Readily processed protonic ceramic fuel cells with high performance at low temperatures

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Because of the generally lower activation energy associated with proton conduction in oxides compared to oxygen ion conduction, protonic ceramic fuel cells (PCFCs) should be able to operate at lower temperatures than solid oxide fuel cells (250°-550°C vs. ≥600°C) on hydrogen and hydrocarbon fuels if fabrication challenges and suitable cathodes can be developed. We fabricated the complete sandwich structure of PCFCs directly from raw precursor oxides with only one moderate-temperature processing step through the use of sintering agents such as copper oxide. We also developed a proton, oxygen-ion, and electron-hole conducting PCFC-compatible cathode material, BaCo0.4Fe0.4Zr0.1Y0.1O3-δ (BCFZY0.1) that greatly improved oxygen reduction reaction kinetics at intermediate to low temperatures. We demonstrated high performance from five different types of PCFC button cells without degradation after 1400 hours. Power densities as high as 445 milliwatt per square centimeter at 500°C on H2 and 142 milliwatt per square centimeter on CH4 were achieved, and operation was possible even at 350°C.

Among the various types of fuel cells, ceramic fuel cells possess several attractive advantages such as fuel flexibility (including the potential to directly use hydrocarbon fuels), high efficiency, and no need for precious-metal catalysts (1–3), but high operating temperatures (700° to 1000°C for conventional “first generation” yttria-stabilized zirconia YSZ-based solid oxide fuel cell (SOFCs)) results in high costs and materials compatibility challenges (4, 5). “Second-generation” SOFCs (5, 6) based on newer oxygen ion conducting electrolytes (such as samarium doped ceria (SDC)), lowered operating temperatures to ~ 600°C (Fig. 1A). Nanostructured “third generation” SOFCs incorporating rare-earth elements such as Eu or Ru, and ultrathin multilayer electrolytes or core-shell nanofiber composite electrodes have achieved exceptional performance at 450° to 600°C (7, 8), but performance drops rapidly with decreasing temperature because the high activation energy Ea associated with oxygen ion conduction (Fig. 1B).

Proton conduction in oxides generally has a lower Ea compared to oxygen ion conduction, so protonic ceramic fuel cells (PCFCs) offer intriguing potential for high-performance (9–13), lower-temperature ceramic fuel cell operation. PCFCs also offer a number of other potential benefits compared to SOFCs, particularly when operating on hydrocarbon fuels. These advantages, illustrated in Fig. 1C, include higher CH4 conversion because of direct proton (hydrogen) removal from the anode and higher carbon cracking resistance because of unfavorable Boudouard Reaction. However, current PCFC performance lags far behind SOFC performance (Fig. 1A), although in the late 1990s, Kreuer et al. provided an important step toward enabling viable PCFCs with the demonstration of stable yttrium-doped barium zirconate (BZY) proton conductors with high (bulk) proton conductivity (14, 15). However, the high grain boundary resistance and fabrication challenges associated with this refractory material system have, until now, constrained its application. Nevertheless, the intrinsic conductivities of currently available protonic ceramic electrolytes suggest that PCFCs can eventually deliver excellent performance between 250° to 550°C. The predicted PCFC performance values based on the limits of current PCFC electrolytes (Fig. 1B) are distributed between 0.2 to 1.6 W cm−2 at 350° to 600°C, based on a 10 μm thick electrolyte (similar to current third-generation SOFCs) and assuming electrode resistances identical to those reported in this paper. Moreover, if epitaxial or “bamboo-structured” PCFC electrolytes can be achieved, thereby mitigating the deleterious effect of blocking grain boundaries, PCFC power densities > 2.0 W cm−2 could be reached.

Two major reasons why PCFCs have lagged their more mature SOFC counterparts are a lack of suitable cathodes expressly designed for PCFC operation and fabrication challenges stemming from the refractory nature of most PCFC electrolytes. Here, we introduce advances that address both of these issues, leading to good PCFC performance at temperatures between 350° to 500°C with power densities of 100-445 mW cm−2. The poor performance of most PCFCs is attributed, in part, to the fact that they use cathodes that were developed for SOFCs operating at much higher temperatures (700° to 1000°C) when target PCFC operation temperatures are near 500°C. We have developed a new perovskite cathode com-
position, BaCo$_{0.4}$Fe$_{0.6}$Zr$_{0.1}$Y$_{0.5}$O$_{3-δ}$ (BCFZY0.1) that is specifically
designed for PCFCs (figs. S2-S3) [see the supporting
online material (SOM)]. BCFZY0.1 is a Y-doped modification of
BaCo$_{0.4}$Fe$_{0.6}$Zr$_{0.1}$O$_{3-δ}$ (BCFZ), which we previously reported
as a highly active and chemically compatible cathode materi-
als for PCFCs (16, 17). BCFZY0.1 is a transition-metal doped
derivative of the well-known proton conducting oxide Ba-
Zr$_{2}$Y$_{1.1}$O$_{3-δ}$ (BZY) (18). Although BZY is an excellent proton
conductor and also exhibits some oxygen ion conductivity in
dry reducing atmospheres (19), its electronic conductivity is
extremely small. By heavily doping the B-site of BZY with
transition metal cations (Co and Fe), the electronic percola-
tion threshold is exceeded, thus activating electronic con-
duction while maintaining ionic conductivity (figs. S4-S6).
The result is a “triple conducting” cathode material (20, 21)
that exhibits simultaneous proton, oxygen ion, and electron
hole conductivity (figs. S7-S8). As illustrated in fig. S9, the
application of conventional SOFC cathodes (which are based
on either electron-conducting oxides or mixed oxygen-ion
electron conducting oxides) to PCFC electrolytes restric-
ts the cathode reaction only to points where the electro-
lyte and electrode phases meet. In contrast, the triple
conducting BCFZY0.1 cathode eliminates the triple-phase
boundary constraints associated with traditional composite
cathode architectures: the entire cathode becomes electro-
chemically active, which offers the chance to lower the via-
able operating window of PCFC devices to <400°C compared
to >700°C today (table S1).

Fabrication complexity has also restrained the com-
mercial development of PCFC technology. The basic structure of
a PCFC consists of a fully dense proton conducting ceramic
electrolyte membrane sandwiched between a porous anode
and a porous cathode. Traditionally (Fig. 2A), the high-
quality componental powders (electrolyte, anode, and cath-
ode) must be synthesized from expensive precursors (e.g.,
nitrates) by complicated wet-chemistry routes (or by time and
energy consuming solid-state reaction procedures) fol-
lowed by multiple drying, grinding, and high-temperature
calcination (≥1000°C) steps. The anode support is then pre-
pared and bisque fired, after which the electrolyte layer is
deposited and the anode/electrolyte “half-cell” is co-fired at
temperatures higher than 1600°C to achieve acceptable elec-
trolyte density. The high sintering temperature required to
achieve densification of the protonic ceramic electrolyte
generally also leads to undesirable coarsening of the anode
structure. Finally, a porous cathode layer is deposited and
the cell is fired a third time to complete the structure. This
separate cathode deposition and firing step frequently leads
to interfacial weakness between the cathode and the electro-
lyte and can constrain the choice of materials options.

Our PCFC fabrication method enables the full cell (i.e.,
porous anode, dense electrolyte, and porous cathode) to be
created in a single reduced-temperature (1400°C) firing step
directly from the raw precursor oxides (Fig. 2B). This ap-
proach leverages the recent development of solid-state reac-
tive sintering (SSRS) (10), whereby carefully selected sinter-
ing aids can be used to assist the conversion of appropri-
ate mixed raw precursor oxides/carbonates (e.g., BaCO$_3$ +
CeO$_2$ + ZrO$_2$ +... etc.) directly into the final phase-pure an-
ode (fig. S10), electrolyte, and cathode perovskite composi-
tions during the single firing step. By using different
sintering aids for the electrolyte vs. the cathode, the former
can be rendered fully dense, while the later can maintain a
highly porous and active nanostructure under the same sinter-
ing conditions (fig. S11). To further improve cathode per-
formance, a second, optional step (Fig. 2B) subsequently
deposits a nanoscale cathode catalyst phase into the porous
cathode bone with solution infiltration followed by calcina-
tion at moderate temperatures (500°C to 900°C). Alternative-
ly, as shown in Fig. 2C, an anode + electrolyte half-cell can
be sintered directly from raw precursor oxides in a first,
moderate-temperature sintering step (~1400°C) with the
subsequent incorporation of a single-phase thin-film cath-
odal via a second lower-temperature (~900°C) sintering step
to ensure high cathode surface area and activity.

To illustrate the versatility of this new approach, we use
the SSRS method to fabricate five different types of PCFC
button cells (Table 1). The button cells feature three differ-
ent well-known PCFC electrolytes: BaZr$_{0.8}$Y$_{0.2}$O$_{3-δ}$ (BZY20),
BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ (BCZY63), and BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-δ}$
(BCZYtYb) in combination with two different sintering aids
(CuO or NiO) and the triple conducting (electron hole, ox-
gen ion, and proton) oxide BCFZY0.1 cathode. These varied
cell compositions demonstrate the generality and reproduc-
ibility of our approach. BZY20, the prototypical PCFC elec-
trolyte material, is notoriously difficult to sinter and densify.
It has excellent stability, but high grain boundary resistance.
BCZY63 provides improved sinterability and lower grain
boundary resistance, but decreased stability compared to
BZY20 (22, 23). BCZYtYb (24) demonstrates one of the high-
est conductivities ever reported for a proton conducting
perovskite, but at the cost of further decreased stability, es-
pecially in H$_2$O or CO$_2$-containing environments (fig. S12).

Nevertheless, successful fabrication of BCZYtYb button cells
by the single-step SSRS fabrication technique demonstrates
that this approach is applicable even to compositionally
complex perovskites (e.g., in this case BCZYtYb has five cat-
ions). Experimental details on the preparation and testing of
the five different PCFC button cells is provided in SOM.

Figure 3 summarizes key results from testing of the five
PCFC button cells. In Fig. 3A, the current-voltage (I-V)
performance of all five cells is compared under H$_2$/air op-
eration at 500°C. The open circuit voltage (OCV) values for all
five cells are higher than 1.05 V, suggesting that both elec-
tronic and mechanical leakages are small. Previous detailed
studies of SSRS-fabricated BCZYtYb-1.0wt%NiO electrolytes
in reducing environments have demonstrated that the elec-
tronic conductivity of these electrolyte materials remains
extremely small (te < 0.01), despite the presence of the NiO
sintering aid, over a wide temperature window (100°C to


800°C) (25). The reduced sintering temperatures enabled by our SSRS fabrication process (≤1450°C) are sufficient to fully densify the thin electrolyte layers in these cells. Fig. S13 shows that dense and defect-free BZY20 electrolytes around 30 μm in thickness can be successfully fabricated using the SSRS method. All cells shown here were fabricated with 20 to 30 μm thick electrolytes and exhibited good reliability and reproducibility.

Figure 3A reveals that cells 1 and 2, which are based on the BCZY63 electrolyte, yield the best performance, with peak power densities of 455 and 405 mW cm$^{-2}$, respectively, at 500°C. Previous reported power densities for PCFCs at this temperature are typically 50-280 mW cm$^{-2}$ (Fig. 1A). These two BCZYYb cells differ primarily in the route used to prepare their cathodes. The highest performing cell (cell 1) was fabricated using the route shown in Fig. 2B while the other BCZYYb cell (cell 2) was fabricated using the route shown in Fig. 2C. The route 2B fabrication process produces a composite two-phase cathode with a highly porous, proton-conducting BCZY63 cathode “backbone” decorated by a nanoparticulate BCFZY0.1 catalyst phase created via a secondary infiltration process (see representative SEM images in fig. S14). In contrast, the route 2C fabrication process uses a single-phase thin-film cathode composed entirely of the BCFZY0.1 catalyst phase without a secondary proton conducting backbone phase (see representative SEM image for this cell in Fig. 3D, additional images provided in fig. S15). The thin-film single-phase cathode provides performance nearly as well as the composite cathode, which substantiates the mixed proton and electronic conduction properties of the BCFZY0.1 cathode material. BCFZY0.1 alleviates the constraints associated with traditional triple-phase boundary composite cathode architectures and enables cells to be produced by the arguably simpler route 2C fabrication process without substantial loss in performance.

Because of the fabrication advantages afforded by the simpler single-phase thin-film cathode design, cells 3, 4, and 5 were also prepared by the route 2C fabrication process. Cells 3 and 4 incorporated a BZY20 electrolyte while cell 5 incorporates a BCZY63 electrolyte. Cell 3 uses 1.0 wt% NiO as a sintering aid, which was mixed with the electrolyte precursors to assist in the phase-formation and densification process, while cells 4 and 5 use 1.4 wt.% and 1.3 wt.% CuO respectively as a sintering aid for the same purpose. We have previously shown (26) that both NiO and CuO are excellent sintering aids for BZY20 and BCZY63. The BZY20 and BCZY63 cells showed modestly decreased performance compared to the BCZYYb cells, which was expected given the lower conductivity of these electrolytes. Although the electrolyte thickness and overall microstructures of cells 3-5 are similar (see figs. S16-S18), the cell prepared with NiO as a sintering aid (cell 3) showed somewhat better performance. The I-V curves in Fig. 3A shows that cell 3 with 1.0wt% NiO as sintering aid has higher OCV which we speculate arose from a lower electronic leak compared with cell 4 which uses 1.4 wt.% CuO as the sintering aid.

Figure 3B provides further details on the performance of cell 2 as an example. The I-V performance of cell 2 as a function of temperature (Fig. 3B) shows that viable power densities (~100 mW cm$^{-2}$) can still be produced at temperatures as low as 350°C. In fact, all five cells produced measurable power at 350°C (the I-V curves of the other four cells as a function of temperature under the same conditions are shown in figs. S16-S19). Exemplary impedance spectroscopy plots of cells 1 and 3 are shown in fig. S20, while the electrolyte and electrode ASRs extracted from these impedance measurements are provided in fig. S21.

Figure 3C demonstrates the stability of the operating voltage and power density during long-term testing of cell 2 under H$_2$/air operation at a constant current density of 300 mA cm$^{-2}$ at 500°C. Both cell voltage and power density actually increased slightly during the course of the 1100 hours test, which we attribute to the continued reduction of the anode during the first 600 hours of operation. The cell was still fully viable after 1100 hours, and its microstructure (Fig. 3D) was virtually identical to that of an untested cell. The cathode/electrolyte and anode/electrolyte interfaces showed no signs of delamination and the well-connected interfacial character was preserved without any visible cracking or pored formation, suggesting good thermal expansion compatibility and stability of the electrodes with the electrolyte. Furthermore, the high-magnification image of the cathode in the inset of Fig. 3D shows that even after long-term testing, the cathode maintained its fine nanostructure.

We investigated whether direct methane operation of several SSRS-fabricated fuel cells could be maintained in the intermediate temperature operating regime. As shown in Fig. 4A, a CuO-sintered BZY20-based cell operating on direct methane fuel attains a peak power density of 240 mW cm$^{-2}$ at 600°C (vs., e.g., 24 mW cm$^{-2}$ at 750°C (27) for previous direct-methane PCFCs). Furthermore, the cell achieved stable operation even at 500°C. The cells also maintain excellent stability. As demonstrated in Fig. 4B and C, the OCV, terminal voltage, and power density for methane fueled BZY20 fuel cells operating at 550° and 500°C remain highly stable during 500 and 1400 hours testing periods, respectively. In both cases, the cells were still fully viable when testing was halted. The microstructure of the BZY20 cell after 1400 hours operation on methane at 500°C (Fig. 4D) revealed no detectable changes in cell morphology, cracking, or delamination, and no evidence of carbon deposition (fig. S22). Long-term stability under OCV condition at 600°C (>400 hours) on methane operation was also measured for a BZY20-based fuel cell sintered with CuO (fig. S23). Based on the higher performance of the NiO-sintered BZY20 cell, its performance on methane was also tested using a H$_2$O/CH$_4$ ratio of 2.5 without fuel dilution by an inert carrier gas. As shown in Fig. 4E, the cell attained peak power densities of 290, 215 and 142 mW cm$^{-2}$ at 600°C, 550°C and 500°C respectively. Figure 4F confirms stability of the cell over 200
hours of testing. These direct methane PCFC single cells achieve unprecedented performance compared with previous results reported in the literature (table S2). Although BCZYYYb-based cells showed better performance on hydrogen, the instability under methanone operation was observed (figs. S12, S24).

By using a densification-aiding sintering additive in the electrolyte layer, a porosity-stabilizing additive in the cathode bone, and poreformer in anode, solid state reactive sintering can be used to produce a complete PCFC single cell directly from raw binary oxides using just one or two combined phase-formation and sintering steps. Low-temperature PCFC performance is further enabled by a new, triple conducting BCFZY0.1 cathode material. The SRRS-fabricated PCFCs attain high power densities at intermediate temperature (as high as 445 mW cm⁻² at 500°C) with viable power density produced at temperatures as low as 350°C and long term durability >1000 hours without loss in performance. Furthermore, SRRS-fabricated PCFCs using BZY20 electrolyte demonstrate very good intermediate-temperature performance and stability under CH₄/air testing for over 1400 hours, underscoring the promise of IT-PCFCs for direct hydrocarbon operation. These results highlight the potential of the SRRS process to provide a commercially practical, simple, and low-cost approach to scalable solid state ceramic devices.

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/cgi/content/full/science.aab3987/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S24
Tables S1 and S2
References for Fig. 1, A and B
References (28–91)
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Fig. 1. Comparison of PCFCs and SOFCs. (A) Performance of current “first-generation” (YSZ-based) SOFCs, “second-generation” (SDC, GDC, and LSGM-based) SOFCs, and “first generation” PCFCs vs. the SSRS-fabricated PCFC with triple-conducting oxide cathode reported here. The new SSRS-based PCFC shows excellent promise in the intermediate and low-temperature regime (350° to 600°C). (B) Performance of recently reported nanostructured “third generation” SOFCs, which generally incorporate exotic elements such as Eu or Ru, ultra-thin multi-layer electrolytes and/or highly nanostructured electrodes vs. predicted performance of PCFCs based on the currently achievable area specific resistance of a 10 μm thick protonic ceramic electrolyte and assuming electrode resistances identical to those reported in this paper. The predicted performance suggests that PCFCs can eventually deliver excellent performance in the IT range (250° to 550°C)—rivaling, if not surpassing, the best third-generation SOFCs. Moreover, the decreased activation energy of PCFC electrolytes compared to SOFC electrolytes suggests PCFCs can be particularly attractive at lower temperatures. (References used for assembling the data points in Fig. 1A, B are provided in the supplementary materials). (C) Schematic illustration of SOFC/PCFC operation. PCFCs can offer a number of other potential benefits compared to SOFCs, particularly when operating on hydrocarbon fuels. These advantages include higher CH₄ conversion because of direct proton (hydrogen) removal from the anode and higher carbon coking resistance due to conditions disfavoring the Boudouard Reaction (Supplementary Text and fig. S1).
Fig. 2. Schematic illustration of the fabrication and structure of PCFC button cells. (A) traditional approach, (B) composite cathode SSRS approach, and (C) thin film cathode SSRS approach.
Fig. 3. Performance and microstructure of selected cells under H₂/air operation. (A) I-V and power density of cells 1-5 under H₂/air at 500°C, (B) I-V and power density of cell 2 under H₂/air at different temperatures, (C) terminal voltage and power density at a current density of 0.3 A cm⁻² at 500°C for cell 2 under H₂/air for over 1100 hours, and (D) a cross-sectional view of cell 2 after operation on H₂ for over 1100 hours (inset figure is the high magnification view of BCFZY0.1 cathode after 1100 hours operation).
Fig. 4. Performance and microstructure of selected cells under CH₄/air operation. (A) I-V and power density for cell 4 under 20vol.% CH₄ + 50vol.% H₂O + 30vol.% Ar/air at 500°, 550° and 600°C. (B) Terminal voltage, open circuit voltage and power density at a current density of 155 mA cm⁻² at 550°C for cell 4 under 20vol.% CH₄ + 50vol.% H₂O + 30vol.% Ar/air for over 500 hours. (C) Terminal voltage, open circuit voltage and power density at a current density of 80 mW cm⁻² at 500°C for cell 4 under 20vol.% CH₄ + 50vol.% H₂O + 30vol.% Ar/air for over 1400 hours. (D) Cross-sectional view of cell 4 after operation under 20vol.% CH₄ + 50vol.% H₂O + 30vol.% Ar/air for over 1400 hours. (E) I-V and power density of cell 3 under 28.6vol.% CH₄ + 71.4vol.% H₂O/air at 500°, 550° and 600°C. (F) Terminal voltage, open circuit voltage and power density of cell 3 at a current density of 150 mA cm⁻² at 500°C under 28.6vol.% CH₄ + 71.4vol.% H₂O/air for over 200 hours.
Table 1. Fabrication method, cell composition, and peak power density of cells 1 to 5.

<table>
<thead>
<tr>
<th>PCFC cells</th>
<th>Fabrication method</th>
<th>Single cell composition</th>
<th>Peak Power density (W/cm²)</th>
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</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>Figure 2B</td>
<td>40wt.% BCZYYb + 60wt.% NiO</td>
<td>BCZYYb + 1.0wt.% NiO</td>
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<tr>
<td>Cell 2</td>
<td>Figure 2C</td>
<td>40wt.% BCZYYb + 60wt.% NiO</td>
<td>BCZYYb + 1.0wt.% NiO</td>
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<tr>
<td>Cell 3</td>
<td>Figure 2C</td>
<td>45wt.% BZY20 + 55wt.% NiO</td>
<td>BZY20 + 1.0wt.% NiO</td>
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<tr>
<td>Cell 4</td>
<td>Figure 2C</td>
<td>45wt.% BZY20 + 55wt.% NiO</td>
<td>BZY20 + 1.4wt.% CuO</td>
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<tr>
<td>Cell 5</td>
<td>Figure 2C</td>
<td>40wt.% BCZYY63 + 60wt.% NiO</td>
<td>BCZYY63 + 1.3wt.% CuO</td>
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