high-current-density PCEC operations.

PCFCs/PCECs are typically prepared by firstly co-sintering hydrogen electrode-electrolyte bi-layer at a high temperature T_1 , and then screen-printing or painting oxygen electrode layer, followed by a second-step sintering at a lower temperature T_2 (**Figure 1a**). However, the protonic ceramic electrolytes are difficult to densify, which require co-sintering at $T_1 \geq 1400$ °C for BZCYYb and ≥ 1500 °C for BZY⁸⁻¹⁰. These temperatures are much higher than what is required to sinter fluorite-structure oxygen ion conductors used in SOFCs/SOECs ($T_1 \sim 1250$ °C for gadolinium-doped ceria and ~ 1300 °C for yttria-stabilized zirconia)¹¹⁻¹³. This contrast exists despite that BaCeO₃ (melting temperature $T_m = 2150$ °C) and BaZrO₃ ($T_m = 2700$ °C) have similar T_m to CeO₂ ($T_m = 2400$ °C) and ZrO₂ ($T_m = 2715$ °C), respectively, and Ce and Zr are the rate-limiting elements for mass transport in both perovskite- and fluorite-structure systems^{14,15}. While seemingly unrelated to the full-cell performance at 400-600 °C, we hypothesize that the low true contact area and high interfacial impedance have the same origin as the poor sinterability, due to slow mass transport. In fact, the situation is even worse for T_2 sintering (~ 1000 °C): A porous oxygen electrode has to be diffusion-bonded to an already well-annealed electrolyte surface (take constrained sintering on a single crystal substrate as an extreme analogy) and T_2 has to be low enough to avoid coarsening of the porous oxygen electrode, to allow gas transport and catalysis. Considering the above, we proposed an acid treatment to rejuvenate the high-temperature annealed electrolyte surface (**Figure 1a**) before bonding with the oxygen electrode. Remarkably, we demonstrated that it can fully recover the theoretical bulk proton conductivity in electrochemical cells and significantly improve the cell performance as well as thermomechanical and electrochemical stabilities.

Interfacial rejuvenation

To prepare the hydrogen electrode-supported half cells, NiO+BZCYYb hydrogen electrode and BZCYYb electrolyte were co-sintered to produce dense electrolyte with a coarse grain structure (**Figure 1b**), a thickness of around 22 μm , and relatively flat surface with a roughness of 0.28 μm (**Figure 1d**, by quantitative atomic force microscopy, AFM). This well-annealed surface impedes oxygen electrode (PrNi_{0.5}Co_{0.5}O_{3- δ} , abbreviated as PNC55) bonding, and results in a mechanically weak oxygen electrode-electrolyte interface with a peeling strength of 18.6 N (**Figure 1f**, **Supplementary Table S1**). To improve the interfacial bonding, we first treated the electrolyte surface of the co-sintered hydrogen electrode-electrolyte bi-layer by nitric acid, before bonding with oxygen electrode (**Figure 1a**). The acid etching initiates along grain boundaries and at specific grains (for 1 min treatment, **Supplementary Figure S1a**) of BZCYYb, indicating heterogeneous surface “inertness” that should be inversely correlated with hetero-oxide bonding. As the treating time increases, the etching proceeds more uniformly and creates a rough surface (**Figure 1c**, **Supplementary Figure S1b-d** and **S2**). We confirmed that the etch does not affect the phase purity of the bulk BZCYYb electrolyte as shown by X-ray diffraction (XRD) in **Supplementary Figure S3**. For chemical uniformity, we conducted energy dispersive spectroscopy (EDS) mapping on the untreated (**Supplementary Figure S4**) and 10 min treated (**Supplementary Figure S5**) electrolyte surface. Spatially uniform elemental distributions were confirmed in both samples, and the inferred compositions (**Supplementary Table S2** and **S3**) agree well with the bulk composition of BZCYYb. For atomic-scale surface chemistry, we

conducted X-ray photoelectron spectroscopy (XPS) analysis on the electrolyte surfaces (**Supplementary Figure S6**) and found weakened signals of Ba 3*d*5 and Y 3*d* peaks at the 10 min treated surface compared to the untreated one. The inferred cation compositions (**Supplementary Table S4**) indicate Y segregation and Ba deficiency at the untreated surface. At the 10 min treated surface, there is no obvious Y segregation, and Ba deficiency becomes more severe. The latter is understandable as acid may preferentially etch away the more reactive BaO units at the surface and leave it terminated with more B-site cations. These chemical features suggest that while the acid treatment does not alter the composition of the bulk region, it drives the nm-scale surface chemistry away from its well-annealed profile, which would benefit atomic-scale diffusion and reaction at the oxygen electrode-electrolyte interface for better hetero-phase diffusional bonding. Indeed, the interface of sintered full cell becomes stronger with etching treatment (**Supplementary Table S1**). A maximum peeling strength of 23.5 N is achieved in 10 min treated cell (Figure 1f), which correlates with a maximum surface roughness of 0.77 μm (**Figure 1e**, **Supplementary Figure S2**).

We conducted aberration-corrected scanning transmission electron microscopy (STEM) and EDS of the 10 min treated-and-diffusion-bonded sample (**Figure 2**). **Figure 2a-j** shows a sample slice (~100 nm thick) near the oxygen electrode-electrolyte interface. While both PNC55 (fine particles on the top, rich in Pr, Ni, Co, and O) and BZCYYb (dense layer on the bottom, rich in Ba, Zr, Ce, Y, Yb, and O) can be clearly observed, there is also some new phase observed in between that is rich in Pr, Ni, Zr, Y, Yb and O, but poor in Co and Ce. To get higher spatial resolution and better statistics, we thinned down another slice from a different location to ~20 nm thickness. As shown in **Figure 2k-t**, in addition to PNC55 (at the upper left corner) and BZCYYb (on the bottom), we again observed a new phase, this time rich in Pr, Zr, Y, Yb, and O. These observations indicate that active chemical reactions take place at the interface during the T_2 sintering. It represents an interfacial version of reactive sintering, which gives better bonding/adhesion under enhanced chemical driving force. Rough and well-bonded features (**Figure 2u&v**) further evidenced the high-quality oxygen electrode-electrolyte interface.

Decreased R_o and R_p : Pre-factor vs. E_a

For electrochemical performance, we first conducted electrochemical impedance spectroscopy (EIS) at open-circuit voltage (OCV) at 400-650 $^{\circ}\text{C}$, for full cells across $\text{H}_2+3\% \text{H}_2\text{O}$ for hydrogen electrode and O_2 for oxygen electrode. As shown in **Figure 3a** (at 600 $^{\circ}\text{C}$; more data at other temperatures in **Supplementary Figure S7**), the acid treatment up to 10 min lowers both the ohmic resistance R_o and polarization resistance R_p , while 15 min treatment increases R_o and R_p due to over-etching. Here, R_o and R_p are assumed to follow an Arrhenius-type temperature dependence

$$R_o = A_o \exp\left(-\frac{E_{a_o}}{k_B T}\right) \quad (1)$$

$$R_p = A_p \exp\left(-\frac{E_{a_p}}{k_B T}\right) \quad (2)$$

where A is the respective pre-exponent term, E_a is the activation energy, the subscripts o and p denote that for ohmic and polarization resistances, respectively, k_B is the Boltzmann constant, and T is the absolute temperature. When plotting $\log R_o$ vs. $1/T$ in **Figure 3b**, we found the curves of

differently treated cells are all parallel to each other; and the same also holds for R_p in **Figure 3c**. This means that the treatment does not affect the activation energy of R_o and R_p (similar activation energy of $E_{a,o}=0.358\pm 0.001$ eV for R_o and $E_{a,p}=0.903\pm 0.003$ eV for R_p are deduced for differently treated cells; **Figure 3d**, fitting details in **Supplementary Table S5**). Instead, it modifies R_o and R_p by changing only A_o and A_p . This is distinct from the practice of enhancing the kinetics by lowering the activation energy. Remarkably, if one calculates the enhancement factor for $1/A_o$ and $1/A_p$ in differently treated cells over the $1/A_o^0$ and $1/A_p^0$ in the untreated cell, the data are all close to the line with a slope of unity in A_o^0/A_o vs. A_p^0/A_p plot in **Figure 3e**. It further allows us to normalize using a dimensionless reduced temperature $k_B T/E_a$ and a dimensionless relative “resistance” R , and collapse all the data into a single curve in Arrhenius plot **Figure 3f**. (See details in **Supplementary Figure S8**.) This indicates a single mechanism responsible for the simultaneously lowered R_o and R_p , and it works by lowering their pre-exponential factor without changing the mechanisms of electrode reactions and proton conduction (inferred by unchanged activation energy). Very likely, it is because of the increased true contact area between oxygen electrode and electrolyte.

Full-cell performance

The lowered cell resistance enhances full-cell performance for PCEC/PCFC operations. In PCEC, the feedstocks are pure H_2 for the hydrogen electrode and $O_2+30\%$ H_2O for the oxygen electrode. When a voltage larger than OCV (e.g., 1.04 V at 600 °C) is applied, the absolute value of the current density j (defined as being negative in PCEC and positive in PCFC) characterizes the cell performance. As shown in **Figure 4a**, at the same applied voltage, larger $|j|$ is achieved in treated cells than in the untreated ones. A 2.8-fold increment over the untreated cell is demonstrated in 10 min treated one at 1.4 V at 600 °C, reaching $|j|=3.07$ A cm^{-2} for PCEC. In addition, the 10 min treated cell demonstrates higher Faradic efficiency (**Supplementary Figure S9a**) and H_2 production rate (**Supplementary Figure S9b**) than the untreated one. In PCFC, the current density (positive) is also higher in treated cells at the same voltage (**Figure 4b**). A 2.5-fold increase over the untreated cell in peak power density P_{max} is demonstrated in 10 min treated one, reaching $P_{max}=1.18$ W cm^{-2} at 600 °C. Again, the 10 min treated cell shows the best electrochemical performance among all the cells within the entire range of investigated temperatures (see more data in **Supplementary Figure S10-S12**).

Notwithstanding the “standard” electrolyte and electrode compositions and readily processed cell architecture, the 10 min treated cell outperforms the reported PCFC data in the literature (**Figure 4c**, filled circles in red), offering P_{max} in the full temperature range for PCFCs^{3,16-19}, despite that our untreated cell lies on the lower end. We also compared the “apparent” proton conductivity σ (inferred from ohmic loss of EIS measurements and normalized by the dimension of the electrolyte membrane) of BZCYYb-based electrolyte in electrochemical cells^{3,20,21}. As shown in **Figure 4d**, σ in the 10 min treated cell (filled circles in red) is not only higher than the literature results, but also fully recovers its intrinsic, theoretical value in bulk BZCYYb samples (reaching ~97% of intrinsic conductivity, vs. only ~44% in the untreated cell).

Suppressed degradations

We next conducted accelerated degradation tests under high-current-density PCEC operations. At a constant applied voltage of 1.4 V at 600 °C, the 10 min treated PCEC has a high initial j of

around -3.24 A cm^{-2} and is stable over 200 h continuous operation (**Supplementary Figure S13a**, with 0.94% decay in $|j|$ in 0-100 h and 0.05% decay in 100-200 h). In comparison, the untreated cell not only has a smaller initial j (-1.35 A cm^{-2}), but also suffers from fast degradation (with 10.2% decay in $|j|$ in 0-100 h and 5.9% decay in 100-200h). (The cycling performances of the cells treated under other conditions and tested under the same PCEC condition are shown in **Supplementary Figure S14**, which are improved over the untreated cells but still worse than the 10 min treated one.) Post-testing analysis of the cell (fractured by us for sample preparation, not from electrochemical testing) revealed a severe delamination problem of the oxygen electrode (**Supplementary Figure S13b**) in the untreated cell after electrochemical cycling. Meanwhile, there is an obvious change in the fracture mode of the BZCYYb electrolyte layer, from intragranular cracking in the untested cell (**Supplementary Figure S15a**) to intergranular cracking. It indicates weakened grain boundary adhesion in the perovskite electrolyte, probably due to the generation of gas bubbles at grain boundaries²²⁻²⁶. In comparison, there is no observable oxygen electrode delamination, and BZCYYb retains its intragranular-cracking behavior in 10 min treated PCEC after 200 h testing (**Supplementary Figure S13c**; same as the untested cell, **Supplementary Figure S15b**). EIS measurements (**Supplementary Figure S16a** and **Table S6**) show increased R_o and R_p for the untreated cell after the PCEC testing, while R_o and R_p are similar for the 10 min treated cell before and after the testing. The polarization curves (**Supplementary Figure S16b**) further confirm the stable PCEC performance of the 10 min treated cell, while the untreated one shows lower initial performance and faster degradation. Therefore, we conclude that the treatment consistently improves the electrochemical, mechanical, and microstructural stabilities because of better interfacial bonding and higher electrochemical activity (lower overpotential in operation).

Optimizations towards lower- T operations

We generalized our findings to other interfaces and optimize the full cells to achieve improved performance at lower operating temperatures. On the electrolyte side, we decreased the thickness of BZCYYb from 22 μm to 16 μm . On the oxygen electrode side, in addition to PNC55, we synthesized the state-of-the-art candidates of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF), explored the compositional space of $\text{PrNi}_x\text{Co}_{1-x}\text{O}_{3-\delta}$ ($0 < x < 1$) to obtain $\text{PrNi}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ (PNC73) with the best performance, and engineered the porous electrode microstructure to obtain 3-dimensional $\text{PrNi}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ mesh (3D PNC73). These materials are tested in full cells (their microstructures shown in **Supplementary Figure S17**) under PCFC (**Supplementary Figure S18**) and PCEC operations (**Supplementary Figure S19**) at 600 °C with and without 10 min acid etching treatment. Our data demonstrate that the treatment effectively improves the cell performance in all cases, increasing the PCFC peak power density by 65%~180% (**Supplementary Figure S20a**; data at other temperatures summarized in **Supplementary Table S7**) and the PCEC current density by 60%~200% (**Supplementary Figure S20b**) at 1.4 V applied voltage. We confirmed the full-cell reliability by conducting the leakage tests (**Supplementary Figure S21**), evaluating fuel flexibility (using CH_4 and C_2H_6 , **Supplementary Figure S22**) and fuel efficiencies ($>98\%$ for all measured cells, **Supplementary Table S8**), and PCFC stability (0.07% decay over 200 h continuous operation at 0.75 V at 600 °C for the 10 min treated cell using PNC73 oxygen electrode, **Supplementary Figure S23**). The protonic full cell made of 16 μm BZCYYb electrolyte and 3D PNC73 oxygen electrode and with

10 min treatment shows exceptional PCFC and PCEC performance (**Figure 4e, 4f**), offering a peak power density of $\sim 1600 \text{ mW cm}^{-2}$ at $600 \text{ }^\circ\text{C}$, $\sim 1250 \text{ mW cm}^{-2}$ at $550 \text{ }^\circ\text{C}$, $\sim 900 \text{ mW cm}^{-2}$ at $500 \text{ }^\circ\text{C}$, $\sim 650 \text{ mW cm}^{-2}$ at $450 \text{ }^\circ\text{C}$, $\sim 470 \text{ mW cm}^{-2}$ at $400 \text{ }^\circ\text{C}$, and $\sim 290 \text{ mW cm}^{-2}$ at $350 \text{ }^\circ\text{C}$ (open stars in red in **Figure 4c**). This presents a major step in the practical utilization of ceramic fuel cells from $600 \text{ }^\circ\text{C}$ down to $350 \text{ }^\circ\text{C}$, which highlights the critical role of interfacial engineering in “all-solid-state” electrochemical devices.

Discussions

The coupled electrochemo-mechanics at the electrode-electrolyte interface affects the thermomechanical integrity, microstructural stability, electrochemical performance, and durability of ceramic electrochemical cells. While much attention has been paid to developing better catalysts and novel architecture of the active electrode, our work highlights the equal importance of properly integrating them with the solid electrolyte so that their “intrinsic” performance can be fully utilized in full cells. The mechanistic study shows that the proposed acid treatment recovers not only the intrinsic bulk proton conductivity of the electrolyte in full cells (considering the decreased ohmic resistance), but also the high activity of the BZCYYb/PNC55/gas triple-phase boundary in light of the decreased R_p . In a previous report³, the former was partially recovered by a 100 nm-thick dense PBSCF inter-layer (which is a mixed ionic-electronic conductor and fabricated by pulsed laser deposition) between the porous oxygen electrode (PBSCF) and the electrolyte ($\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$). Yet, the polarization resistance remained unchanged, which is different from the present study for the PNC55 model system. We believe the difference lies in the mechanism of the oxygen-electrode half reaction. In the case of PBSCF electrode, the half reaction primarily takes place at PBSCF/gas double-phase boundary, as demonstrated by dimensional analysis in **Ref. 3**. Furthermore, with the pulsed-laser-deposited dense inter-layer in full cells, there is no triple-phase boundary, as the electrolyte is not in direct contact with the inlet gas of the oxygen electrode. In the case of PNC55, the fact that R_o and R_p can be simultaneously decreased with similar ratios demonstrates that the half-reaction primarily takes place near the triple-phase boundary, given the somewhat lower proton conductivity in PNC55 compared to BZCYYb. It further suggests that the mixed-conductive PNC55 may have a weaker proton conductivity than PBSCF, thus its activity in full cells is more critically dependent on the oxygen electrode-electrolyte interface. This offers a plausible explanation for the lowered ohmic loss by interfacial modification: For the untreated cell, PNC55 has poor bonding and limited contact area with the BZCYYb electrolyte (**Supplementary Figure S24a**). So there are not enough reaction sites near the oxygen electrode-electrolyte interface, and a large portion of the interfacial reactions may need to happen at the surface of PNC55 particles relatively far away from the interface, enabled by proton conduction in PNC55 lattice. Such proton conduction in PNC55 would contribute to the ohmic loss of the full cell. In contrast, with the proper acid treatment, PNC55 now has good bonding and abundant contacts with the BZCYYb electrolyte (**Supplementary Figure S24b**). This means that there are sufficient reaction sites near the interface, and no extended proton conduction in PNC55 is required. Therefore, the intrinsic bulk proton conductivity can be achieved in full cells.

Regarding the improved interfacial bonding, there is an apparent contribution from the surface roughness. To mimic such a physical effect, we used sandpapers to mechanically polish the electrolyte surface before bonding the oxygen electrode. While polishing does increase the

surface roughness (**Supplementary Figure S25, S26**), we found that coarse-grit sandpapers can easily damage the electrolytes and cause gas leakage (**Supplementary Figure S27**); fine-grit sandpaper polishing only offers marginal performance benefits compared to the untreated cell, which is still much worse than the acid-treated one (**Supplementary Figure S28**). This demonstrates pronounced chemical rejuvenation effects in the acid treatment assisted interfacial bonding, in the removal of segregating elements and reactive bonding. The acid treatment is a simple and generic approach, and we believe it can be combined with other materials and architectures to enable more efficient and robust protonic ceramic devices.

Conclusions

To summarize, we demonstrated a simple acid treatment, which is completely compatible with the state-of-the-art multilayer processing technique of ceramic fuel/electrolysis cells, can rejuvenate the high-temperature annealed electrolyte surface, improve hetero-oxide bonding, and recover the intrinsic conductivity and activity of the components for maximum performance. The underlying mechanism is revealed, and the “unidentified origin” of residual ohmic losses is now understood. The scientific understanding, the practical solution, and the applicability to various interfaces provided here can help the rapid insertion of protonic ceramic electrochemical cells into the sustainable energy infrastructure, such as nuclear-heat-and-electricity driven production of chemical fuels for seasonal energy storage, and CO₂ capture and utilization, in an electrical grid strongly influenced by intermittent solar and wind generations. Beyond ceramic fuel cells, interfacial engineering and specially designed processing techniques are also critical to other electrochemical materials and devices, such as oxide cathodes of lithium-ion batteries²⁷⁻²⁹, all-solid-state batteries³⁰, and metal-ceramic interfaces.

Methods

Materials synthesis

BZCYYb was synthesized by a solid-state reaction method. Stoichiometric amounts of BaCO₃ (99.8% purity, Alfa Aesar), ZrO₂ (99% purity, Alfa Aesar), CeO₂ (99.9% purity, Alfa Aesar), Y₂O₃ (99.9% purity, Alfa Aesar), and Yb₂O₃ (99.9% purity, Alfa Aesar) were mixed by ball milling in ethanol for 12 h, followed by drying, grinding, and heat treatment at 1100 °C for 8 h to obtain phase-pure BZCYYb powders. PNC55 was synthesized by a Pechini method. Stoichiometric Pr(NO₃)₃·6H₂O (99.9% purity, Alfa Aesar), Ni(NO₃)₂·6H₂O (99% purity, Alfa Aesar), and Co(NO₃)₂·6H₂O (99% purity, Alfa Aesar) were dissolved in deionized water to prepare an aqueous solution containing 0.05 mol L⁻¹ Pr³⁺, 0.025 mol L⁻¹ Ni²⁺, and 0.025 mol L⁻¹ Co²⁺. 0.2 mol L⁻¹ glycol (99% purity, ACROS Organics) and 0.1 mol L⁻¹ citric acid (99% purity, Alfa Aesar) were next added. The prepared solution was heated to 80 °C on a hot plate with continuous stirring until converted to a gel. The obtained gel was heated to 350 °C, followed with an auto-ignition process to produce a black foamy intermediate product. Final PNC55 powders were obtained by annealing the intermediate product at 1100 °C for 4 h. LSCF, PBSCF, and PNC73 were similarly synthesized by the same Pechini method following their stoichiometries, with additional chemicals Sr(NO₃)₂ (99.0% purity, Alfa Aesar), Ba(NO₃)₂ (ACROS Organics), and Fe(NO₃)₃·9H₂O (99.95% purity, Sigma-Aldrich). 3D PNC73 was fabricated by a template-derived method. Stoichiometric Pr(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O were dissolved in deionized water to prepare a nitrate precursor solution containing 0.05 mol L⁻¹ Pr³⁺,

0.035 mol L⁻¹ Ni²⁺, and 0.015 mol L⁻¹ Co²⁺. A piece of fabric textile (Telio, Montreal, CA) was immersed into the precursor solution for 24 h and then heat-treated at 750 °C for 2 h to form the 3D PNC73 mesh.

Cell fabrication

Hydrogen electrode-supported cells were fabricated by a tape-casting process. To prepare green tapes of the hydrogen electrode, NiO and BZCYYb powders were mixed with 6:4 weight ratio by ball milling in ethanol and toluene for 24 h. Binder of polyvinyl butyral (PVB; Tape Casting Warehouse, Inc), plasticizer of butyl benzyl phthalate (BBP; Tape Casting Warehouse, Inc), and dispersant of fish oil (Tape Casting Warehouse, Inc) were next added, followed by ball milling for an additional 24 h to yield the desired slip rheology. Tape casting was performed using a laboratory tape casting machine. The thickness of hydrogen-electrode green tapes was controlled to be ~1 mm after drying at 37.8 °C for 4 h. Green tapes of electrolyte were prepared similarly without adding NiO and by controlling the thickness to ~0.12 mm (for the 22 μm thick BZCYYb electrolyte after sintering) or ~0.08 mm (for the 16 μm thick BZCYYb electrolyte after sintering) after drying. Three pieces of hydrogen-electrode green tapes and one piece of electrolyte green tape were laminated by a hot press at 70 °C under 4 ton for 5 h. Laminated green tapes were punched with 7/16-inch diameter and pre-sintered at 920 °C for 3 h to remove the organics. The co-sintering of hydrogen electrode-electrolyte bi-layer was conducted at $T_1=1400$ °C at 5 h (heating rate: 1 °C min⁻¹ to 1000 °C and 2 °C min⁻¹ to 1400 °C), followed by a furnace cooling. To treat the surface, 0.3 mL (0.53 mL/cm²) concentrated nitric acid (Alfa Aesar) was dropped on electrolyte surface of co-sintered hydrogen electrode-electrolyte bi-layer, waited for different times from 1 min to 15 min, and then washed by deionized water. To fabricate full cells, slurry of oxygen electrodes was prepared by mixing oxygen electrode powders with ethanol and a texanol-based binder (ESL ElectroScience) by ball milling and then brush-painted on electrolyte surface of the co-sintered hydrogen electrode-electrolyte bi-layer. For 3D PNC73 electrode, the heat-treated mesh was firstly bonded to electrolyte surface using a thin layer of painted PNC73 slurry. The surface area of oxygen electrode was controlled at ~0.178 cm². The painted cells were sintered at $T_2=1000$ °C for 4 h (heating rate: 3 °C min⁻¹), followed by furnace cooling.

Cell assembly and testing

Full cells were sealed in house-made reactor using Aremco cerambond 552 sealant with oxygen electrode-side up. Silver mesh was used as the current collector with attached silver wires as leads. After assembly, the cell was heated up to 600 °C (heating rate: 1 °C min⁻¹). When a temperature of 600 °C was reached, H₂ (flow rate: 20 mL min⁻¹) was fed into the hydrogen electrode to reduce NiO to metallic Ni. When the reduction process was completed, a bubbler was connected between gas inlet of hydrogen electrode and inward gas to hydrolyze H₂ with 3% steam. EIS measurements were conducted at OCV conditions at 400-650 °C, with a frequency range from 10⁵ to 0.1 Hz, an AC amplitude of 10 mV, and zero DC bias. Electrochemical tests of PCFCs and PCECs were conducted individually by a Solartron 1400 electrochemical working station after a stable OCV was observed at the set temperature. Current density-voltage curves and current density-power density curves under fuel-cell mode were measured by a Solartron 1400 & 1470 electrochemical working station after stable OCV was observed at the set temperature. Feedstock in oxygen electrode was pure O₂. Feedstock in hydrogen electrode was H₂ with 3% steam. Electrochemical

data under fuel-cell mode were collected at voltage range from OCV to 0.2 V at the set temperature. Continuous fuel cell operation was conducted at a constant applied voltage of 0.75 V at 600 °C up to 200 h. Under electrolysis mode, the feedstock was pure H₂ (flow rate: 20 mL min⁻¹) in hydrogen electrode and O₂ with 30% steam in oxygen electrode. Electrochemical tests were conducted after stable OCV was observed at the set temperature, at voltage range from 1.5 V to OCV. Continuous electrolysis operation was conducted at a constant applied voltage of 1.4 V at 600 °C up to 200 h. PCFCs using CH₄ and C₂H₆ fuels were tested at 600 °C, using CH₄ or C₂H₆ (flow rate: 20 mL min⁻¹) with 3% steam as the feedstock of the hydrogen electrode and pure oxygen (flow rate: 60 mL min⁻¹) as the feedstock of oxygen electrode. Leakage tests were conducted at 600 °C with the feedstock of pure hydrogen (flow rate: 20 mL min⁻¹) for hydrogen electrode and air (flow rate: 60 mL min⁻¹) for oxygen electrode.

Characterizations

XRD measurements were conducted on a D8ADVANCE/Germany Bruker X-ray diffractometer using Ni-filter Cu K_α radiation (wavelength: 0.154056 nm). Microstructures and EDS mapping were inspected under a scanning electron microscope (SEM, JEOL 6700F). Surface chemistry was analyzed by XPS using Physical Electronics Versaprobe II X-ray Photoelectron Spectrometer. Surface roughness was inspected under AFM (Dimension Fastscan Atomic Force Microscopy, Bruker) using a tapping mode. To measure the peeling strength of the oxygen electrode-electrolyte interface, double-sided tapes were attached to both sides of full cells with a rectangular shape (length: 1.18 inch, width: 1 inch). The hydrogen-electrode side was stuck to the testing bed with oxygen electrode facing up and a scotch tape was next attached to the double-sided tape on the oxygen-electrode side. During peeling tests, oxygen electrode was peeled off from electrolyte while the force was recorded and converted to peeling strength. Cross-sectional samples for STEM were prepared using a Thermo Fisher Helios 600 focused ion beam (FIB)/SEM microscope. The samples were firstly coated with 10 nm carbon using a Denton DV502A Evaporator to minimize the beam damage and charging effects. Additive protective layers included an e-beam-deposited Pt layer (100 nm) and an ion-beam-deposited carbon layer (1 μm). The samples were thinned step by step by lowering ion voltages from 30 kV to 2 kV and currents from 0.92 nA to 89 pA. The surface damage caused by FIB was removed by Ar⁺ milling using a Fischione 1051 TEM Mill at room temperature with a voltage of 100 V and an angle of 7°. The HAADF images and EDS mapping were taken on a Thermo Fisher Themis Z-STEM with an acceleration voltage of 200 kV.

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Author contributions

W.B., W.W., Y.D., J.L., and D.D. conceived the project. W.B. and W.W. fabricated the cells and conducted electrochemical measurements. Y.D. conducted the theoretical analysis. Y.D. and W.B. analyzed the data. B.W. contributed to STEM characterizations. W.T. contributed to cell fabrications and SEM characterizations. M.Z. contributed to AFM characterizations. C.J. contributed to peeling test. H.D. contributed to development of oxygen electrode. W.F. contributed to XPS measurement. W.B., W.W., Y.D., J.L., and D.D. wrote the paper. All author discussed and contributed to writing. These authors contributed equally: Wenjuan Bian, Wei Wu.

Author information

Corresponding authors: Correspondence to Wei Wu (wei.wu@inl.gov), Yanhao Dong (dongyh@mit.edu), Ju Li (liju@mit.edu), Dong Ding (dong.ding@inl.gov). The authors declare no competing financial interests.

Data availability statement

Data supporting the findings in the present work are available in the manuscript or supplementary information. Additional data are available from the corresponding authors upon reasonable request.

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Figure legends

Figure 1 | Rejuvenated surface improves oxygen electrode-electrolyte interfacial strength. **a**, Schematic PCFC/PCEC fabrication process. **b,c**, Microstructure for untreated (**b**) and 10 min treated (**c**) electrolyte surface of co-sintered hydrogen electrode-electrolyte bi-layer. **d,e**, AFM for untreated (**d**) and 10 min treated (**e**) electrolyte surface. **f**, Peeling strength of cathode-electrolyte interface. Top inset of (**f**): Photo for peeling strength measurement.

Figure 2 | Reactive sintering at oxygen electrode-electrolyte interface improves interfacial bonding. **a-j**, High-angle annular dark-field (HAADF)-STEM image (**a**) of a sample slice near the oxygen electrode-electrolyte interface and the corresponding EDS mapping of Pr (**b**), Ni (**c**), Co (**d**), O (**e**), Ba (**f**), Zr (**g**), Ce (**h**), Y (**i**), and Yb (**j**). **k-t**, HAADF-STEM image (**k**) of a thinned sample slice at another region near the interface and the corresponding EDS mapping of Pr (**l**), Ni (**m**), Co (**n**), O (**o**), Ba (**p**), Zr (**q**), Ce (**r**), Y (**s**), and Yb (**t**). **u,v**, High-resolution HAADF-STEM of the two regions marked in (**k**), showing rough and well-bonded interface.

Figure 3 | Correlation between simultaneously lowered ohmic and polarization resistance. **a**, EIS at OCV at 600 °C. Z' and Z'' denote the real and imaginary parts of the complex impedance, respectively. R_o is taken from left intercept of the EIS curve with x -axis and R_p is taken from right intercept of the EIS curve with x -axis minus R_o . **b,c**, Arrhenius plot of ohmic (**b**) and polarization (**c**) resistance for differently treated cells. **d**, Calculated activation energy. **e**, Correlation between enhanced kinetics A_o^0/A_o vs. A_p^0/A_p . Dash line with a slope of unity is for the guidance of eyes. **f**, Arrhenius plot of relative “resistance” R against the inverse of reduced temperature $k_B T/E_a$. Cells made up of 22 μm thick BZCYYb electrolyte and PNC55 oxygen electrode and with different etching treatment conditions.

Figure 4 | Boosted electrochemical performance with modified oxygen electrode-electrolyte interface. **a**, Polarization curve in PCEC operations at 600 °C. **b**, Polarization and power density curves in PCFC operations at 600 °C. Cells made up of 22 μm thick BZCYYb electrolyte and PNC55 oxygen electrode and with different etching treatment conditions. Solid and open symbols in (**b**) are for left y -axis voltage and right y -axis power density P , respectively. **c,d**, Comparison of P_{max} (**c**) and σ (**d**) with literature data^{3,16-21}. Dissolved/doped NiO in protonic electrolytes were reported to lower the proton conductivity¹⁰. This phenomenon is not seen in our BZCYYb electrolyte in full cells, as it fully recovers the bulk value. **e,f**, Polarization curve in PCEC operations (**e**), and polarization and power density curves in PCFC operations (**f**) of cells made up of 16 μm thick BZCYYb electrolyte and 3D PNC73 oxygen electrode and with 10 min etching treatment before oxygen electrode was attached. P_{max} obtained in (**f**) were plotted as open stars in red in (**c**) for comparison.