Direct electrosynthesis of pure aqueous H₂O₂ solutions up to 20% by weight using a solid electrolyte

Chuan Xia,* Yang Xia,* Peng Zhu, Lei Fan, Haotian Wang†

Hydrogen peroxide (H₂O₂) synthesis generally requires substantial postreaction purification. Here, we report a direct electrochemistry strategy that delivers separate hydrogen (H₂) and oxygen (O₂) streams to an anode and cathode separated by a porous solid electrolyte, wherein the electrochemically generated H+ and HO₂− recombine to form pure aqueous H₂O₂ solutions. By optimizing a functionalized carbon black catalyst for two-electron oxygen reduction, we achieved >90% selectivity for pure H₂O₂ at current densities up to 200 milliamperes per square centimeter, which represents an H₂O₂ productivity of 3.4 millimoles per square centimeter per hour (3660 moles per kilogram of catalyst per hour). A wide range of concentrations of pure H₂O₂ solutions up to 20 weight % could be obtained by tuning the water flow rate through the solid electrolyte, and the catalyst retained activity and selectivity for 100 hours.

H₂ oxidation reaction (HOR):
H₂ → 2H⁺ + 2e⁻ (2)

H₂O₂ formation: HO₂− + H⁺ → H₂O₂ (3)

In the electrochemical process, O₂ and H₂ can be kept safely separated and introduced in pure form to accelerate the reaction. The synthesis can proceed under ambient conditions for on-site H₂O₂ generation and could potentially even output electricity. Although there have been selective catalysts such as noble metals or carbon materials developed for the 2e⁻ ORR pathway (14–18), the H₂O₂ product has typically been generated in a mixture, with solutes in traditional liquid electrolytes ranging from acidic to alkaline pH. Extra separation processes to recover pure H₂O₂ solutions were therefore required. Other designs including the use of deionized (DI) water or a polymer electrolyte membrane as the ion-conducting electrolyte have been explored on a preliminary basis for obtaining pure H₂O₂ solutions, but they generally suffered from low reaction rates, product concentrations, or Faradaic efficiencies (FEs) (supplementary text, note 1) (19–21).

Here, we report a porous solid electrolyte design to realize direct electrolysiss of pure H₂O₂ solutions. As illustrated in Fig. 1B and figs. S1 and S2, independent H₂ and O₂ streams were respectively delivered to HOR and 2e⁻-ORR catalysts coating gas diffusion layer (GDL) electrodes. The anode and cathode “sandwiched” the cation exchange membrane (CEM) and anion exchange membrane (AEM) layers (see materials and methods for details) to avoid flooding by direct contact with liquid water. In the center, a thin and porous solid electrolyte layer facilitated ionic recombination of H⁺ and HO₂− ions crossing from the anode and cathode with small ohmic losses; a flowing DI water stream confined to this middle layer could then dissolve the pure H₂O₂ product with no introduction of ionic impurities. By tuning the HO₂− generation rate or the DI water flow rate, a wide range of H₂O₂ concentrations (from hundreds of parts per million to tens of percent) could be directly obtained with no need for further energy-consuming downstream purification.

To deliver efficient conversion, electrocatalysts with high activity and selectivity for 2e⁻-ORR and HOR are a prerequisite. We chose the state-of-the-art platinum on carbon (Pt/C) catalyst for HOR at the anode, which affords high H₂-to-H⁺ conversion rates at small overpotentials (22–24). For the cathode, however, electrocatalysts with high activity and selectivity for 2e⁻-ORR toward H₂O₂ have been much less thoroughly explored than the extensively studied fuel-cell catalysts for 4e⁻-ORR to H₂O. Recent studies on noble metal catalysts such as Au-Pd or Pd-Hg (14, 25), as well as carbon materials such as grapheme, carbon nanotubes, or porous carbon (15, 16, 26–29), have demonstrated high selectivity toward the 2e⁻ pathway. Nevertheless, practical current densities (hundreds of milliamperes per square centimeter) with high FEs, particularly at neutral pH for the purpose of pure H₂O₂ generation, have not yet been achieved. We chose commercial carbon black as the starting material because of its low cost, its high surface area (fig. S3) for high mass activity, and, especially, its nanoparticulate morphology (fig. S3) to facilitate O₂ diffusion from the GDL (layer-by-layer stacking of graphene nanosheets, by contrast, can hinder gas transport). Surface functional groups such as ethers (C-O-C) and carboxylic acids (HO-C=O) have previously been postid to activate the adjacent carbon atomic sites for selective 2e⁻-ORR (15, 16).

Hence, we treated the carbon black nanoparticles with nitric acid to introduce such oxidized functionality (see materials and methods and supplementary text, note 2). No morphological changes were observed for these carbon black nanoparticles after acid treatment (fig. S3); however, high-resolution x-ray photoelectron spectroscopy (XPS) (fig. S4) confirmed that acid treatment enriched the particles with oxygen-containing functional groups, including C=O/C=O and HO-C=O, as deconvolved from carbon and oxygen 1s signals.

We found that surface oxidation strongly correlated with H₂O₂ selectivity and activity (fig. S5). The selectivity rose from <80% for the oxidized particles to >95% for even relatively low surface oxygen coverage (2.11%). Although the H₂O₂ selectivity was similar upon further increasing the surface oxygen coverage from 2.11 to 11.62% as shown in fig. S5B, we found that the 2e⁻-ORR catalytic activity gradually improved (fig. S5C), which we ascribe to the increased concentration of active sites. After optimization, we selected carbon black with ~10% surface oxygen coverage (CB-10%) as the
cathode catalyst for further development of the full cell. We first used a standard three-electrode rotation ring-disc electrode (RRDE) system in neutral pH (0.1 M Na₂SO₄) to evaluate the intrinsic activity of CB-10% for benchmark comparisons (see materials and methods). The catalyst presented an impressive H₂O₂ generation performance, with a maximal H₂O₂ selectivity of ~98% and an onset potential of 0.438 V versus reversible hydrogen electrode (RHE), to deliver a 0.1 mA cm⁻² H₂O₂ generation current (fig. S7), with potentials calibrated to the RHE scale. The results (fig. S8B) indicate that there were no obvious negative or positive impacts on H₂O₂ selectivity of the CB-10% catalyst when switching from traditional liquid electrolyte to our solid electrolyte. Next, we systematically investigated the H₂O₂ production performance of CB-10% using a two-electrode cell with porous solid electrolyte, as shown schematically in Fig. 1B. Figure 2A shows the current-voltage (I-V) curve of a CB-10%//SE//Pt-C cell with O₂ and H₂ gas streams delivered to the cathode and anode, respectively. The DI water flow rate was fixed at 27 ml hour⁻¹ for this 4-cm² electrode cell to prevent substantial product accumulation, particularly under large currents. H₂O₂ was readily detected starting from a cell voltage of ~0.54 V, suggesting an early onset considering the equilibrium voltage of ~0.76 V (37). The H₂O₂ selectivity remained >90% across the entire cell voltage range, reaching a maximum of 95% (Fig. 2B). An H₂O₂-generation current of ~30 mA cm⁻² was achieved, whereas high FE was still maintained in neutral solutions, better than the highest O₂-to-H₂O₂ conversion rates yet observed (30).

The porous solid electrolyte layer comprises either an anion or cation solid conductor, which can consist of ion-conducting polymers with different functional groups (31), inorganic compounds (32), or other types of solid electrolyte materials such as ceramics, polymer–ceramic hybrids, or solidified gels (33). Among these different solid conductors, polymer ion conductors have been widely used for electrochemistry applications because of their fast ion conduction at room temperature, high reliability, and ease of processing (34). Because proton conduction is generally faster than anion conduction (35), here, we chose to use styrene-divinylbenzene copolymer microspheres (fig. S7), functionalized with sulfonic acid groups for cation (H⁺) conduction along their interconnected surfaces; in addition, the micrometer pores formed between these stacked spheres allow for DI water flow and product release (fig. S7). We first studied the impact of the solid electrolyte on H₂O₂ selectivity by the CB-10% catalyst in a standard three-electrode setup (fig. S8A), with potentials calibrated to the RHE scale. The results (fig. S8B) indicate that there would be no obvious negative or positive impacts on H₂O₂ selectivity of the CB-10% catalyst when switching from traditional liquid electrolyte to our solid electrolyte. Next, we systematically investigated the H₂O₂ production performance of CB-10% using a two-electrode cell with porous solid electrolyte, as shown schematically in Fig. 1B. Figure 2A shows the current-voltage (I-V) curve of a CB-10%//SE//Pt-C cell with O₂ and H₂ gas streams delivered to the cathode and anode, respectively. The DI water flow rate was fixed at 27 ml hour⁻¹ for this 4-cm² electrode cell to prevent substantial product accumulation, particularly under large currents. H₂O₂ was readily detected starting from a cell voltage of ~0.54 V, suggesting an early onset considering the equilibrium voltage of ~0.76 V (37). The H₂O₂ selectivity remained >90% across the entire cell voltage range, reaching a maximum of 95% (Fig. 2B). An H₂O₂-generation current of ~30 mA cm⁻² was achieved, whereas high FE was still maintained in neutral solutions, better than the highest O₂-to-H₂O₂ conversion rates yet observed (30).

Table 1. Performance metrics of different H₂O₂ generation methods

<table>
<thead>
<tr>
<th></th>
<th>Purity</th>
<th>Productivity (mol kg⁻¹ cat⁻¹ hour⁻¹)</th>
<th>Productivity (mmol cm⁻² hour⁻¹)</th>
<th>Selectivity (%)</th>
<th>Stability</th>
<th>Max. concentration (ppm)</th>
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<tbody>
<tr>
<td>Our method</td>
<td>Pure</td>
<td>3660</td>
<td>3.4</td>
<td>90 – 95</td>
<td>&gt;100 hours</td>
<td>200,000</td>
</tr>
<tr>
<td>Direct synthesis</td>
<td>Mixture (8, 9, 45–47)</td>
<td>60.8 – 180</td>
<td>N/A</td>
<td>80.7 – 96</td>
<td>Up to 4 cycles or 4 hours</td>
<td>5300</td>
</tr>
<tr>
<td>Electrochemical syn.</td>
<td>Mixture (48–53)</td>
<td>N/A</td>
<td>0.05 – 1.2</td>
<td>47 – 93.5</td>
<td>2 – 6 hours</td>
<td>3400 – 60,000</td>
</tr>
<tr>
<td>Electrochemical syn.</td>
<td>Pure (19–21)</td>
<td>N/A</td>
<td>0.16 – 0.289</td>
<td>26.5 – 30</td>
<td>6 – 72 hours</td>
<td>1400 – 80,000</td>
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Fig. 1. Schematic illustration of the two different H₂O₂ synthesis methods using H₂ and O₂. (A) Synthesis of H₂O₂ using diluted H₂ and O₂ under high pressure. Methanol used to improve the solubility of the reacting gases in the medium (44) must then be removed downstream. Other studies that avoid alcohols have been performed in acidic solutions of either HCl or H₂SO₄, with NaBr or NaCl as promoters (44). (B) Electrolysis of H₂O₂ using pure H₂ and O₂ streams separately introduced to the anode and cathode, respectively. SE represents a solid electrolyte, which consisted in this study of either functionalized styrene–divinylbenzene copolymer microspheres or inorganic CsₓH₉₋ₓPW₁₂O₄₀ (see materials and methods). Electrochemically generated cations (H⁺) and anions (HO₂⁻), driven by the electric field, cross in the porous SE layer and recombine to form H₂O₂. DI water flowing through the porous SE layer then dissolves the H₂O₂ with no impurities.
(0.53 mmol cm\(^{-2}\) hour\(^{-1}\)) could be obtained under 0 V (no external energy input). Moreover, a potential of only 0.61 V was required to deliver a current density of 200 mA cm\(^{-2}\) with an H\(_2\)O\(_2\) FE of -90%. This current represents an H\(_2\)O\(_2\)-generation rate of 3.4 mmol cm\(^{-2}\) hour\(^{-1}\), or 3660 mol kg\(^{-1}\) cat hour\(^{-1}\) considering both cathode and anode catalyst (see materials and methods; a comparison with literature benchmarks is given in Table 1 and fig. S9). No H\(_2\) byproduct (potentially from H\(_2\) evolution at large overpotentials) was detected from the cathode side under such a high current density (fig. S10A), indicating exclusive selectivity for ORR. Other types of solid electrolyte with different material properties, including polymeric conductors for HO\(_2^-\) conduction and inorganic Cs\(_x\)H\(_{3-x}\)PW\(_{12}\)O\(_{40}\) for cation conduction, were also demonstrated to be effective for pure H\(_2\)O\(_2\) solution generation (fig. S11), which suggests the wide tunability and versatility of our solid electrolyte design.

Under a fixed DI water flow rate of 27 ml hour\(^{-1}\), the H\(_2\)O\(_2\) concentration from our 4-cm\(^2\)

![Fig. 2. Direct electrosynthesis of pure H\(_2\)O\(_2\) using H\(_2\) and O\(_2\) with porous solid electrolyte.](http://science.sciencemag.org/)

(A) I-V curve of CB-10%/SE/Pt-C cell with an H\(^{+}\)-conducting porous solid electrolyte. We define the cell voltage as negative when the cell can output energy during the production of H\(_2\)O\(_2\). The positive cell voltage therefore indicates that energy input is required for the reactor. The cell voltages were \(iR\) (current × resistance) compensated (see materials and methods).

(B) Corresponding FEs and production rates of H\(_2\)O\(_2\) under different cell voltages. (C) Dependence of H\(_2\)O\(_2\) concentration on the DI water flow rate at an overall current density of 200 mA cm\(^{-2}\). Up to 20 wt % pure H\(_2\)O\(_2\) solutions could be continuously generated for immediate use. The data points in (A) to (C) each represent the mean of two independent measurements.

(D) Removal of TOC in Houston rainwater using the H\(_2\)O\(_2\) solution generated at a fixed current density of 200 mA cm\(^{-2}\) and a fixed DI water flow rate of 27 ml hour\(^{-1}\) in our 4-cm\(^2\) electrode device. A high rainwater treatment rate of 0.88 liters hour\(^{-1}\) (0.22 liters cm\(^{-2}\) electrode hour\(^{-1}\) or 2200 liters m\(^2\) electrode hour\(^{-1}\)) was achieved to meet the drinking water standards (TOC < 2 ppm according to the Texas Commission on Environmental Quality). (E and F) Stability tests for continuous generation of pure H\(_2\)O\(_2\) solutions with concentrations >1000 and 10,000 ppm, respectively. No degradation of cell voltage or H\(_2\)O\(_2\) concentration was observed over the 100-hour continuous operation. The cell currents and DI flow rates were (E) 60 mA and 27 ml hour\(^{-1}\) and (F) 120 mA and 5.4 ml hour\(^{-1}\), respectively.
the O2/SE/H2O cell. (80 cm² electrode, no scaled-up unit cell module.) We ascribe the observed decrease in apparent FE (98% at 0.3 wt % versus 70% at 6.6 wt %) to the following two possible processes. First, the higher concentration of H2O2 product in the solid electrolyte layer could shift the equilibrium of the 2e⁻-ORR while enhancing the selectivity of the competing 4e⁻ pathway to H2O2 product, thereby lowering intrinsic H2O2 selectivity. Second, while H2O2 formation proceeds, a fraction of the generated H2O2 might not be detected, particularly at high product concentration, because of a potentially increased bimolecular decomposition rate and/or increased crossover to the anode, as frequently observed in methanol or formic acid fuel cells (38–40); this would result in an apparent decrease in H2O2 selectivity. Possible impurities in the product solution, such as sodium (common in water), iron (from the device), sulfur (from the SE), and platinum (from the anode), were quantified to be at or below ppm levels determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) (table S1 and supplementary text, note 3). Therefore, the electrochemically synthesized H2O2 solutions could be put to immediate use out of the cell without any further purification, lowering cost substantially compared with other methods and simplifying the setup for the deployment of on-site generation technology. Long-term stability is another important metric for evaluating catalysis. Our device produced ~1200 and ~11,000 ppm H2O2 solutions continuously in 100-hour test runs with no degradation in activity or selectivity (Fig. 2, E and F). XPS characterization of the CB-10% catalyst after the reaction revealed that the surface oxygen functionality was robust and did not appear to have been electrochemically reduced during the operation of the ORR (fig. S10B).

As a representative demonstration of on-site application, we used the as-synthesized H2O2 from our device for rainwater purification (Fig. 2D and fig. S13). Compared with traditionally used chlorine compounds, which may produce carcinogens in the processed drinking water (41), H2O2 is safe for both human and environmental health when disinfecting and decomposing organic contaminants, typically assessed as removal of total organic carbon (TOC) (42). The use of electrochemically generated H2O2 is not only economical (see supplementary text, note 4), but also avoids the transportation and storage of hazardous bulk H2O2. We directly mixed the generated H2O2 stream (200 mA cm⁻², 27 ml hour⁻¹ DI water flow) from our 4-cm² electrode device with the rainwater stream (feeding rate ranging from 18.32 to 0.05 liters hour⁻¹) to optimize the purification efficiency. The TOC of the pristine rainwater collected at the Rice University campus in Houston was detected to be ~5 ppm (see materials and methods), which is above the Texas treated-water standard of ~2 ppm (43). Decreasing the rainwater feeding rate gradually lowered the TOC remaining (Fig.

**Fig. 3. Electrosynthesis of pure H2O2 solutions by 2e⁻-ORR and water oxidation.** (A) I-V curve for an O2/SE/H2O cell in which H2O is oxidized at the anode side to form protons and O2. A 0.5 M aqueous H2SO4 solution was used to improve ionic conductivity on the anode side and was not consumed during electrosynthesis. (B) Corresponding FEs of the O2/SE/H2O cell. (C) I-V curve and FEs for an air/SE/H2O cell generating pure H2O2 solutions. Pure H2O2 solutions were generated at a high production rate of 2.3 mmol cm⁻² hour⁻¹ (2490 mol kg⁻¹ cat⁻¹ hour⁻¹) using only air and water as cathode and anode feedstock, respectively. (D) I-V curve of the scaled-up unit cell module (80 cm² electrode, no IR compensation), and (E) the corresponding H2O2 FEs. (F) Dependence of H2O2 concentration (up to ~20 wt %) on the DI water flow rate at a constant overall current of 8 A. The data points in (A) to (E) each represent the mean of two independent measurements.
2D), demonstrating the efficacy of the generated H₂O₂ solution in water treatment. A maximal processing rate of 0.88 liter hour⁻¹ (0.22 liter cm⁻² electrode hour⁻¹ or 2200 liters m⁻² electrode hour⁻¹) was achieved in lowering the TOC level to meet the drinking water standards, making our design economically and environmentally appealing for practical rainwater treatment when scaled up.

We also demonstrated that the oxidation reaction on the anode side could be flexibly modified to be coupled with the cathodic 2e⁻/ORR for applications where H₂ is not available (Fig. S14). Water oxidation to O₂ with concurrent proton release might be easier to access than hydrogen oxidation. A 0.5 M aqueous sulfuric acid solution on the anode side was used to lower the ionic resistance; H₂SO₄ was not consumed during the reaction and was continuously circulated (see materials and methods). The CEM membrane blocked crossover of the H₂SO₄ into the porous solid electrolyte layer, ensuring the formation of pure H₂O₂ solutions. This was confirmed by pH and ICP-OES measurements: The pH of the generated H₂O₂ solution was ~6 to 7 (pure H₂O₂ solutions show a sign), we extended the electrode area from 4 cm² to 80 cm² (Fig. 3F and fig. S12B).

Given the wide variety of liquid products amenable to electrochemical synthesis, our solid electrolyte design could in principle be extended beyond H₂O₂ generation to other important electrochemical applications.

REFERENCES AND NOTES


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Direct electrosynthesis of pure aqueous H$_2$O$_2$ solutions up to 20% by weight using a solid electrolyte

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**A direct route to pure peroxide**

Despite the widespread use of hydrogen peroxide as an oxidant and disinfectant, its commercial synthesis still requires inefficient concentration and purification steps. Xia *et al.* now report an electrochemical approach to synthesizing pure peroxide solutions straight from hydrogen and oxygen. Using a solid-state electrolyte, they avoid contamination of the product solution by extraneous ions. Varying the flow rate of water through the electrochemical cell tunes the final concentration over a range from 0.3% to 20% by weight.

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