Supporting Online Material

Methods and Materials

CsH₂PO₄ preparation. Cesium dihydrogen phosphate powder was synthesized by methanol-induced precipitation from aqueous solutions of stoichiometric quantities CsCO₃ and H₃PO₄. The resulting precipitate was dried under vacuum at 100 °C.

Thermal analysis. Simultaneous gravimetric analysis and differential scanning calorimetry was performed using a Netzsch Jupiter 449c, equipped with a Balzers AMU 200 mass spectrometer for exhaust gas analysis. Data were collected from 30 to 400 °C at a heating rate of 5 °C min⁻¹. Samples were heated under 60 cm³ min⁻¹ flowing gas, with gas compositions of 4 vol % H₂ in Ar and 15 vol % O₂ in Ar for the first and second experiment, respectively.

Dehydration experiment. Equilibrium dehydration pressures were measured by placing a small quantity of CsH₂PO₄ and various amounts of H₂O in an enclosed, heated chamber equipped with a humidity sensor. The pressure in the chamber was recorded as a function of temperature and the onset of dehydration marked by a rapid increase in \( p_{\text{H}_2\text{O}} \).

MEA fabrication. Single-cell fuel cells, or MEAs were fabricated using carbon Toray paper as electrodes and a mixture of Pt, CsH₂PO₄, carbon, naphthalene in a 10:6:1:1 weight ratio in the electrocatalyst layer (18 mg Pt cm⁻²). In the case of the direct methanol fuel cell, the anode electrocatalyst layer was replaced with a mixture of Pt₀.₅Ru₀.₅ alloy, CsH₂PO₄, C, naphthalene in an 8:6:1:2 weight ratio (13 mg PtRu cm⁻²). The multi-layer structure was cold-pressed under uniaxial pressure at 340 MPa. Upon
heating to the temperature of fuel cell operation, naphthalene sublimed, ideally leaving behind a porous electrode structure. Electrochemical characterization was carried out on three different H\textsubscript{2}/O\textsubscript{2} cells and one DMFC cell.

**Electrochemical measurements.** The sample was placed in an in-house constructed fuel cell measurement station and polarization curves collected using a Keithley 2420 Source Meter. In the case of the H\textsubscript{2}/O\textsubscript{2} cell, humidification was maintained by passing oxygen and hydrogen through water held at 69-72 °C, in order to obtain the desired water partial pressure of 0.3 atm. For the direct methanol fuel cell, argon was passed through hot water (70 °C), and gaseous methanol was added to the humidified argon stream. The CH\textsubscript{3}OH:H\textsubscript{2}O molar ratio was held at 0.92. The water partial pressure at the cathode was maintained at 0.33 atm. Humidity levels were monitored with an accuracy of 1 % using an EdgeTech 650 capacitance-based sensor.

**Supporting Text**

**Consequence of water partial pressure on fuel cell operation**

In order to confirm the necessity for controlling water partial pressure when operating CsH\textsubscript{2}PO\textsubscript{4} electrolyte fuel cells at elevated temperatures, a CsH\textsubscript{2}PO\textsubscript{4}-based membrane electrode assembly was fabricated and measured in an H\textsubscript{2}/O\textsubscript{2} fuel cell configuration. The cell was operated at 242 °C under humidified 50 sccm flowing gasses, \( p_{H_2O} = 0.3 \) atm. The water partial pressure was decreased stepwise, measuring polarizations curves (current density versus cell voltage) at each step. Below \( p_{H_2O} = 0.105 \) atm, the cell became non-operational. From Fig. 1 in the main text, the onset of dehydration at 242 °C is not expected until \( p_{H_2O} = 0.06 \) atm, however, factoring a ± 3 °C error in the measured
temperature, these values are reconcilable. These results show that it is essential to maintain the appropriate water partial pressure to suppress the dehydration of CsH$_2$PO$_4$ when operating a CsH$_2$PO$_4$ electrolyte fuel cell at elevated temperatures.
Supporting Figures

H₂/O₂ fuel cell stability measurement for 35 hours

Fig. S1. H₂/O₂ fuel cell performance with CsH₂PO₄-based electrolyte. (A) Cell voltage and water partial pressure as a function of time while drawing 100 mA cm⁻² continuous current for 35 h. (B) Cell voltage and power density versus current density before and after 35 h measurement. The cell was operated at 235 °C under humidified (p₃O₂ = 0.3 atm) 50 sccm flowing H₂ and O₂ gases at the anode and the cathode, respectively. Electrolyte thickness was 260 µm and catalyst loading 18 mg cm⁻² Pt. During the continuous measurement, the voltage very gradually increased from 0.538 to 0.567 V, with an average of 0.561 V. Water generated at the cathode was in correspondence with that expected from drawing 100 mA cm⁻² current (Fig. S2). The polarization curves obtained before and after the long-term evaluation were similar to one another, although not identical. The open cell voltage (OCV) was initially 0.986 and dropped to 0.960 V after 35 hr measurement. An initial drop in OCV has been observed in similar cells and is attributed to evolution of the electrocatalyst layer.
Water generated at the cathode for H$_2$/O$_2$ fuel cell

**Fig S2.** Cathode water partial pressure as a function of time for a CsH$_2$PO$_4$ electrolyte H$_2$/O$_2$ fuel cell while 100 mA cm$^{-2}$ of current was drawn continuously for 35 h. The cell was operated at 235°C. Flowing 50 sccm humidified, $p_{H_2O}$ of 0.302 atm (initial—dotted line), H$_2$ and O$_2$ gases were fed to the anode and cathode, respectively. While drawing current the average $p_{H_2O}$ was 0.316 atm (measured—solid line). The water partial pressure was measured with an accuracy of ±1%. The water generated at the cathode corresponding to 100 mA cm$^{-2}$ current is $7.06 \times 10^{-5}$ mol min$^{-1}$ H$_2$O, $p_{H_2O}$ of 0.320 atm (calculated—dashed line), which is within experimental error of $5(3) \times 10^{-5}$ mol min$^{-1}$ H$_2$O measured from the change in water partial pressure.
Ohmic loss due to electrolyte resistance

Fig. S3. The current density versus cell voltage for a CsH$_2$PO$_4$-based H$_2$/O$_2$ fuel cell operated at 235°C, $p_{H_2O} = 0.3$ atm. The cell was composed of a 260 µm thick CsH$_2$PO$_4$ electrolyte. The $iR$-corrected result (dashed line), and upper and lower limit (dotted lines) are calculated from the initial (solid line) measured cell voltage $E$, current density $i$, and area specific resistance of the electrolyte $R_A$, $iR$-corrected = $E - iR_A$. The area specific resistance of the electrolyte $R_A$ is calculated from the electrolyte thickness $t$ and conductivity $\sigma$, $R_A = t/\sigma$. Values of conductivity were obtained from the Arrhenius relationship: $\sigma(T) = A/T \exp(-\Delta H_a/k_B T)$, where the pre-exponential factor $A$ and activation enthalpy $\Delta H_a$ obtained from Baranov et al. (1) are $2.7 \times 10^{-3}$ Ω$^{-1}$ cm$^{-1}$ K and 0.29(1) eV, respectively. Using these values, the conductivity of CsH$_2$PO$_4$ is $1.5 \times 10^{-2}$ Ω$^{-1}$ cm$^{-1}$ at 235°C, with an upper and lower limit of $1.9 \times 10^{-2}$ and $1.2 \times 10^{-2}$ Ω$^{-1}$ cm$^{-1}$, respectively. As seen from above, the accuracy of the $iR$-corrected result is heavily dependent upon accurate values of conductivity. Nonetheless, the majority of voltage losses can be attributed to the resistance of the electrolyte.
Onset of dehydration in CsH$_2$PO$_4$

Fig. S4. (A) Water partial pressure ($p_{H_2O}$) as a function of temperature for CsH$_2$PO$_4$ powder at various initial starting water partial pressures. (B) Arrhenius plot of $p_{H_2O}$ as a function of temperature. Powder samples of CsH$_2$PO$_4$ at ten different starting water partial pressures were heated at 0.4 °C min$^{-1}$ to ~300 °C in a closed volume container. Accuracy of recorded temperature was ±3 °C. Onset of dehydration ($T_d$), indicated by a discontinuous change in the slope of $p_{H_2O}$ as a function of temperature, is shown in (A). In (B), no clear Arrhenius behaviour was observed that would indicate a single dehydration reaction and corresponding Gibbs free energy ($\Delta G_r$) for the dehydration CsH$_2$PO$_4$. Though a clear change in slope is expected at 230 °C resulting from the change in entropy through the superprotonic phase transition, unexpected, and indicative of the formation of an intermediate compound, was the observation of a liquid phase at ~290 °C, a temperature well below the melting point of CsH$_2$PO$_4$ or CsPO$_3$. It is likely that the dehydration of CsH$_2$PO$_4$ takes place via a series of polymorphic intermediates which melt at relatively low temperatures. This conclusion is, in part, substantiated both by the absence of Arrhenius behaviour upon heating and a of a reverse reaction upon cooling.
Supporting Tables

Table I. Summary of performance characteristics of three additional CsH₂PO₄-based H₂/O₂ fuel cells. Each cell was prepared in the same fashion, with a CsH₂PO₄ electrolyte thickness of 260 µm, catalyst loading of 18 mg cm⁻² Pt, and humidified gasses (\(P_{\text{H}_2\text{O}} = 0.3\) atm).

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Open Circuit Voltage (V)</th>
<th>Short Circuit Current Density (mA cm⁻²)</th>
<th>Peak Power Density (mW cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.960 – 0.986</td>
<td>308 – 348</td>
<td>61.7 – 65.4</td>
</tr>
<tr>
<td>2</td>
<td>1.003 – 1.027</td>
<td>308 – 383</td>
<td>49.3 – 60.3</td>
</tr>
<tr>
<td>3</td>
<td>0.915 – 0.948</td>
<td>323 – 361</td>
<td>50.5 – 58.1</td>
</tr>
</tbody>
</table>

Supporting References and Notes