

# Lowering the operating temperature of protonic ceramic electrochemical cells to <math><450^{\circ}\text{C}</math>

Fan Liu<sup>1</sup>, Hao Deng<sup>1</sup>, David Diercks<sup>2</sup>, Praveen Kumar<sup>2</sup>, Mohammed Hussain Abdul Jabbar<sup>3</sup>, Cenk Gumeçi<sup>3</sup>, Yoshihisa Furuya<sup>3</sup>, Nilesh Dale<sup>3</sup>, Takanori Oku<sup>4</sup>, Masahiro Usuda<sup>4</sup>, Pejman Kazempoor<sup>5</sup>, Liyang Fang<sup>1</sup>, Di Chen<sup>1</sup>, Bin Liu<sup>1</sup>, Chuancheng Duan<sup>1,\*</sup>

## Affiliations:

1. Department of Chemical Engineering, Kansas State University, Manhattan, KS, United States
2. Shared Instrumentation Facility, Colorado School of Mines, Golden, CO, United States
3. Nissan Technical Centre North America (NTCNA), Farmington Hills, MI, United States
4. Nissan Research Center, Nissan Motor Company Limited, Yokosuka, Kanagawa, Japan
5. School of Aerospace and Mechanical Engineering, University of Oklahoma, Norman, OK, United States

Corresponding author: [cduan@ksu.edu](mailto:cduan@ksu.edu)

## Abstract

Protonic ceramic electrochemical cells (PCECs) can be employed for power generation and sustainable hydrogen production. Lowering the PCEC operating temperature can facilitate its scaleup and commercialization. However, achieving high energy efficiency and long-term durability at low operating temperatures is a long-standing challenge. Herein, we report a simple and scalable approach for fabricating ultrathin, chemically homogeneous, and robust proton-conducting electrolytes and demonstrate an in-situ formed composite positive electrode,  $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}\text{-Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ , which significantly reduces ohmic resistance, positive electrode-electrolyte contact resistance, and electrode polarization resistance. The PCECs attain high power densities in fuel cell mode ( $\sim 0.75\text{ W cm}^{-2}$  at  $450^{\circ}\text{C}$  and  $\sim 0.10\text{ W cm}^{-2}$  at  $275^{\circ}\text{C}$ ) and exceptional current densities in steam electrolysis mode ( $-1.28\text{ A cm}^{-2}$  at  $1.4\text{ V}$  and  $450^{\circ}\text{C}$ ). At  $600^{\circ}\text{C}$ , the PCECs achieve a power density of  $\sim 2\text{ W cm}^{-2}$ . Additionally, we demonstrate the direct utilization of methane and ammonia for power generation at  $<450^{\circ}\text{C}$ . Our PCECs are also stable for power generation and hydrogen production at  $400^{\circ}\text{C}$ .

## Main text

### Introduction

Ceramic electrochemical cells based on both oxygen-ion conductors and proton-conducting oxides have been demonstrated for efficient power generation and green hydrogen production<sup>1-4</sup>. Ceramic electrochemical cells have key merits, including fuel flexibility in fuel cell mode and higher energy efficiency in steam electrolysis mode

compared to low-temperature polymer electrolyte membrane electrochemical cells<sup>5-8</sup>. However, the scaleup and commercialization of ceramic electrochemical cells have lagged behind those of polymer electrolyte membrane electrochemical cells, which is mainly ascribed to the high operating temperature of ceramic electrochemical cells (>500°C)<sup>9</sup>. Therefore, creating low-temperature ceramic electrochemical cells has been one of the primary challenges and opportunities in this research field (Figure 1a).

The operating temperature of solid oxide electrochemical cells based on oxygen-ion conductors (O-SOECs) has been successfully reduced to ~500°C<sup>10-14</sup>. However, due to the relatively high activation energy of oxygen-ion conduction, reducing the operating temperature of O-SOECs to <450°C is challenging<sup>10,15,16</sup>. Due to proton conduction having a lower activation energy than oxygen-ion conduction, protonic ceramic electrochemical cells (PCECs) have been recurrently researched and proposed to operate at <450°C<sup>17,18</sup>.

Only a handful of studies have reported that PCECs can operate at <450°C<sup>17-20</sup>. Depositing a dense interfacial layer between the electrolyte and positive electrode can reduce the ohmic resistance and increase the peak power density (PD) to 0.36 W cm<sup>-2</sup> on H<sub>2</sub>-air at 450°C<sup>19</sup>. To reduce the electrode polarization resistance, a highly porous PrBa<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>O<sub>6-δ</sub> (PBSCF-1) positive electrode using a complicated template method, which improved the mass transport kinetics, leading to a PPD of 0.41 W cm<sup>-2</sup> on H<sub>2</sub>-O<sub>2</sub> at 400°C<sup>20</sup>. A recent study reported that employing an acid-etched electrolyte and a positive electrode fabricated via this template method further increased the PPD to 0.65 W cm<sup>-2</sup> on H<sub>2</sub>-O<sub>2</sub> at 450°C<sup>18</sup>. Furthermore, most of these approaches that have been validated are either complicated or unscalable. Therefore, it is urgent to demonstrate straightforward and scalable methods to fabricate PCECs with low-resistance electrolytes and active positive electrodes to achieve good PCEC performance at <450°C.

Supplementary Figure 1 shows a PCEC ohmic conductivity analysis, estimated by dividing the electrolyte thickness by the ohmic area specific resistance ( $ASR_o$ ). There is a discrepancy between intrinsic electrolyte conductivity and PCEC ohmic conductivity, implying that PCEC devices contribute additional ohmic resistance, mainly high electrolyte-grain boundary resistance and positive electrode-electrolyte contact resistance. Therefore, PCECs should be better fabricated to optimize their microstructure, aiming to minimize grain boundary resistance while enhancing the bonding between the electrode and electrolyte, particularly the weakly bonded positive electrode-electrolyte interface created in a separated high-temperature step. Figure 1b indicates that the electrode polarization area specific resistance ( $ASR_p$ ) accounts for 70-90% of the total resistance at 450°C. Furthermore, it has been widely recognized that the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which occur at the positive electrode, tend to be more sluggish with decreasing operating temperatures. These results suggest that both the electrolyte and positive electrode should be optimized to enhance PCEC performance at <450°C.

Herein, we report approaches for overcoming these challenges and fabricating high-performance low-temperature (<450°C) PCECs (LT-PCECs). We demonstrate PCECs that achieve a high fuel cell power density of ~0.75 W cm<sup>-2</sup> at 450°C. At an operating temperature of as low as 275°C, a practical power density of ~0.10 W cm<sup>-2</sup> is achieved.

Moreover, at 1.4 V and 450°C, our PCECs attain a promising current density of -1.28 A cm<sup>-2</sup> in steam electrolysis mode. Furthermore, durable operation at 400°C in both fuel cell and electrolysis modes are demonstrated.

### Strategies to validate PCECs run at <450°C

To validate PCECs that can run at <450°C, LT-PCECs with ultrathin, bamboo-structured (single-grain thick), and chemically homogeneous electrolytes were first fabricated via a scalable and cost-effective ultrasonic spray-coating process, which minimizes the resistance of proton conduction across the grain boundary (Figure S2), reducing the  $ASR_O$  attributed to the electrolyte (Figure 1c). Second, we demonstrate an *in-situ* formed positive electrode composed of Ba<sub>0.62</sub>Sr<sub>0.38</sub>CoO<sub>3-δ</sub>-Pr<sub>1.44</sub>Ba<sub>0.11</sub>Sr<sub>0.45</sub>Co<sub>1.32</sub>Fe<sub>0.68</sub>O<sub>6-δ</sub> (BSC+PBSCF). This positive electrode reduces the coefficient of thermal expansion (CTE), improves the positive electrode-electrolyte bonding, and reduces the contact resistance, further reducing the  $ASR_O$ . Additionally, this positive electrode simultaneously facilitates the surface oxygen exchange and bulk oxygen-ion diffusion, particularly at low operating temperatures, which significantly decreases the  $ASR_P$  (Figure 1d), allowing an extraordinarily low  $ASR_P$  of 0.38 Ω cm<sup>2</sup> to be achieved at 450°C [versus the 0.76 Ω cm<sup>2</sup>  $ASR_P$  of the state-of-the-art positive electrode]. The LT-PCECs with low-resistance electrolytes and the positive electrodes developed in this work exhibit remarkable performance at <450°C (Figure 1e). For example, at 400°C, a fuel cell PPD of ~0.34 W cm<sup>-2</sup> is achieved using H<sub>2</sub>, which doubles the PPD of the current state-of-the-art PCECs. In the steam electrolysis mode, a durable current density of -1.28 A cm<sup>-2</sup> is obtained at 1.4 V and 450°C. We demonstrated PCEC fuel cell operation at 275°C, with a practical PPD of ~0.1 W cm<sup>-2</sup> achieved on H<sub>2</sub>-O<sub>2</sub>. Good stability is also demonstrated at 400°C in terms of both power generation (degradation rate <0.07 mV/h) and hydrogen production (degradation rate <0.15 mV/h). Figure 1f and Table S1 show that LT-PCECs can produce hydrogen with a comparable or higher rate and electrolysis energy efficiency at 400°C compared to the previously reported PCECs that operate at >500°C (supplementary video 1).

### Readily fabricated ultrathin proton-conducting electrolyte

Poor sinterability and Ba evaporation are two main challenges associated with proton-conducting electrolyte fabrications<sup>21</sup>. It is also well known that the grain boundary is less conductive than the grain bulk (Supplementary Figure 3)<sup>22,23</sup>. Therefore, fabricating PCECs with ultrathin, large-grain, and chemically homogeneous electrolytes is one of the most essential steps for realizing high performance. Herein, we employed an ultrasonic spray coating system to coat electrolyte on the negative electrode (Figure 2a), which is scalable and reproducible (supplementary video 2). Additionally, high-quality PCECs with relatively large areas have been fabricated using the ultrasonic spray coating system, which yields dense and defect-free PCEC electrolytes with a uniform thickness of ~3.5 μm, further validating the feasibility of employing this process for large-scale PCEC manufacturing (Supplementary Figures 4-9, supplementary video 3). Furthermore, the ultrasonic spray coating improves the PCEC electrolyte microstructure and conductivity compared to the traditional compressed air spray coater (Supplementary Figures 10-11).

The SEM images of the electrolyte cross-section show that the electrolyte layer is dense, with a uniform thickness of  $\sim 3 \mu\text{m}$  (Figure 2b). Figure 2b and Supplementary Figure 2a show that the electrolyte exhibits a bamboo structure, leading to a low  $ASR_O$ . PCECs manufactured via this simple coating and cosintering process are reproducible (Supplementary Figure 12). Figure 2c shows the electrolyte surface has an average grain size of  $\sim 8 \mu\text{m}$ , much larger than the electrolyte thickness ( $\sim 3 \mu\text{m}$ ). Therefore, the PCEC obtained via this process has a quasi-2D electrolyte, which exhibits a low grain boundary area and reduces  $ASR_O$  (Figure 2d).

The high-angle annular dark field (HAADF) image (Figure 2e) also displays that the ultrathin electrolyte layer exhibits a bamboo structure where the grain boundaries appear perpendicular to the negative electrode. Moreover, the energy dispersive X-ray spectroscopy (EDS) line scanning profile (Figure 2f) and mapping images (Figures 2g and 2h) at both the microscale and nanoscale indicate that this thin electrolyte layer is chemically homogeneous. No element segregation or depletion was observed across the electrolyte or at the grain boundary. The EDS line scanning profile (Supplementary Figure 13) across the electrolyte also shows a homogeneous elemental distribution, implying that the chemical composition is consistent throughout the electrolyte. Element segregation at the grain boundary can lead to a positive potential, which decreases proton conduction<sup>24,25</sup>. Figures 2h and 2i show that the chemical composition of the grain boundary appears to be homogenous within the bulk at the nanoscale, which is beneficial for high proton conductivity. The PCECs fabricated in this work achieved an  $ASR_O$  that is lower or comparable to that of PCECs fabricated via costly and complicated PLD (Figure 1c).

### **Reduced $ASR_P$ with in-situ formed positive electrode**

Many positive electrode materials and advanced electrode processing techniques have been demonstrated to enhance the electrocatalytic activity of positive electrodes and reduce  $ASR_P$ <sup>2,17,26-32</sup>. However, one of the state-of-the-art positive electrodes,  $\text{Gd}_{0.3}\text{Ca}_{2.7}\text{Co}_{3.82}\text{Cu}_{0.18}\text{O}_{9-\delta}$ , exhibited an  $ASR_P$  of  $>0.7 \Omega \text{ cm}^2$  on  $\text{H}_2$ -air at  $450^\circ\text{C}$ <sup>32</sup>. The target of this study was to reduce the  $ASR_P$  to  $<0.4 \Omega \text{ cm}^2$  at  $450^\circ\text{C}$ , which would further improve the PCEC performance at  $<450^\circ\text{C}$ . Herein, we aimed to develop an in-situ formed composite positive electrode (BSC+PBSCF) composed of a perovskite phase ( $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ , PBSCF-2) and  $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$  (BSC) nanoparticles dispersed on (or mixed with) the perovskite phase to reduce the  $ASR_P$ . This composite positive electrode is denoted as in-situ formed BSC+PBSCF (or BSC+PBSCF). As shown in Figure 3a and Supplementary Table 2, the XRD Rietveld refinement results confirm that BSC+PBSCF consists of a PBSCF-2 phase (space group: P4/mmm, 69.4 wt. %,  $a=b=3.83 \text{ \AA}$ ;  $c=7.72 \text{ \AA}$ ) and a BSC phase (space group: P63/mmc, 30.6 wt. %,  $a=b=5.56 \text{ \AA}$ ;  $c=4.75 \text{ \AA}$ ). The obtained compositions are in good agreement with the subsequently obtained EDS results (Figures 3c-e and Supplementary Table 3), which show that BSC+PBSCF is composed of  $\sim 30$  wt. % BSC and  $\sim 70$  wt. % PBSCF-2.

Transmission electron microscopy (TEM) and EDS were performed to further determine the microstructure, crystal structure, and composition of BSC+PBSCF. As displayed in Figure 3b, BSC+PBSCF exhibits a particle size of  $\sim 20$ - $40 \text{ nm}$ . The high-resolution TEM

(HR-TEM) images shown in Figure 3c confirm that BSC+PBSCF is composed of two fully crystallized phases, PBSCF-2 and BSC. Four main lattice planes with interplanar distances of 0.199 nm, 0.270 nm, 0.340 nm, and 0.283 nm were observed, which corresponded to PBSCF-2 (200), PBSCF-2 (102), BSC (101), and BSC (110), respectively. The d-spacings determined by TEM are consistent with those calculated using the XRD refinement results (Table S2), affirming that the chemical compositions used for XRD refinement are reliable. Additionally, the EDS mapping images show that the BSC phase is Ba-rich and contains a negligible amount of Pr and Fe (Figure 3d). Both PBSCF-2 and BSC contain high amounts of Sr and Co. Therefore, the region where Ba is sparse, whereas Pr and Fe are abundant, is assumed to be the PBSCF-2 phase (Figure 3d). Moreover, the areas that contain Ba, Sr, and Co but not Pr and Fe are assumed to be the BSC phase. The EDS spectra shown in Figure 3e indicate the composition of PBSCF-2 is close to  $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ , while that of BSC is identified as  $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$  (Table S3). The stoichiometries of these two phases were then used for the XRD refinement shown in Figure 3a. Additionally, according to the mole balance of Pr and the EDS results, it was determined that BSC+PBSCF contains ~30.0 wt. % BSC and ~70.0 wt.% PBSCF-2, consistent with the results obtained from the XRD refinement (~30.6 wt. % BSC and ~69.4 wt.% PBSCF-2), affirming that the stoichiometries and chemical compositions are valid. Additional TEM and EDS mapping images shown in Supplementary Figures 14-15 further affirm the composition of BSC+PBSCF.

As presented in Figure 4a and Supplementary Figure 16, we determined the  $ASR_p$ , which clearly shows that BSC+PBSCF has an improved electrocatalytic activity. At 400°C, the  $ASR_p$  of BSC+PBSCF is 1.22  $\Omega\text{ cm}^2$ , which is 14.5% of the  $ASR_p$  achieved with PBSCF-1 (8.37  $\Omega\text{ cm}^2$ ). Additionally, the Arrhenius plots shown in Figure 4a indicate that BSC+PBSCF exhibits a smaller activation energy (86 kJ/mol) than PBSCF-1 (103 kJ/mol), suggesting that BSC+PBSCF can function as a promising positive electrode at lower operating temperatures. Oxygen temperature-programmed desorption ( $\text{O}_2$ -TPD) experiments were conducted to investigate the oxygen mobility and diffusion of BSC+PBSCF and PBSCF-1 (Figure 4b). Two main peaks were observed for both positive electrode materials, possibly due to the oxygen molecules adsorbed on the surfaces exhibiting different binding energies. The corresponding peak temperatures of BSC+PBSCF (231°C and 292°C) are lower than those of PBSCF-1 (322°C and 388°C), indicating that the surface oxygen on BSC+PBSCF is more easily released from the surface than that on PBSCF-1, which leads to enhanced oxygen surface oxygen exchange kinetics<sup>33</sup>. Both surface oxygen exchange and bulk oxygen-ion diffusion kinetics are essential for high OER and ORR activities, which were determined by electrochemical conductivity relaxation (ECR) experiments (Figures 4c-4d and Supplementary Figures 17-18). Figure 4c shows that BSC+PBSCF has higher bulk oxygen-ion diffusion coefficients ( $D_{chem}$ ) than PBSCF-1, suggesting that BSC+PBSCF has enhanced oxygen-ion diffusion in the bulk. Furthermore, the surface oxygen exchange coefficient ( $k_{chem}$ ) of BSC-coated PBSCF-2 (BSC+PBSCF) is much higher than that of PBSCF-1 (Figure 4d). At 550°C, the  $k_{chem}$  of BSC+PBSCF is more than twice that of PBSCF-1, implying that the BSC phase is beneficial for accelerating the surface oxygen exchange kinetics. This is also consistent with the  $\text{O}_2$ -TPD profiles. Figures 4c and 4d show that the activation energies of BSC+PBSCF associated with  $D_{chem}$  and  $k_{chem}$  are both lower than those of PBSCF-1, further highlighting its promising activity at lowered

operating temperatures. Therefore, the synergy between PBSCF-2 and BSC results in improved electrocatalytic activity, especially at <450°C.

Figure 4e displays the electrochemical impedance spectroscopy (EIS) of PCECs with different positive electrodes collected at 450°C under OCV conditions. With BSC+PBSCF applied as the positive electrode, the ASRp is reduced by a factor of five. The corresponding distribution of relaxation time (DRT) analysis was conducted and presented in Figure 4f. The DRT plots can be divided into three main regions, including the low-frequency (LF, <100 Hz), intermediate-frequency (MF, 100-10000 Hz), and high-frequency (HF, >10000 Hz) regions, which correspond to oxygen mass transport, oxygen exchange on the positive electrode, and the charge transfer process, respectively<sup>34,35</sup>. First, BSC+PBSCF exhibits substantially smaller LF peaks, indicating that oxygen gas diffusion is accelerated over BSC+PBSCF, which is attributed to the porous structure of the BSC+PBSCF electrode. The BET-measured surface area of BSC+PBSCF is 9.2 m<sup>2</sup>/g (Supplementary Figure 19 and Supplementary Table 4), which is ~2 times as high as that of PBSCF-1 (4.8 m<sup>2</sup>/g), agreeing well with the LF peak results. Second, the MF peaks, which are associated with the surface exchange processes, of BSC+PBSCF are also much smaller than those of PBSCF-1, further affirming that BSC+PBSCF has enhanced surface oxygen exchange kinetics, which is consistent with the ECR results (Figure 4d). Additionally, both BSC+PBSCF and PBSCF-1 show similar HF peaks, which are smaller than the LF and MF peaks, indicating that the charge transfer processes on both electrodes are not rate-limiting steps.

Spin-polarized DFT calculations were performed to investigate bulk oxygen vacancy formation ( $\Delta E_{Ov}$ ) and oxygen diffusion in PBSCF-1, PBSCF-2, and BSC to understand the observed experimental behaviors (Supplementary note 2).  $\Delta E_{Ov}$  associated with Ov1 and Ov2 follow a decreasing order of PBSCF-1 > PBSCF-2 > BSC, indicating a gradual increase in the likelihood of oxygen vacancy formation. As shown in Figure 5a-b, the oxygen atom located at the Ov2 site of PBSCF-1 is bonded with four Sr and two Co atoms, while the Ov1 site in PBSCF-1, the Ov1 and Ov2 sites in PBSCF-2 are surrounded by four Sr, one Co, and one Fe atoms. Hence, based on DFT calculations, we can conclude that a higher concentration of Sr and a proper mixing of Fe help stabilize Ov and lower the oxygen vacancy formation energies. The chemical environment for Ov1 and Ov2 in the hexagonal BSC cell is different, in which they are surrounded by two Ba, two Sr, and two Co atoms (Figure 5c).

BSC+PBSCF displays a superior ORR performance owing to the higher oxygen diffusivity. As shown in Figure 5d, the energy barriers ( $E_{a,bulk}$ ) exhibit a decreasing order of BSC (1.05 eV) > PBSCF-1 (0.88 eV) > PBSCF-2 (0.51 eV). The  $E_{a,bulk}$  in PBSCF-2 is 0.37 eV lower than in PBSCF-1. The energy differences will have a meaningful impact on atomic oxygen diffusion and correlate very well with the measured diffusivities (Figure 4c).

Using the DFT results, we also attempted to understand the observed surface exchange rates (Figure 4d). It has been reported that<sup>36</sup> the oxygen surface exchange coefficient ( $k_{chem}$ ) varies linearly against the bulk oxygen vacancy formation energy ( $\Delta E_{Ov}$ ). Furthermore, a lower  $\Delta E_{Ov}$  would indicate a higher  $k_{chem}$ . As such, the high  $k_{chem}$  observed

in BSC can also be successfully explained based on the trends in the calculated oxygen vacancy formation energies.

Combining the trends in oxygen diffusivity and the surface exchange coefficients, a synergistic effect may be supported in the BSC+PBSCF system, in which the BSC top layer facilitates surface oxygen exchange. Then, PBSCF-2 enhances the bulk diffusions with low  $E_{a,bulk}$ , both owing to the promoted oxygen vacancy formations.

### Enhanced positive electrode-electrolyte interfacial bonding

Figure 6a presents the  $ASR_O$  of PCECs equipped with the developed BSC+PBSCF and PBSCF-1 positive electrodes, which indicates that BSC+PBSCF simultaneously reduces the ohmic resistance and the corresponding activation energy. The  $ASR_O$  of PCECs with BSC+PBSCF is reduced from  $0.233 \Omega \text{ cm}^2$  to  $0.169 \Omega \text{ cm}^2$  at  $500^\circ\text{C}$ . Additionally, the activation energy of the  $ASR_O$  decreases to  $30 \text{ kJ/mol}$  [versus  $33 \text{ kJ/mol}$  for the PCEC with PBSCF-1 positive electrode]. The dilatometry results (Figure 6b) indicate that BSC+PBSCF positive electrode has a lower coefficient of thermal expansion (CTE,  $18.0 \times 10^{-6} \text{ K}^{-1}$ ) than that of the PBSCF-1 positive electrode ( $23.4 \times 10^{-6} \text{ K}^{-1}$ ), which can improve the positive electrode-electrolyte compatibility and interfacial bonding. Additionally, the *in-situ* formed BSC+PBSCF achieves a much lower CTE than other Co-based positive electrodes reported in the literature (Supplementary Figure 20). Peeling strength testing was then conducted to quantify the positive electrode-electrolyte bonding strength and determine the coherence of the positive electrode-electrolyte interface (Figure 6c, Supplementary Figures 21 and 22). A more uniform and stronger peeling strength was obtained by using the BSC+PBSCF positive electrode, indicating that BSC+PBSCF leads to a positive electrode-electrolyte interface with improved chemical bonding and coherence, which reduces the positive electrode-electrolyte contact resistance and consequently decreases the  $ASR_O$ . As summarized in Figure 6d, the BSC+PBSCF positive electrode exhibits an average peeling strength of  $6.8 \text{ N}$ ,  $42\%$  higher than that of the PBSCF-1 positive electrode ( $4.8 \text{ N}$ ). Therefore, the BSC+PBSCF positive electrode simultaneously improves the electrochemical performance and reduces the ohmic resistance at lower operating temperatures. Figure 6e displays the HAADF and EDS images of the positive electrode-electrolyte interface. At the interface, both BSC and PBSCF-2 were observed, which might enhance the chemical bonding of the positive electrode with the electrolyte, thus, reducing  $ASR_O$ .

### LT-PCEC electrochemical performance and long-term durability

Fabricating PCECs via tape-casting followed by an ultrasonic spray-coating process and employing the in-situ formed BSC+PBSCF as the positive electrode allowed the creation of high-performance PCECs operated at  $<450^\circ\text{C}$  (Supplementary Figure 23). The open-circuit voltages (OCVs) for all PCECs under fuel cell operation are higher than  $1.05 \text{ V}$  (Figures 7a-7b), indicating that the PCECs with an ultrathin and bamboo-structured electrolyte do not exhibit obvious electronic leakage or gas leakage. The created LT-PCECs achieve a much higher fuel cell performance than the PCECs with the PBSCF-1 positive electrode and literature results (Figure 1e, Figure 7c). With air fed to the positive electrode, a PPD of  $1.64 \text{ W cm}^{-2}$  is attained at  $600^\circ\text{C}$  (Figure 7a), greater than that of previously reported PCEC fuel cells in the literature<sup>17,19,21,31,32,37-39</sup>. To compare these

PCECs with the most recently developed PCECs<sup>18</sup>, oxygen is fed to the positive electrode, and a PPD of  $\sim 2.0 \text{ W cm}^{-2}$  is achieved at  $600^\circ\text{C}$  (Supplementary Figures 24-25), which is higher than that of PCECs with acid-etched electrolytes and 3D positive electrodes<sup>18</sup> (Supplementary Figure 26). The PCECs also achieve remarkable performance at  $<450^\circ\text{C}$ . For example, a PPD of  $\sim 0.77 \text{ W cm}^{-2}$  is reached at  $450^\circ\text{C}$  (Figure 7b). Additionally, at  $450^\circ\text{C}$ , the BSC+PBSCF positive electrode facilitates an  $\sim 2.7$ -fold increase in PPD compared to the PBSCF-1 positive electrode ( $0.77 \text{ W/cm}^2$  versus  $0.29 \text{ W/cm}^2$ ; Figure 7c). This work also demonstrated that PCEC operated at  $275^\circ\text{C}$  delivers a practical fuel cell PPD of  $\sim 0.1 \text{ W cm}^{-2}$  on  $\text{H}_2\text{-O}_2$  (Figure 7b). Several LT-PCECs were tested to validate the reproducibility (Figures 7a-7d and Supplementary Figures 27-34).

The PCECs operating at  $<450^\circ\text{C}$  also present good fuel flexibility. With ammonia fed to the anode, without using any additional ammonia cracking catalysts, the PCECs achieve PPDs of  $0.65 \text{ W cm}^{-2}$  at  $500^\circ\text{C}$ ,  $0.28 \text{ W cm}^{-2}$  at  $450^\circ\text{C}$ , and  $0.16 \text{ W cm}^{-2}$  at temperatures as low as  $400^\circ\text{C}$  (Figure 7e, Supplementary Figure 35). The direct-ammonia PCECs also attain outstanding performance at  $600\text{-}500^\circ\text{C}$ , achieving a PPD of  $1.38 \text{ W cm}^{-2}$  at  $600^\circ\text{C}$ , which well exceeds the results reported in the literature (Figure 7f)<sup>40-46</sup>. After conducting the performance evaluation under ammonia, there is no evidence of grain boundary fractures, indicating that the ultrathin electrolyte fabricated in this work is robust under ammonia (Supplementary Figure 35c). The PCEC performance on ammonia is comparable to that on  $\text{H}_2$  (Supplementary Figure 36), indicating that the negative electrode is active for ammonia cracking, which suggests that ammonia can serve as a  $\text{H}_2$  carrier for power generation in PCECs.

PCECs can directly utilize methane for power generation. Herein, a rationally designed internal steam methane reforming (SMR) catalyst,  $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ , was coated on a PCEC negative electrode to further achieve high performance using methane as the fuel at low operating temperatures. Its catalytic activity was first evaluated in a packed bed reactor, which indicates that the synergy between Ni and Ru enhances the SMR activity<sup>47,48</sup>. For example, as shown in Figure 7g,  $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_2$  achieves the highest  $\text{CH}_4$  conversion at  $500^\circ\text{C}$ , which is  $\sim 35\%$  higher than that of  $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$  and  $\sim 26\%$  higher than that of  $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$ . At  $450^\circ\text{C}$ , the  $\text{CH}_4$  conversion achieved over  $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_2$  reaches  $\sim 27\%$ , suggesting that the PCEC equipped with this catalyst can deliver viable power density. At  $500^\circ\text{C}$ , as shown in Figure 7h, we demonstrate a PPD of  $0.55 \text{ W cm}^{-2}$  on methane [versus, e.g.,  $0.37 \text{ W cm}^{-2}$  at  $500^\circ\text{C}$  for state-of-the-art intermediate-temperature solid oxide fuel cells (SOFCs); Figure 7i], which approaches the PPD performance of PCECs on pure  $\text{H}_2$  (Supplementary Figure 37). The PCEC fuel cell performance on methane shows that a viable PPD is still achieved at  $400^\circ\text{C}$ . The LT-PCEC fuel-cell performance using both ammonia and methane validates the fuel flexibility of PCECs operating at  $<450^\circ\text{C}$ .

We also evaluated the PCECs for hydrogen production in electrolysis mode at  $<450^\circ\text{C}$ . Figure 7j shows the PCECs attain a current density of  $-1.28 \text{ A cm}^{-2}$  at  $1.4 \text{ V}$  and  $450^\circ\text{C}$  [versus, e.g.,  $1.04 \text{ A cm}^{-2}$  at  $450^\circ\text{C}$  for the state-of-the-art PCECs<sup>18</sup>]. Furthermore, Figure 7k shows that the PCECs achieve reasonable Faradaic efficiency ( $\text{FE}\% > 80\%$ , Supplementary note 3). Moreover, at  $400^\circ\text{C}$  and a current density of  $0.6 \text{ A cm}^{-2}$ , the cell-level electrical energy-to-chemical energy conversion efficiency reaches  $77\%$  (Figure 7l,

Supplementary Figure 38), validating the feasibility of producing hydrogen with PCECs at <math><450^{\circ}\text{C}</math>.

We then tested PCEC stability for power generation and hydrogen production at <math><450^{\circ}\text{C}</math>. At a current density of <math>300\text{ mA cm}^{-2}</math> and <math>400^{\circ}\text{C}</math>, the PCEC continuously operated in fuel cell mode for 100 h, achieving a degradation rate of <math><0.07\text{ mV/h}</math> (Figure 8a). After the stability test, there is no observable change in the microstructure and no electrolyte cracking (Figure 8b and Supplementary Figure 39). The positive electrode-electrolyte interfaces show no delamination, suggesting that the interfacial bonding is good and the thermal expansions are compatible.

Figure 8c shows the long-term stability test data of the PCECs in electrolysis mode at <math>400^{\circ}\text{C}</math>. The PCEC operated at a current density of <math>-0.6\text{ A cm}^{-2}</math> for >250 h, achieving a low degradation in the applied voltage (<math><0.15\text{ mV/h}</math>) and FE. These results validate the feasibility of durable  $\text{H}_2$  production with PCECs at <math>400^{\circ}\text{C}</math>, dramatically reducing the required operating temperature and exceeding previous PCEC performance. The stable terminal voltage and FE suggest no noticeable degradation. Postmortem microstructural analysis shows no evidence of degradation after this long-term durability testing (Figure 8d). Specifically, no cracking was observed on the electrolyte, essential for high Faradaic efficiencies. No evidence of positive electrode decomposition or electrolyte-positive electrode delamination is shown in the SEM images, highlighting the robustness of the PCECs for  $\text{H}_2$  production.

## Conclusions

By fabricating ultrathin, single-grain thick, chemically homogeneous, and low-resistance electrolytes and developing an *in-situ* formed composite positive electrode, we successfully fabricated high-performance PCECs capable of both power generation and hydrogen production at <math><450^{\circ}\text{C}</math>. The PCEC electrolyte fabricated via the simple and scalable process achieves a resistance comparable to or lower than that of PCECs prepared via costly and complicated processes. Both experimental and computational studies have revealed that this *in-situ* formed BSC+PBSCF positive electrode has a significantly improved electrocatalytic activity and reduced positive electrode-electrolyte contact resistance. At <math>450^{\circ}\text{C}</math>, the PCECs developed in this work achieve exceptional performance in both fuel cell and steam electrolysis modes. The PCECs display long-term durable fuel cell performance and remarkable durability in electrolysis mode at <math>400^{\circ}\text{C}</math>. These reproducible results further highlight the promise of using PCECs for efficient power generation and hydrogen production at a large scale.

## Methods

### Negative electrode powder with low Ba deficiency

The negative electrode powder was composed of  $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (BCZYYb7111), NiO, and corn starch with a weight ratio of 2:3:1. BCZYYb7111 was synthesized via a fast-heating solid-state sintering (SSS) method. In brief, a stoichiometric amount of  $\text{BaCO}_3$ ,  $\text{CeO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and 1 wt. % NiO (the amount of NiO was

based on the total weight of crystallized BCZYYb7111) was first ball-milled for 48 h. After drying at 120°C for 24 h, the homogeneous mixture was calcined at 1350°C with a fast-heating rate of 10°C/min for 5 h in the air to crystallize BCZYYb7111, which was then crushed into a fine powder. The obtained BCZYYb7111 powder was then ball-milled again and dried at 120°C overnight. The as-synthesized BCZYYb7111 fine powder was then ball-milled with NiO and corn starch for 48 h. After drying at 120°C, a negative electrode powder with a low Ba deficiency was synthesized.

### **Negative electrode functional layer powder**

The negative electrode functional layer powder was composed of 40 wt.% BaCe<sub>0.7</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub> (BCZYYb7111) and 60 wt.% NiO. The powder synthesis procedure was the same as that of the abovementioned negative electrode powder synthesis process. The only difference was that no corn starch was added.

### **BaCe<sub>0.4</sub>Zr<sub>0.4</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub> (BCZYYb4411) electrolyte powder**

BCZYYb4411 was synthesized via a wet-chemistry method<sup>49</sup> using Y<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O, and zirconyl nitrate solution (35 wt. % in diluted nitric acid) as the precursors. Briefly, the calculated amounts of Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> were first dissolved in 20 wt.% diluted nitric acid solution at 100°C to obtain yttrium and ytterbium nitrate solutions. Stoichiometric amounts of Ba(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O, and zirconyl nitrate were subsequently added into the yttrium and ytterbium nitrate solution, which was stirred for 30 mins. The complexing and chelating agents, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were added to the above solution with a CA:EDTA:total cation molar ratio of 2:2:1, which was continuously stirred for 1 h at room temperature for complete complexation. The pH was adjusted to ~9 by adding an aqueous NH<sub>4</sub>OH solution. The obtained solution was heated at 250°C on a hot plate until a gel was formed. The gel was then dried at 175°C for 24 h in a drying oven, followed by calcining the powder at 1250°C for 5 h to obtain the BCZYYb4411 electrolyte powder.

### **In-situ formed positive electrode Ba<sub>0.62</sub>Sr<sub>0.38</sub>CoO<sub>3-δ</sub>+Pr<sub>1.44</sub>Ba<sub>0.11</sub>Sr<sub>0.45</sub>Co<sub>1.32</sub>Fe<sub>0.68</sub>O<sub>6-δ</sub> (BSC+PBSCF)**

The *in-situ* formed BSC+PBSCF positive electrode powder was synthesized via a wet-chemistry method<sup>49</sup> using stoichiometric amounts of Pr<sub>6</sub>O<sub>11</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, and Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O as the precursors. Briefly, the calculated amount of Pr<sub>6</sub>O<sub>11</sub> was first dissolved in 20 wt.% diluted nitric acid solution at 100°C to obtain the praseodymium nitrate solution. Stoichiometric amounts of Ba(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, and Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O were subsequently added into the praseodymium nitrate solution, which was stirred for 30 mins. The complexing and chelating agents, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA), were added to the above solution with a CA:EDTA:total cation molar ratio of 2:2:1, which was continuously stirred for 1 h at

room temperature for complete complexation. The pH was adjusted to ~9 by adding an aqueous  $\text{NH}_4\text{OH}$  solution. The solution was then heated at  $250^\circ\text{C}$  on a hot plate until a gel was formed. The gel was immediately placed in a drying oven at  $175^\circ\text{C}$  for 24 h. The obtained black powder was then calcined under air at  $600^\circ\text{C}$  for 5 h, followed by ball-milling in ethanol for 1 day and then drying at  $100^\circ\text{C}$  for the following positive electrode ink preparation. Upon sintering at  $765^\circ\text{C}$ , the calcined powder will be crystallized to BSC+PBSCF powder.

### **$\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$ (PBSCF-1) positive electrode powder**

The PBSCF-1 powder was synthesized via the same method as BSC+PBSCF. Briefly, after obtaining the powder calcined at  $600^\circ\text{C}$ , the powder will be subsequently sintered at  $950^\circ\text{C}$  and crystallized to PBSCF-1.

### **Electrical conductivity relaxation (ECR) samples**

Three materials were synthesized for ECR experiments, which include  $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$  (PBSCF-1),  $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$  (PBSCF-2), and  $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$  (BSC). Their synthesis procedures were the same as the abovementioned wet-chemistry method. BSC was prepared using stoichiometric amounts of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the precursors. After drying at  $175^\circ\text{C}$ , the obtained powder was then calcined under air at  $600^\circ\text{C}$  for 5 h, followed by ball-milling in ethanol for 24 h. After evaporating the ethanol at  $100^\circ\text{C}$ , the obtained powder was ready for subsequent ink preparation. PBSCF-2 was also synthesized with the same method. The precursors and procedures were the same as those for BSC+PBSCF.

### **$\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (SDC-Ni-Ru) steam methane reforming (SMR) catalyst**

The SDC-Ni-Ru catalyst was prepared via the above wet-chemistry method using a stoichiometric amount of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and ruthenium(III) nitrosyl nitrate solution ( $\text{HN}_4\text{O}_{10}\text{Ru}$ ) as the precursors. Similarly, after drying at  $175^\circ\text{C}$  for 24 h, the obtained powder was then calcined under air at  $600^\circ\text{C}$  for 5 h. The calcined powder was then ball-milled in ethanol for 24 h and dried in air at  $100^\circ\text{C}$ . The obtained powder was used for the following SMR catalyst ink preparation.

### **BCZYYb4411 electrolyte ink for ultrasonic spray-coating**

The BCZYYb4411 electrolyte powder was mixed with 1 wt.% NiO (NiO functions as the sintering aid, the amount of which was based on the mass of BCZYYb4411) and binders (e.g., fish oil, b-98 polyvinyl butyral, di-n-butyl phthalate, and ethanol). After ball-milling using yttria-stabilized zirconia (YSZ) beads ( $d=5$  mm) for 4 days, the prepared

BCZYYb4411 electrolyte ink was ready for ultrasonic spray-coating. The particle size distribution of the electrolyte powder in ink was evaluated using a Malvern Zetasizer Nano S. The obtained data were analyzed utilizing the Mie theory<sup>50</sup>.

### **Positive electrode slurry preparation**

Five grams of  $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$  (PBSCF-1) or BSC+PBSCF powder, 1 g dispersant (20 wt.% solspere 28000 (Lubrizol) dissolved in  $\alpha$ -terpinol), and 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved in  $\alpha$ -terpinol) were well mixed and ground by mortar and pestle to make the positive electrode slurry.

### **SDC-Ni-Ru catalyst slurry preparation**

Five grams of SDC-Ni-Ru, 1 g dispersant (20 wt.% solspere 28000 (Lubrizol) dissolved in  $\alpha$ -terpinol), and 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved in  $\alpha$ -terpinol) were well mixed and ground by mortar and pestle to make the slurry for SMR.

### **BSC slurry preparation for electrochemical conductivity relaxation (ECR) testing**

Similarly, 5 grams of BSC was mixed with 1 g dispersant (20 wt.% solspere 28000 (Lubrizol) dissolved in  $\alpha$ -terpinol) and 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved in  $\alpha$ -terpinol). The slurry was well grounded by mortar and pestle to make the slurry for the following ECR testing.

### **Negative electrode slurry preparation**

The composite powder, BCZYYb7111 + NiO + corn starch, was first mixed with organic materials (menhaden fish oil, b-98 polyvinyl butyral, polyethylene glycol 400, cyclohexanone, di-n-butyl phthalate, xylenes) and ethanol. The resulting mixture was then ball-milled using yttria-stabilized zirconia (YSZ) beads ( $d=10$  mm) for 24 h to obtain the negative electrode slurry.

### **Negative electrode functional layer slurry preparation.**

Similarly, the negative electrode functional layer slurry was also prepared by mixing and ball-milling BCZYYb7111 + NiO and the above organic materials and ethanol. Detailed information on the chemicals used in this work can be found in Supplementary Table 6.

### **PCEC half-cell manufacturing**

PCEC half-cells were manufactured with both tape-casting and spray-coating methods. First, the prepared negative electrode function layer slurry (BCZYYb7111 + NiO) was coated on Mylar via tape-casting. After drying in air for 5 h, the negative electrode slurry was then cast on the negative electrode function layer. The obtained two layers were dried in air for 48 h and then presintered at 800°C for 30 mins to thermally degrade all the organic materials.

A lab-scale ultrasonic coating system (Siansonic, model: UC330) was used to fabricate the ultrathin (quasi-two dimensional), chemically homogeneous, and robust proton-conducting electrolyte. The BCZYYb4411 electrolyte ink was loaded into an ultrasonic syringe. The flow rate of the electrolyte ink fed to the ultrasonic nozzle was controlled using a syringe pump. An ultrasonic nozzle installed on the x-y-z robotic arm was used for coating the ultrathin electrolyte layer. The coating time, spray spot size, coating speed, ultrasonic power, and substrate temperature were optimized to achieve the desired electrolyte thickness and density. The obtained PCECs were cosintered at 1450°C for 5 h to fabricate the PCEC half-cells.

### **Current collection and single-cell testing**

The electrochemical button cell was sealed on an alumina tube using the MO·SCI glass sealant (OL-GL1709P/-45). Gold paste was painted on both electrodes. A silver grid was then applied to the gold paste to strengthen the current collection. The thermocouple was inserted into the reactor near the PCECs, to ensure accurate temperature readings. Upon sealing the PCECs on an alumina tube, the negative electrodes (anode in the fuel cell mode; cathode in the electrolysis mode) of all PCECs were first reduced under H<sub>2</sub> (20 sccm) at 600°C for 20 min. In this work, the heating/cooling rate was set as 4°C/min. At each testing temperature, before collecting the results, the cells were held for 15 min to ensure that the PCECs achieved a steady state. The effective electrode area of all PCECs was 0.5 cm<sup>2</sup>. All electrochemical measurements were conducted using a Princeton Applied Research potentiostat. All the cells tested in this work were numbered; detailed information can be found in Supplementary Table 7.

### **PCECs with PrBa<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>O<sub>6-δ</sub> (PBSCF-1) positive electrodes**

The PBSCF-1 ink was first brush-painted on the electrolyte side and then fired at 950°C for 5 h to obtain the PBSCF-1 positive electrode. After sealing the cell according to the abovementioned process, the PCEC temperature was increased to 765°C to melt the sealing glass (OL-GL1709P/-45). The PCEC temperature was then reduced to 600°C for performing electrochemical measurements. Hydrogen was used as the fuel, and air was used as the oxidant, with flow rates of 80 sccm and 200 sccm, respectively.

### **PCECs with in-situ formed BSC+PBSCF positive electrodes**

After brush-painting the BSC+PBSCF ink on the electrolyte, the PCEC single-cell was then directly sealed on the alumina tube without presintering the positive electrode. The PCEC temperature was first increased to 765°C to melt the sealing glass (OL-GL1709P/-45), whereby BSC+PBSCF was simultaneously obtained. The PCEC performance was evaluated at temperatures ranging from 600°C to 300°C. Air or O<sub>2</sub> with a flow rate of 200 sccm was fed to the positive electrode as the gas stream. To evaluate the PCEC fuel-cell performance on hydrogen, a hydrogen stream with a flow rate of 80 sccm was fed to the negative electrode. To determine the PCEC fuel-cell performance using ammonia as the fuel, the ammonia flow rate, which was set as 40 sccm at 600°C, 35 sccm at 550°C, 30 sccm at 500°C, 25 sccm at 450°C, 20 sccm at 400°C, and 10 sccm at 400°C, was varied with the operating temperature to maximize the fuel utilization rate. To test the PCEC fuel-cell performance on methane, the SDC-Ni-Ru ink was brush-painted on the negative electrode as a catalytic reforming layer. A mixture of methane with steam at a methane-to-steam ratio of 1:1 was fed to the negative electrode. Herein, the CH<sub>4</sub> flow rate, which was set as 16 sccm at 500°C, 12 sccm at 450°C, and 8 sccm at 400°C, was also varied with the operating temperatures.

The SMR catalytic activities of Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ni<sub>0.1</sub>Ru<sub>0.05</sub>O<sub>2-δ</sub>, Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ni<sub>0.15</sub>O<sub>2-δ</sub>, and Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ru<sub>0.15</sub>O<sub>2-δ</sub> were first evaluated in packed bed reactors. A total of 120 mg of each catalyst was loaded into a quartz tubular reactor with an inner diameter of 0.28 inches at 1 atm. A thermocouple was loaded close to the catalyst to measure the operating temperature. The catalyst was first reduced under 20% H<sub>2</sub> balanced with Ar (100 sccm) at 600°C for 30 mins. After reduction, the reactor temperature was decreased to 500°C, and 15 sccm CH<sub>4</sub> gas was flowed through a heated water bubbler to obtain a steam-to-carbon (S/C) ratio of 1:1, and this gas flow was subsequently fed to the reactor. The outlet gas compositions were determined using inline gas chromatography (INFICON 3000 Micro GC) from 500 to 450°C. Before measurement, the reactor was kept at each temperature for approximately 30 min to reach equilibrium. The CH<sub>4</sub> conversion ( $X_{CH_4}$ ) was calculated as equation (1):

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (1)$$

where  $F_{in}$  and  $F_{out}$  represent the flow rate of inlet gas or outlet gas, respectively.

To evaluate the PCEC electrolysis performance for hydrogen production, a mixture of steam and nitrogen was supplied to the positive electrode with a steam concentration of 40%. The steam concentration was controlled by bubbling nitrogen (100 sccm) through a customized temperature-controlled bubbler. Pure hydrogen gas (15 sccm) was fed to the negative electrode as the sweep gas. To evaluate the Faradaic efficiency (FE), the negative electrode outlet gas was mixed with a nitrogen gas stream, which was then injected into an online gas chromatograph (INFICON 3000 Micro GC) to quantify the hydrogen production rate (Supplementary note 4). The FE (%) was calculated using equation (2):

$$FE(\%) = \frac{n_{H_2,measured}}{n_{H_2,theoretical}} = \frac{n_{H_2,measured} \times (n \times F)}{I} \times 100\% \quad (2)$$

where  $FE$  (%) is the Faradaic efficiency at different current densities,  $n_{H_2,measured}$  is the measured hydrogen production rate (mol/s),  $n$  is 2,  $F$  is the Faradaic constant (96485 C mol<sup>-1</sup>), and  $I$  is the applied current (A).

The electrolysis energy efficiency,  $EEE$  (%), was calculated based on the lower heating value of H<sub>2</sub> (LHV), according to the equation (3):

$$EEE (\%) = \frac{\Delta H_{H_2,LHV} \times n_{H_2,measured}}{I \times V} = \frac{n_{H_2,measured} \times (n \times F)}{I \times V} \times 100\% \quad (3)$$

where  $EEE$  (%) is the LHV  $EEE$  of PCECs,  $\Delta H_{H_2,LHV}$  is the LHV reaction enthalpy for steam electrolysis with a value of 241.8 kJ mol<sup>-1</sup>,  $n_{H_2,measured}$  is the measured hydrogen production rate (mol s<sup>-1</sup>),  $I$  is the applied current (A),  $V$  is the response voltage (V), and  $F$  is the Faradaic constant (96485 A s mol<sup>-1</sup>)

### Peeling strength testing

The peeling strength of the positive electrodes (BSC+PBSCF and PBSCF-1) was measured according to the ASTM D903 180-degree peeling strength testing standard. PCEC full cells with different positive electrodes were tested under the same testing conditions. Briefly, the specimen was placed in the peeling strength test machine by fixing the negative electrode using heavy-duty double-sided tape. One end of a piece of rectangular tape was stuck on the positive electrode, while the other end was fixed to the peeling strength testing machine. By pulling the tape back in a “U” shape (180°) at the same speed, the applied force was recorded as a function of time.

### Dilatometry testing

The dilatometry experiments were carried out using the Netzsch DIL 402 Expedis instrument to determine the linear thermal expansion profiles of the positive electrode samples. Cylindrical samples were used in this experiment. Briefly, 0.6 g of each sample powder was first dry pressed by using a carbonized stainless-steel die set under a pressure of 50 bar for 1 min, producing a green cylinder. The cylinders were then sintered in air to get the desired sample composition (BSC+PBSCF cylinder was calcined at 765°C for 5 min; PBSCF-1 cylinder was calcined at 950°C for 5 h). The linear thermal expansion profiles of the samples were measured using a heating and cooling rate of 10°C/min. The dilatometer was calibrated and corrected for each measurement.

### BCZYYb4411 electrolyte pellet conductivity testing

The conductivity of PCEC electrolytes was measured by using the EIS and a comprehensive analysis of the EIS spectra was performed to determine the grain bulk and grain boundary conductivity. BCZYYb4411 powder was subjected to uniaxial dry pressing to form a 20 mm diameter pellet at a pressure of 150 bar, which was then

sintered for 5 hours at 1450°C. The resulting pellet was polished with sandpaper to attain a flat surface with a thickness of ~1 mm. Platinum (Pt) paste was applied on both sides of the pellet (with an effective area of 0.5 cm<sup>2</sup>) as the current collector via brush painting, which was then calcined at 350°C for 30 minutes. The ohmic resistance of this BCZYYb4411 electrolyte pellets was measured by performing EIS under a humidified argon atmosphere (3% steam) from 500 to 250°C. Before each measurement, the pellet was held at each temperature for approximately 1 hour to achieve a steady state.

The EIS spectra were collected using a Gamry 1010 interface. The obtained impedance spectra were then analyzed using Zview software to separate and analyze the bulk and grain boundary resistances. The “brick layer model”<sup>22,23</sup> was used to calculate the bulk and grain boundary conductivities.

### **Electrical conductivity relaxation (ECR) testing.**

Two samples were prepared for the ECR testing, which include PBSCF-1 and PBSCF-2 coated with BSC. The PBSCF-1 powder was first axially pressed at 100 bar for 2 min using a 2 cm (diameter) die, followed by sintering at 1250°C for 3 h to densify the pellets. A bar was prepared using a high-precision diamond saw. For comparison, PBSCF-2 was also prepared with the same procedure. BSC was then uniformly coated on PBSCF-2 bar, followed by sintering at 1000 °C for 2 h. ECR measurement was conducted at 700°C, 650°C, 600°C, 550°C, and 500°C. At each temperature, the oxygen concentration was initially set as 2 vol.% (10 sccm O<sub>2</sub> + 490 sccm Ar). ECR was measured via a four-probe method with a current of 40 mA applied and voltage measured. Once the voltage reached equilibrium, the oxygen concentration was immediately changed from 2 vol.% to 20 vol.%. The voltage response was recorded. The relative conductivity change data was calculated using the NETL ECR analysis tool<sup>51</sup>, which determines the surface exchange coefficient ( $k_{\text{chem}}$ ) and bulk diffusion coefficient ( $D_{\text{chem}}$ ).

### **Structural characterization**

The crystal structure of the as-synthesized powders was measured using X-ray diffraction (XRD) (Rigaku MiniFlex diffractometer with a Cu K $\alpha$  radiation source operated at 30 kV and 15 mA). The scan speed was 1°/min. The morphology, microstructure, and chemical composition of BSC+PBSCF were examined using transmission electron microscopy (TEM, FEI Tecnai Osiris 200 Kv S/TEM system and Talos F200X S/TEM system operated at 200 kV, equipped with an FEG (field emission gun) cathode and four in-column Super-X energy dispersive X-ray spectrometer (EDS) detectors with a total collection angle of 0.9 sr). The microstructure of the PCECs was examined by using scanning electron microscopy (Hitachi/S-3400 N). Nitrogen Brunauer–Emmett–Teller (BET) surface area analysis and O<sub>2</sub>-temperature-programmed desorption (O<sub>2</sub>-TPD) were conducted using a ChemBET Pulsar chemisorption analyser.

**Data availability:** The authors declare that [the/all other] data supporting the findings of

this study is available within the paper [and its supplementary information files].

### Acknowledgments

This work was financial supported by the Nissan Motor Co., Ltd (A22-0455-001, C.D.), Department of Energy grant (DE-FE0032005, DE-SC0021505, DE-FE0032235 and DE-FE0032300, C.D.), and The National Aeronautics and Space Administration grant (80NSSC21C0220, C.D.).

### Author Contributions Statement

Conceptualization: C.D., F.L.; Methodology: C.D., F.L., D.D., H.D., B.L.; Investigation: C.D., F.L., H.D., D.D., P. Kumar, M.J., C.G., Y.F., N.D., T.O., M.U., P.Kazempoor, L.F., D.C., B.L.; Visualization: C.D., F.L.; Funding acquisition: C.D.; Project administration: C.D.; Supervision: C.D.; Writing – original draft: C.D., F.L.; Writing – review & editing: C.D., F.L., H.D., D.D., P. Kumar, M.J., C.G., Y.F., N.D., T.O., M.U., P.Kazempoor, L.F., D.C., B.L.

### Competing Interests Statement

Authors declare no competing interests.

### Figure Legends/Captions

**Figure 1. Lowering the operating temperature of PCECs to <450°C.** (a) Motivations for lowering the operating temperature of PCECs to <450°C. Intermediate-temperature protonic ceramic electrochemical cells (IT-PCECs); Balance of plants (BOPs); High-temperature solid oxide cells (HT-SOCs). (b) Comparison of  $ASR_P/(ASR_O+ASR_P)$  of PCECs at OCV condition, suggesting that  $ASR_P$  is dominant at low temperatures (<450°C). 2021, Lee et al., PBSCF<sup>21</sup>; 2018 Haile et. al., PBSCF (PLD)<sup>19</sup>; 2018, Lee et. al., BSCF<sup>37</sup>; 2015 Duan et. al., BCFZY<sup>17</sup>; 2021 Park et. al., GCCCO<sup>32</sup>; 2019 Shao et. al., BCCY<sup>38</sup>; 2018 Shim et. al., LSC (PLD)<sup>39</sup>; 2022, Liu et. al., BCFN<sup>31</sup>. (c) Comparison of  $ASR_O$  (This work, cell 1) of PCECs with the literature results. PCECs readily fabricated in this work achieve  $ASR_O$  that are comparable to the PCECs fabricated using the costly and complicated pulsed laser deposition (PLD) method. (d) Comparison of  $ASR_P$  of PCECs (This work, Cell 1) with the literature results. The developed positive electrode in this work leads to the lowest  $ASR_P$ . (e) Comparison of PCEC fuel cell peak power densities (Cell 1 and Cell 6) with literature results. (f) Comparison of PCEC energy efficiency in electrolysis mode (as a function of H<sub>2</sub> production rate) with the literature results at 400-700°C (Supplementary Table 1, Cell 2). This work has demonstrated PCECs for hydrogen production at 400°C, which achieve comparable or higher electrolysis energy efficiency and hydrogen production rate than previous PCECs operated at >500°C.

**Figure 2. Readily fabricated ultrathin proton-conducting electrolyte using ultrasonic spray coating and negative electrode with low Ba deficiency (Supplementary note 1).** (a) Schematic illustration of the ultrasonic spray coating process for applying electrolyte. (b) The cross-section SEM image of PCEC full cell, which shows an ultrathin (~3 μm), dense, and bamboo-structured electrolyte layer can be fabrication via ultrasonic spray coating (Cell 2). (c)

The SEM image of PCEC electrolyte surface, which displays an average grain size of 8  $\mu\text{m}$  (Cell 3). **(d)** An illustration of the ultrathin ( $\sim 3 \mu\text{m}$ ), dense, and bamboo-structured electrolyte layer, which shows the quasi-2D feature. The grain size is much bigger than the thickness, which could be considered as a quasi-2D electrolyte. The proton flux (green arrows) does not cross grain boundaries, reducing the  $ASR_o$ . **(e)** High-angle annular dark field (HAADF) image of the electrolyte and anode. GB: grain boundary. **(f)** Energy-dispersive X-ray spectroscopy (EDS) line scan profile along the red line shown in (e). **(g)** HAADF image and EDS mapping for constituent cations at the microscale, which include Ba, Ce, Zr, Y, Yb, and Ni. The scale bar is 1  $\mu\text{m}$ . **(h)** HAADF image of an electrolyte grain boundary at the nanoscale and the corresponding EDS mapping for constituent elements, including Ba, Ce, Zr, Y, Yb, and O. **(i)** EDS line scan profile along the red line shown in (h). The results from (e)-(i) are based on Cell 4.

**Figure 3. Crystalline structure, morphology, microstructure, and chemical composition of in-situ formed BSC+PBSCF positive electrode.** **(a)** XRD pattern and the Rietveld refinement results, which show BSC+PBSCF contains  $\sim 30.6 \text{ wt. } \%$  BSC and  $\sim 69.4 \text{ wt. } \%$  PBSCF-2. **(b)** TEM image of BSC+PBSCF. **(c)** High-resolution TEM image of BSC+PBSCF, which confirms that BSC+PBSCF is composed of PBSCF-2 and BSC. **(d)** High-angle annular dark-field (HAADF) image and corresponding energy dispersive spectroscopy (EDS) mapping images, which further affirm that BSC+PBSCF is composed of PBSCF-2 and BSC. The scale bar is 20 nm. **(e)** EDS spectra at Area 1 and Area 2 (Figure 3d), which identify the stoichiometry of BSC is  $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$  and the stoichiometry of PBSCF-2 is  $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ . The analysis of EDS results also confirms the weight percent of BSC phase is  $\sim 30.0 \text{ wt. } \%$  and PBSCF-2 is  $\sim 70.0 \text{ wt. } \%$ , which is consistent with the XRD refinement results.

**Figure 4. In-situ formed BSC+PBSCF positive electrode reduces  $ASR_p$ .** **(a)** The area-specific electrode polarization resistance ( $ASR_p$ ) of PCECs equipped with BSC+PBSCF and PBSCF-1 positive electrodes under OCV conditions (Cell 1, Cell 5, Cell 6, and Cell 7). **(b)**  $\text{O}_2$ -TPD profiles of BSC+PBSCF and PBSCF-1. **(c)** Bulk oxygen-ion diffusion coefficient ( $D_{\text{chem}}$ ) of BSC+PBSCF and PBSCF-1 as a function of operating temperature. **(d)** Surface oxygen exchange coefficient ( $k_{\text{chem}}$ ) of BSC+PBSCF and PBSCF-1 as a function of operating temperature. **(e)** EIS spectra of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes, which were measured under OCV conditions at  $450^\circ\text{C}$  (Cell 1 and Cell 6).  $\text{H}_2$  was fed to the negative electrode and air was fed to the positive electrode. **(f)** Corresponding distribution of relaxation times (DRT) analysis of the EIS spectra shown in (e).

**Figure 5. DFT calculations to study the bulk oxygen vacancy formation and oxygen diffusion of PBSCF-1, PBSCF-2 and BSC.** Lattice structures of (a) PBSCF-1, (b) PBSCF-2 and (c) BSC. The Pr, Ba, Sr, Co, Fe, and O atoms are yellow, scarlet, green, blue, brown, and red, respectively. Their lattice constants are listed in Supplementary Table 5. The most stable oxygen vacancy (Ov1) and the second stable vacancy (Ov2) sites are marked with black circles. The oxygen diffusion pathways are indicated by the arrows. The initial state (IS, black), final state (FS, black), and transition state (TS, green) are also marked. The  $\Delta E_{\text{Ov}}$  corresponding to Ov1 and Ov2 and  $E_{a,\text{bulk}}$  are labeled and shown in (d).

**Figure 6. In-situ formed BSC+PBSCF reduces the positive electrode-electrolyte contact resistance.** **(a)** The area-specific ohmic resistance ( $ASR_o$ ) of PCECs equipped with BSC+PBSCF and PBSCF-1 positive electrodes (Cell 1, Cell 5, Cell 6, and Cell 7). **(b)** Linear thermal expansion profiles of positive electrodes as a function of temperature during heating and

cooling, and the corresponding CTEs. **(c)** Representative peeling strength measurement profiles for BSC+PBSCF and PBSCF-1 positive electrodes (Cell 8 and Cell 9). **(d)** The average peeling strength of positive electrodes. The BSC+PBSCF positive electrode leads to a more coherent and stronger bonding with the electrolyte than PBSCF-1 (Cell 8 and Cell 9). **(e)** High-angle annular dark field (HAADF) image of the BSC+PBSCF positive electrode-electrolyte interface and the corresponding energy dispersive X-ray spectroscopy (EDS) mapping images of Pr, Ba, Sr, Co, Fe, and O. The horizontal dashed line shows the positive electrode-electrolyte interface. The white dashed box shows the PBSCF-2 phase formed at the interface. The red dashed box shows the BSC phase formed at the interface. The scale bar in Figure 6e quantitatively shows the concentration of elements, where black indicates the lowest concentration while red displays the highest concentration. The results from (e) are based on Cell 10.

**Figure 7. LT-PCECs attain exceptional fuel-cell and electrolysis performance. (a)** *I-V* and *I-P* curves of a representative LT-PCEC at 350-600°C. H<sub>2</sub> was fed to the negative electrode and air was fed to the positive electrode (Cell 7). **(b)** *I-V* and *I-P* curves of a representative LT-PCEC at 275-450°C (Cell 11). H<sub>2</sub> was fed to the negative electrode and O<sub>2</sub> was fed to the positive electrode. **(c)** Comparison of fuel cell peak power densities (PPDs) of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes (Cell 1, Cell 5, Cell 6, and Cell 7). **(d)** EIS spectra of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes, which were measured under OCV conditions at 400°C (Cell 1 and Cell 6). H<sub>2</sub> was fed to the negative electrode and air was fed to the positive electrode. **(e)** *I-V* and *I-P* curves of a representative LT-PCEC using ammonia as the fuel. (Our work: Cell 12) The LT-PCEC is equipped with BSC+PBSCF as the positive electrode. NH<sub>3</sub> was fed to the negative electrode and air was fed to the positive electrode. **(f)** Comparison of PCEC fuel-cell performance on ammonia with literature results<sup>40-46</sup> (Our work: Cell 12). **(g)** CH<sub>4</sub> conversion over three SMR catalysts, including Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ni<sub>0.1</sub>Ru<sub>0.05</sub>O<sub>2-δ</sub>, Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ni<sub>0.15</sub>O<sub>2-δ</sub>, and Sm<sub>0.2</sub>Ce<sub>0.7</sub>Ru<sub>0.15</sub>O<sub>2-δ</sub>, which were tested in a packed bed reactor. The steam-to-carbon ratio is 1:1. **(h)** *I-V* and *I-P* curves of a representative LT-PCEC on methane. (Our work: Cell 13). The LT-PCEC is equipped with BSC+PBSCF as the positive electrode. A mixture of methane and steam was fed to the negative electrode and air was fed to the positive electrode. The steam-to-carbon ratio is 1:1. **(i)** Comparison of PCEC fuel cell performance on methane with literature results<sup>17,47,52,53</sup> (Our work: Cell 13). **(j)** Polarization curves of the LT-PCEC in electrolysis mode for hydrogen production at 350-450°C (Cell 14). 40 vol.% H<sub>2</sub>O + 60 vol.% N<sub>2</sub> was fed to the positive electrode. **(k)** Faradaic efficiency of LT-PCEC in electrolysis mode at 400°C (Cell 2, Supplementary note 3). **(l)** Energy efficiency of LT-PCEC in electrolysis mode at 400°C (Cell 2).

**Figure 8. Stability of LT-PCECs with in-situ formed BSC+PBSCF as the positive electrode for power generation in fuel cell mode and green H<sub>2</sub> production in electrolysis mode. (a)** The stability testing of the LT-PCEC on H<sub>2</sub>-Air at 400°C (Cell 15). The discharging current density is 400 mA cm<sup>-2</sup>. **(b)** The SEM image of the LT-PCEC after stability testing on H<sub>2</sub>-Air (Cell 15). **(c)** Long-term stability testing of a LT-PCEC in electrolysis mode at 400°C with a charging current density of 600 mA cm<sup>-2</sup> (Cell 16). **(d)** The SEM image of the LT-PCEC after stability testing in electrolysis mode (Cell 16).

## References

- 1 Hauch, A. *et al.* Recent advances in solid oxide cell technology for electrolysis. *Science* **370**, eaba6118, doi:<https://10.1126/science.aba6118> (2020).

- 2 Duan, C. *et al.* Highly efficient reversible protonic ceramic electrochemical cells for power generation and fuel production. *Nature Energy* **4**, 230-240, doi:<https://doi.org/10.1038/s41560-019-0333-2> (2019).
- 3 Liu, F. *et al.* Process-intensified protonic ceramic fuel cells for power generation, chemical production, and greenhouse gas mitigation. *Joule* **7**, 1308-1332, doi:<https://doi.org/10.1016/j.joule.2023.05.009> (2023).
- 4 Song, Y. *et al.* Nanocomposites: A New Opportunity for Developing Highly Active and Durable Bifunctional Air Electrodes for Reversible Protonic Ceramic Cells. *Advanced Energy Materials* **11**, 2101899, doi:<https://doi.org/10.1002/aenm.202101899> (2021).
- 5 Zhang, W. *et al.* A Solid Oxide Fuel Cell Runs on Hydrocarbon Fuels with Exceptional Durability and Power Output. *Advanced Energy Materials* **n/a**, 2202928, doi:<https://doi.org/10.1002/aenm.202202928> (2022).
- 6 Liu, F., Fang, L., Diercks, D., Kazempoor, P. & Duan, C. Rationally designed negative electrode for selective CO<sub>2</sub>-to-CO conversion in protonic ceramic electrochemical cells. *Nano Energy* **102**, 107722, doi:<https://doi.org/10.1016/j.nanoen.2022.107722> (2022).
- 7 Clark, D. *et al.* Single-step hydrogen production from NH<sub>3</sub>, CH<sub>4</sub>, and biogas in stacked proton ceramic reactors. *Science* **376**, 390-393, doi:<https://doi.org/10.1126/science.abj3951> (2022).
- 8 Li, M. *et al.* Switching of metal–oxygen hybridization for selective CO<sub>2</sub> electrohydrogenation under mild temperature and pressure. *Nature Catalysis* **4**, 274-283, doi:<https://doi.org/10.1038/s41929-021-00590-5> (2021).
- 9 Wachsman, E. D. & Lee, K. T. Lowering the Temperature of Solid Oxide Fuel Cells. *Science* **334**, 935-939, doi:<https://doi.org/10.1126/science.1204090> (2011).
- 10 Zhang, J., Ricote, S., Hendriksen, P. V. & Chen, Y. Advanced Materials for Thin-Film Solid Oxide Fuel Cells: Recent Progress and Challenges in Boosting the Device Performance at Low Temperatures. *Adv. Funct. Mater.* **32**, 2111205, doi:<https://doi.org/10.1002/adfm.202111205> (2022).
- 11 Song, Y. *et al.* A Cobalt-Free Multi-Phase Nanocomposite as Near-Ideal Cathode of Intermediate-Temperature Solid Oxide Fuel Cells Developed by Smart Self-Assembly. *Adv. Mater.* **32**, 1906979, doi:<https://doi.org/10.1002/adma.201906979> (2020).
- 12 Shin, S. S. *et al.* Multiscale structured low-temperature solid oxide fuel cells with 13 W power at 500 °C. *Energy & Environmental Science* **13**, 3459-3468, doi:<https://doi.org/10.1039/D0EE00870B> (2020).
- 13 Kuai, X. *et al.* Boosting the Activity of BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> Perovskite for Oxygen Reduction Reactions at Low-to-Intermediate Temperatures through Tuning B-Site Cation Deficiency. *Advanced Energy Materials* **9**, 1902384, doi:<https://doi.org/10.1002/aenm.201902384> (2019).
- 14 Zhang, Y. *et al.* Recent Progress on Advanced Materials for Solid-Oxide Fuel Cells Operating Below 500 °C. *Adv. Mater.* **29**, 1700132, doi:<https://doi.org/10.1002/adma.201700132> (2017).
- 15 Baek, J. D., Yoon, Y.-J., Lee, W. & Su, P.-C. A circular membrane for nano thin film micro solid oxide fuel cells with enhanced mechanical stability. *Energy & Environmental Science* **8**, 3374-3380, doi:<https://doi.org/10.1039/C5EE02328A> (2015).
- 16 Evans, A. *et al.* Low-Temperature Micro-Solid Oxide Fuel Cells with Partially Amorphous La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> Cathodes. *Advanced Energy Materials* **5**, 1400747, doi:<https://doi.org/10.1002/aenm.201400747> (2015).

- 17 Duan, C. *et al.* Readily processed protonic ceramic fuel cells with high performance at low temperatures. *Science* **349**, 1321-1326, doi:<https://10.1126/science.aab3987> (2015).
- 18 Bian, W. *et al.* Revitalizing interface in protonic ceramic cells by acid etch. *Nature* **604**, 479-485, doi:<https://10.1038/s41586-022-04457-y> (2022).
- 19 Choi, S. *et al.* Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells. *Nature Energy* **3**, 202-210, doi:<https://10.1038/s41560-017-0085-9> (2018).
- 20 Bian, W. *et al.* Regulation of Cathode Mass and Charge Transfer by Structural 3D Engineering for Protonic Ceramic Fuel Cell at 400 °C. *Adv. Funct. Mater.* **31**, 2102907, doi:<https://doi.org/10.1002/adfm.202102907> (2021).
- 21 Choi, M. *et al.* Exceptionally high performance of protonic ceramic fuel cells with stoichiometric electrolytes. *Energy & Environmental Science* **14**, 6476-6483, doi:<https://10.1039/D1EE01497H> (2021).
- 22 Haile, S. M., West, D. L. & Campbell, J. The role of microstructure and processing on the proton conducting properties of gadolinium-doped barium cerate. *J. Mater. Res.* **13**, 1576-1595, doi:<https://10.1557/JMR.1998.0219> (1998).
- 23 Haile, S. M., Staneff, G. & Ryu, K. H. Non-stoichiometry, grain boundary transport and chemical stability of proton conducting perovskites. *Journal of Materials Science* **36**, 1149-1160, doi:<https://10.1023/A:1004877708871> (2001).
- 24 Clark, D. R. *et al.* Probing Grain-Boundary Chemistry and Electronic Structure in Proton-Conducting Oxides by Atom Probe Tomography. *Nano Lett.* **16**, 6924-6930, doi:<https://10.1021/acs.nanolett.6b02918> (2016).
- 25 Diercks, D. R., Gorman, B. P., Manerbino, A. & Coors, G. Atom Probe Tomography of Yttrium-Doped Barium–Cerium–Zirconium Oxide with NiO Addition. *J. Am. Ceram. Soc.* **97**, 3301-3306, doi:<https://doi.org/10.1111/jace.13093> (2014).
- 26 Choi, S., Davenport, T. C. & Haile, S. M. Protonic ceramic electrochemical cells for hydrogen production and electricity generation: exceptional reversibility, stability, and demonstrated faradaic efficiency. *Energy & Environmental Science* **12**, 206-215, doi:<https://10.1039/C8EE02865F> (2019).
- 27 Ding, H. *et al.* Self-sustainable protonic ceramic electrochemical cells using a triple conducting electrode for hydrogen and power production. *Nature Communications* **11**, 1907, doi:<https://10.1038/s41467-020-15677-z> (2020).
- 28 Vøllestad, E. *et al.* Mixed proton and electron conducting double perovskite anodes for stable and efficient tubular proton ceramic electrolyzers. *Nature Materials* **18**, 752-759, doi:<https://10.1038/s41563-019-0388-2> (2019).
- 29 Zhai, S. *et al.* A combined ionic Lewis acid descriptor and machine-learning approach to prediction of efficient oxygen reduction electrodes for ceramic fuel cells. *Nature Energy*, doi:<https://10.1038/s41560-022-01098-3> (2022).
- 30 Wang, Z. *et al.* Rational design of perovskite ferrites as high-performance proton-conducting fuel cell cathodes. *Nature Catalysis*, doi:<https://10.1038/s41929-022-00829-9> (2022).
- 31 Pei, K. *et al.* Surface restructuring of a perovskite-type air electrode for reversible protonic ceramic electrochemical cells. *Nature Communications* **13**, 2207, doi:<https://10.1038/s41467-022-29866-5> (2022).

- 32 Saqib, M. *et al.* Transition from perovskite to misfit-layered structure materials: a highly oxygen deficient and stable oxygen electrode catalyst. *Energy & Environmental Science* **14**, 2472-2484, doi:[https://10.1039/D0EE02799E](https://doi.org/10.1039/D0EE02799E) (2021).
- 33 Liu, Z. *et al.* One-pot derived thermodynamically quasi-stable triple conducting nanocomposite as robust bifunctional air electrode for reversible protonic ceramic cells. *Applied Catalysis B: Environmental* **319**, 121929, doi:<https://doi.org/10.1016/j.apcatb.2022.121929> (2022).
- 34 Chen, Y. *et al.* A Highly Efficient Multi-phase Catalyst Dramatically Enhances the Rate of Oxygen Reduction. *Joule* **2**, 938-949, doi:[https://https://doi.org/10.1016/j.joule.2018.02.008](https://doi.org/10.1016/j.joule.2018.02.008) (2018).
- 35 Niu, Y. *et al.* Highly Active and Durable Air Electrodes for Reversible Protonic Ceramic Electrochemical Cells Enabled by an Efficient Bifunctional Catalyst. *Advanced Energy Materials* **12**, 2103783, doi:[https://https://doi.org/10.1002/aenm.202103783](https://doi.org/10.1002/aenm.202103783) (2022).
- 36 Lee, Y.-L., Kleis, J., Rossmeisl, J., Shao-Horn, Y. & Morgan, D. Prediction of solid oxide fuel cell cathode activity with first-principles descriptors. *Energy & Environmental Science* **4**, 3966-3970, doi:[https://10.1039/C1EE02032C](https://doi.org/10.1039/C1EE02032C) (2011).
- 37 An, H. *et al.* A  $5 \times 5$  cm<sup>2</sup> protonic ceramic fuel cell with a power density of 1.3 W cm<sup>-2</sup> at 600 °C. *Nature Energy* **3**, 870-875, doi:[https://10.1038/s41560-018-0230-0](https://doi.org/10.1038/s41560-018-0230-0) (2018).
- 38 Song, Y. *et al.* Self-Assembled Triple-Conducting Nanocomposite as a Superior Protonic Ceramic Fuel Cell Cathode. *Joule* **3**, 2842-2853, doi:<https://doi.org/10.1016/j.joule.2019.07.004> (2019).
- 39 Bae, K., Kim, D. H., Choi, H. J., Son, J.-W. & Shim, J. H. High-Performance Protonic Ceramic Fuel Cells with 1 μm Thick Y:Ba(Ce, Zr)O<sub>3</sub> Electrolytes. *Advanced Energy Materials* **8**, 1801315, doi:<https://doi.org/10.1002/aenm.201801315> (2018).
- 40 Zhang, H. *et al.* An efficient and durable anode for ammonia protonic ceramic fuel cells. *Energy & Environmental Science* **15**, 287-295, doi:[https://10.1039/D1EE02158C](https://doi.org/10.1039/D1EE02158C) (2022).
- 41 He, F. *et al.* A New Pd Doped Proton Conducting Perovskite Oxide with Multiple Functionalities for Efficient and Stable Power Generation from Ammonia at Reduced Temperatures. *Advanced Energy Materials* **11**, 2003916, doi:<https://doi.org/10.1002/aenm.202003916> (2021).
- 42 Aoki, Y. *et al.* High-Efficiency Direct Ammonia Fuel Cells Based on BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>/Pd Oxide-Metal Junctions. *Global Challenges* **2**, 1700088, doi:<https://doi.org/10.1002/gch2.201700088> (2018).
- 43 Miyazaki, K., Muroyama, H., Matsui, T. & Eguchi, K. Impact of the ammonia decomposition reaction over an anode on direct ammonia-fueled protonic ceramic fuel cells. *Sustainable Energy & Fuels* **4**, 5238-5246, doi:[https://10.1039/D0SE00841A](https://doi.org/10.1039/D0SE00841A) (2020).
- 44 Zhang, L. & Yang, W. Direct ammonia solid oxide fuel cell based on thin proton-conducting electrolyte. *J. Power Sources* **179**, 92-95, doi:<https://doi.org/10.1016/j.jpowsour.2007.12.061> (2008).
- 45 Lin, Y. *et al.* Proton-conducting fuel cells operating on hydrogen, ammonia and hydrazine at intermediate temperatures. *Int. J. Hydrogen Energy* **35**, 2637-2642, doi:<https://doi.org/10.1016/j.ijhydene.2009.04.019> (2010).
- 46 Yang, J. *et al.* Electrochemical and Catalytic Properties of Ni/BaCe<sub>0.75</sub>Y<sub>0.25</sub>O<sub>3-δ</sub> Anode for Direct Ammonia-Fueled Solid Oxide Fuel Cells. *ACS Applied Materials & Interfaces* **7**, 7406-7412, doi:[https://10.1021/acsami.5b01048](https://doi.org/10.1021/acsami.5b01048) (2015).

- 47 Chen, Y. *et al.* A robust fuel cell operated on nearly dry methane at 500 °C enabled by synergistic thermal catalysis and electrocatalysis. *Nature Energy* **3**, 1042-1050, doi:<https://doi.org/10.1038/s41560-018-0262-5> (2018).
- 48 Tang, Y. *et al.* Synergy of Single-Atom Ni<sup>1</sup> and Ru<sup>1</sup> Sites on CeO<sub>2</sub> for Dry Reforming of CH<sub>4</sub>. *J. Am. Chem. Soc.* **141**, 7283-7293, doi:<https://doi.org/10.1021/jacs.8b10910> (2019).
- 49 Duan, C. *et al.* Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. *Nature* **557**, 217-222, doi:<https://doi.org/10.1038/s41586-018-0082-6> (2018).
- 50 Mie, G. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Annalen der physik* **330**, 377-445 (1908).
- 51 Abernathy, H., Yang, T., Liu, J. & Na, B. NETL Electrical Conductivity Relaxation(ECR) Analysis Tool. doi:<https://doi.org/10.18141/1762415> (2021).
- 52 Konwar, D., Park, B. J., Basumatary, P. & Yoon, H. H. Enhanced performance of solid oxide fuel cells using BaZr<sub>0.2</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> thin films. *J. Power Sources* **353**, 254-259, doi:<https://doi.org/10.1016/j.jpowsour.2017.04.010> (2017).
- 53 Lei, L., Keels, J. M., Tao, Z., Zhang, J. & Chen, F. Thermodynamic and experimental assessment of proton conducting solid oxide fuel cells with internal methane steam reforming. *Applied Energy* **224**, 280-288, doi:<https://doi.org/10.1016/j.apenergy.2018.04.062> (2018).

