

Supporting Information

Optimization and scaling-up of porous solid electrolyte electrochemical reactors for hydrogen peroxide electrosynthesis

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S1. The assembling and operating schematic of PSE reactors

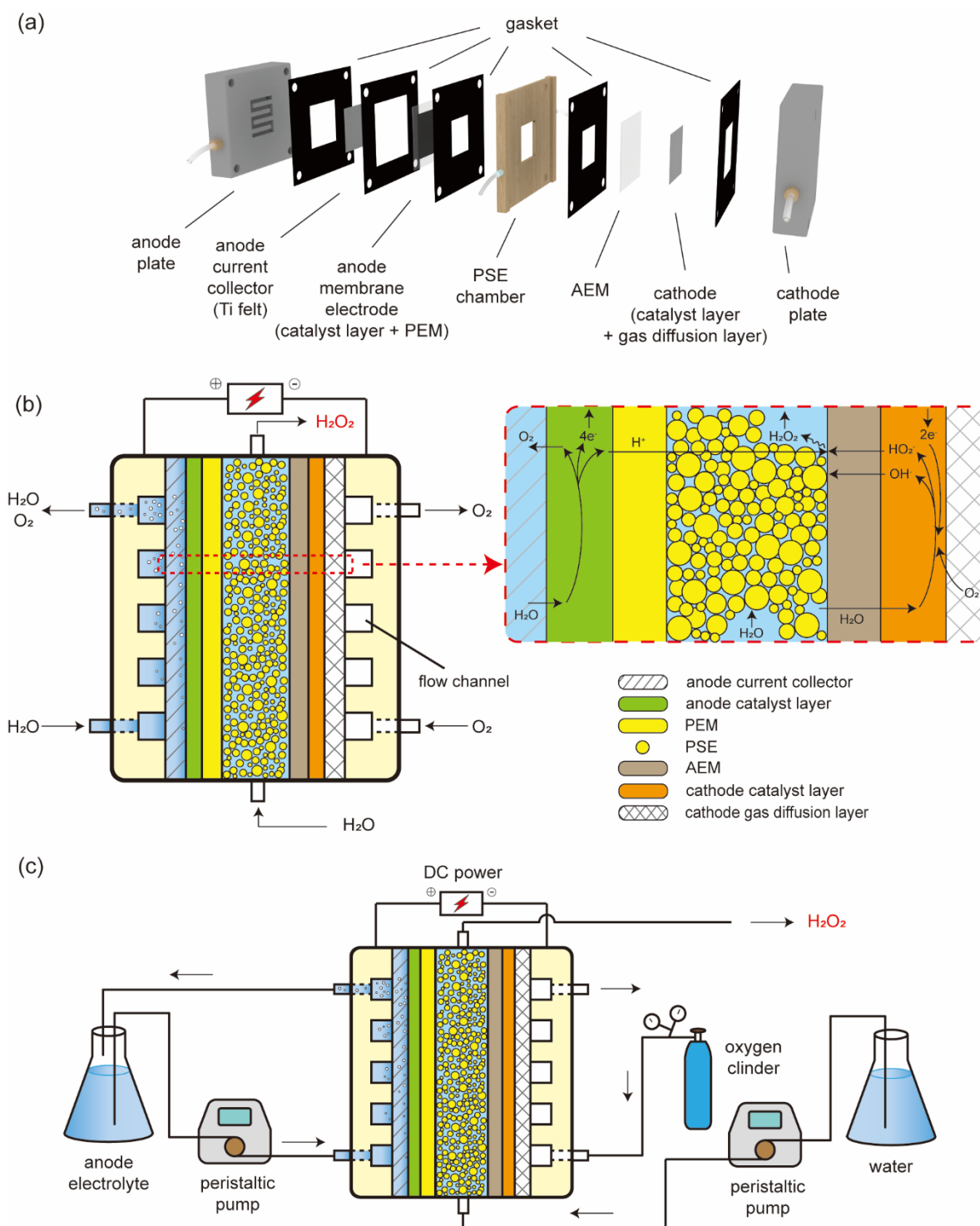


Fig. S1. Setup and operation schematics of PSE reactor. (a) The components and assembling strategy, (b) H_2O_2 production principle, and (c) operating schematic of the PSE reactor.

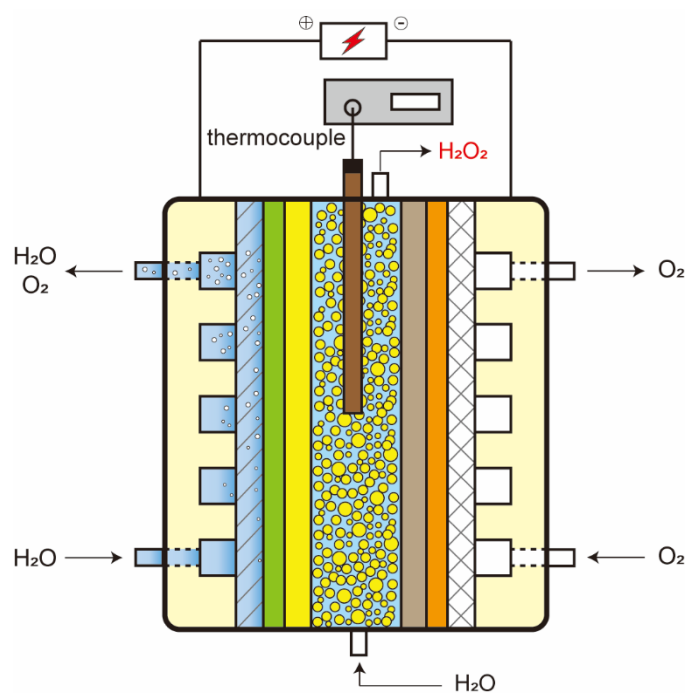


Fig. S2. The schematic of the temperature detection inside the PSE reactor.

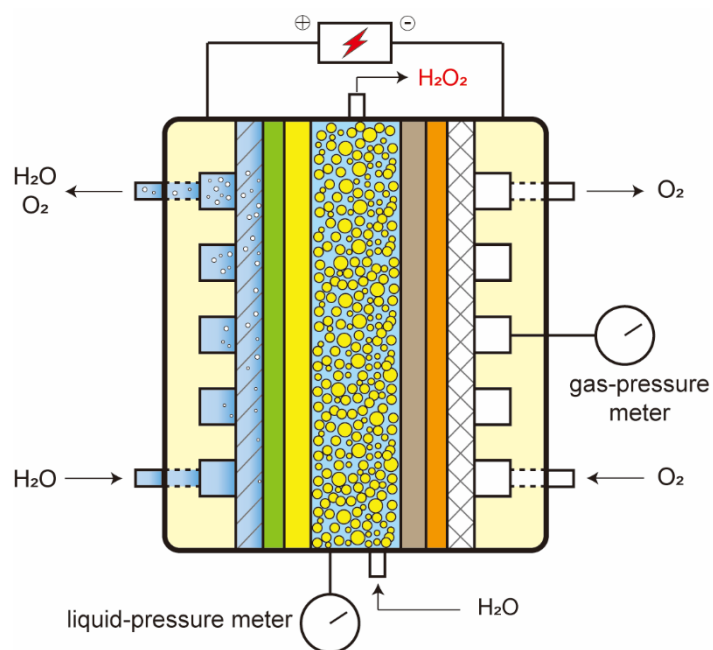


Fig. S3. The schematic of the pressure detection.

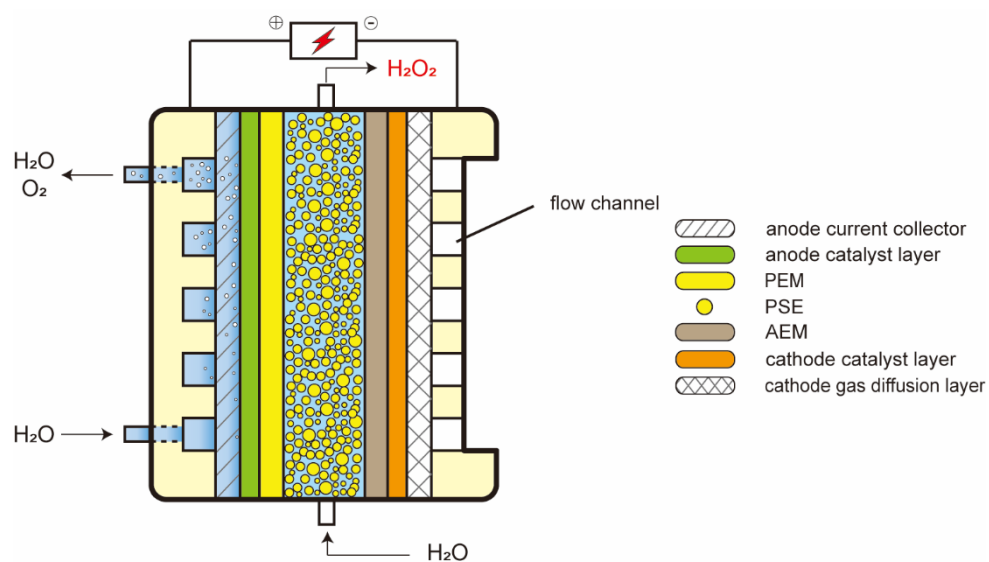


Fig. S4. PSE reactor in natural air diffusion mode.

S2. Carbon black catalyst

To quantify the ORR performance of carbon black, a rotating ring-disk electrode (RRDE) was employed at 1600 rpm in 0.1 M KOH. The loading amount of carbon black was 0.3 mg/cm², and the scan rate was 5 mV/s. Fig. S5 exhibits the RRDE result, which shows that the H₂O₂ selectivity of carbon black is higher than ~80% over the potential range from 0.2 to 0.7 V vs. RHE. This result proves carbon black is a good 2e-ORR catalyst and can be used in PSE reactor.

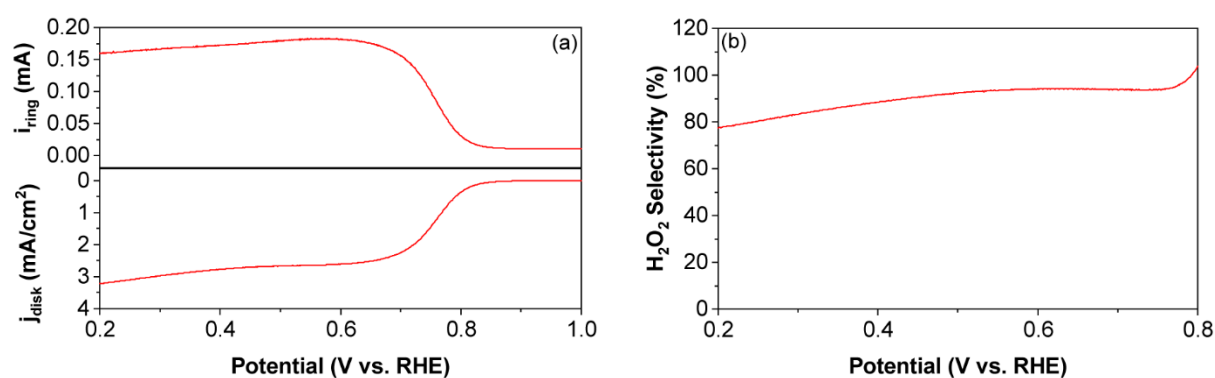


Fig. S5. The performance of carbon black catalyst without iR-correction. (a) Linear sweep voltammetry (LSV) results, (b) H₂O₂ selectivity. Source data for Fig. S5 are provided as a Source Data file.

S3. Effects of PSE on H₂O₂ electrosynthesis

Fig. S6 shows the energy consumption (EC) during H₂O₂ electrosynthesis with the various PSEs. Corresponding to the different R_s of H⁺ conduction, EC increased in the order of Dowex 50W×8, Amberlite IR 120H, Sennate D001×7, and Purolite CT-175 when a given current density was applied during H₂O₂ electrosynthesis (see Fig. 1 for more information).

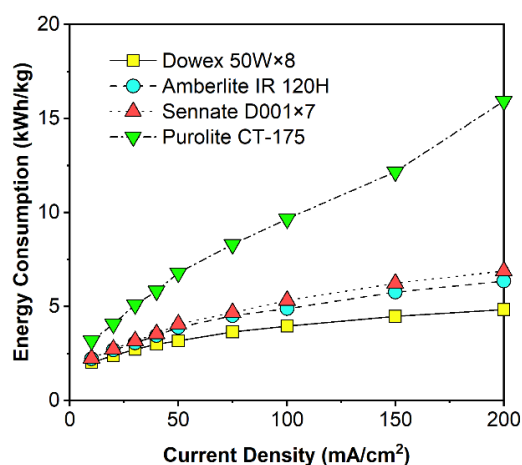


Fig. S6. Energy consumption during H₂O₂ electrosynthesis with various PSEs. Source data for Fig. S6 are provided as a Source Data file.

Fig. S7 presents the SEM images and S EDS mapping results of various PSEs. The substantially lower S density of Purolite CT-175 demonstrates a lower surface SA group density compared with other PSE.

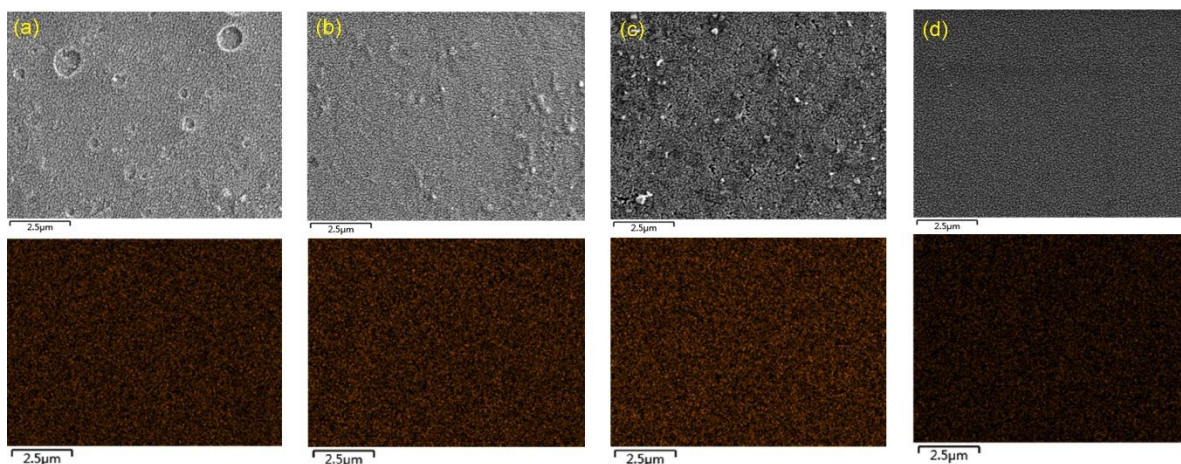


Fig. S7. SEM images and S EDS mapping results of (a) Dowex 50W×8, (b) Amberlite IR 120H, (c) Sennate D001×7, and (d) Purolite CT-175.

The ion transfer resistance of PSE was measured using a modified method that has been used to measure the ionic conductivity of proton exchange membrane (PEM),¹ as depicted in Fig. S8. Briefly, PSE particles were filled into the test slot ($7\text{ mm} \times 7\text{ mm} \times 1\text{ mm}$) with a packing density of $\sim 1100\text{ mg/mL}$. Two Pt sheet electrodes were then used to cover the PSE and then sandwiched by two PTFE endplates. The electrochemical impedance spectroscopy (EIS) test and fitting were conducted with an AC amplitude of 5 mV around the open-circuit potential from 10 kHz to 1 Hz using a CS-1350 electrochemical workstation (Correst Co., Ltd., China). When applying a voltage oscillation of 5 mV to two Pt electrodes, the double-layer capacitance on the electrode surface is approximately short-circuited at higher frequencies, thereby eliminating the electron transfer step. Therefore, the intersection of the Nyquist plot with the real axis (Z') represents the ion transfer resistance (R_s) of the PSE.

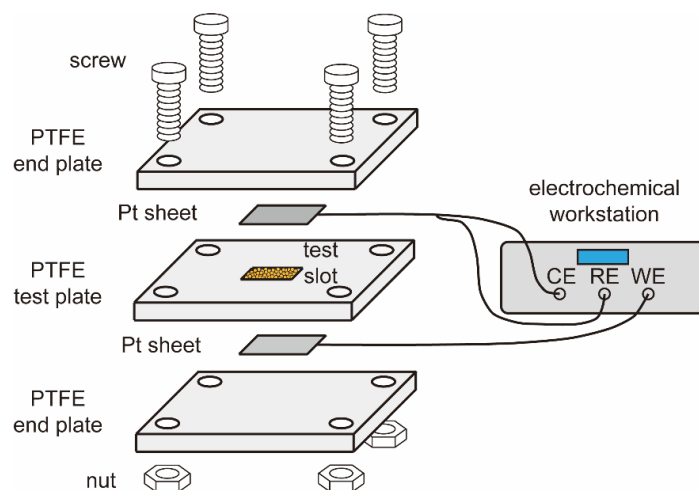


Fig. S8. The experimental schematic of the ion transfer resistance of PSE.

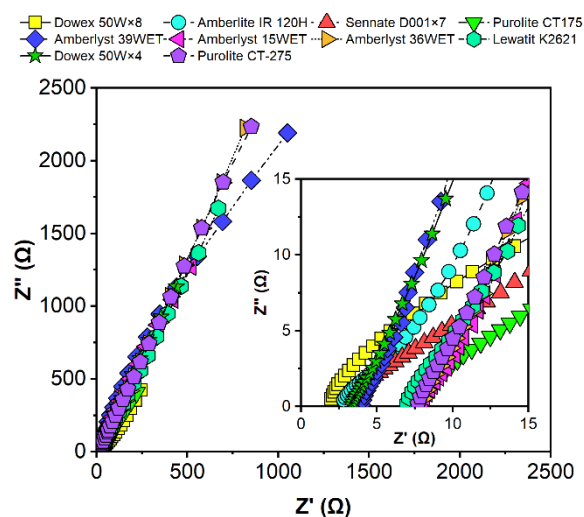


Fig. S9. Nyquist plots of various PSEs. Source data for Fig. S9 are provided as a Source Data file.

During H_2O_2 electrosynthesis, the temperature inside the PSE reactor increased quickly to a stable level within a few minutes (Fig. S10a). Moreover, the steady temperatures increased with increasing applied current densities due to the more significant Joule heating effect at higher currents (Fig. S10b). Furthermore, the R_s of PSEs has a significant effect on the reactor temperature. Under an applied current density of 200 mA/cm^2 , the stabilized temperatures were $\sim 26\text{--}28^\circ\text{C}$ during H_2O_2 electrosynthesis with Dowex $50\text{W}\times 8$, Amberlite IR 120H, and Sennate $\text{D001}\times 7$, but reached $\sim 45^\circ\text{C}$ with Purolite CT-175 (Fig. S10c) because of its considerably

higher R_s than the other PSEs (see Table 1). Additionally, a homogenous temperature field of the PSE reactor can be observed with various PSEs, evidenced by the infrared thermal imaging (Fig. S10d).

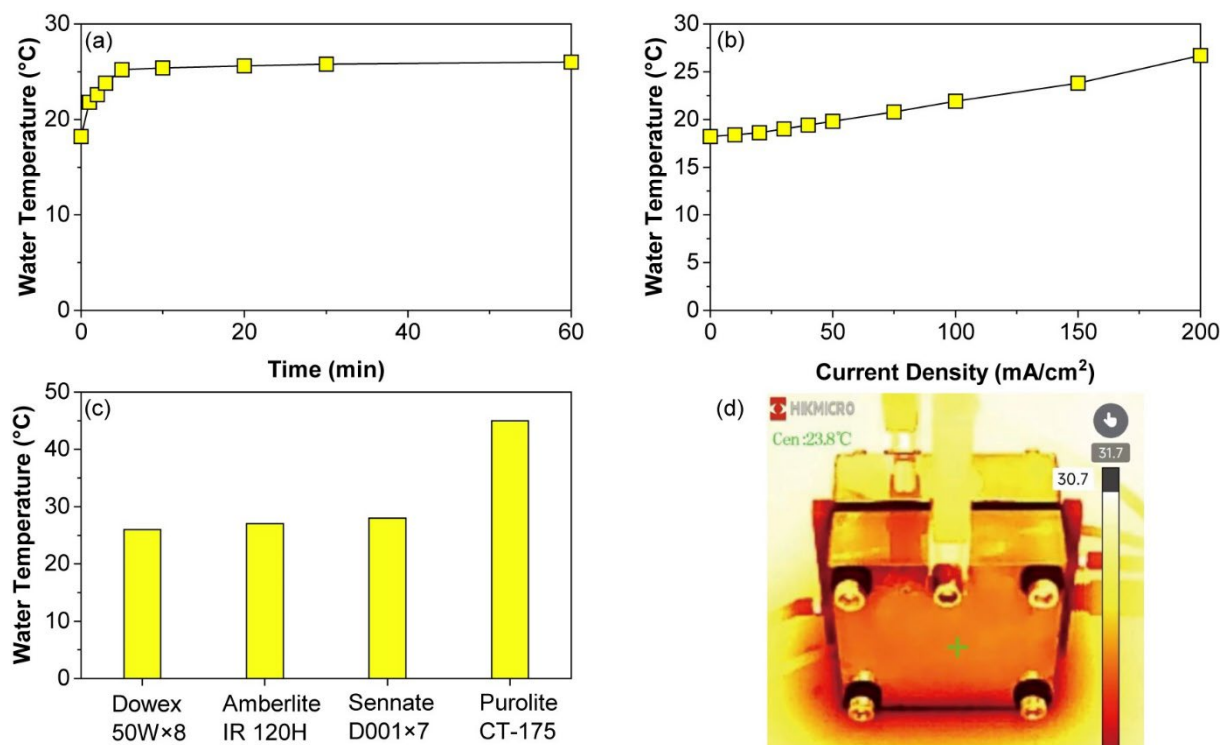


Fig. S10. Reactor temperatures as a function of (a) operation time, (b) current density, and (c) PSE type during H_2O_2 electrosynthesis, (d) infrared thermal imaging of the PSE cell. Operating conditions: PSE = Dowex 50W×8 for Figs. S10a, b, and d; current density = 200 mA/cm² for Figs. S10a, c, and d. Source data for Fig. S10a–c are provided as a Source Data file.

The effects of PSE microsphere diameter and packing density on the performance of H_2O_2 electrosynthesis are shown in Fig. S11 and S12, respectively. In a cubic space of 1 mm × 1 mm × 1 mm, a maximum of eight PSE microspheres with a diameter of 500 μm can be packed, yielding a total of 12 contact points (Fig. S11a). Assuming a current density of 100 mA/cm² and a faradaic efficiency (FE) of 100%, this configuration results in the transfer of approximately 6.25×10^{17} protons per second, equating to a task of 5.2×10^{16} proton transfers per second per contact point. In comparison, when the diameter of PSE microspheres is

decreased to 100 μm , the number of PSE microspheres in the space can reach 1000. Consequently, a total contact points of 2700 can be obtained, which leads to each contact point transfers 2.3×10^{14} protons per second. This is two orders of magnitude lower than the proton transfer requirement for 500 μm microspheres. Consequently, R_s of H^+ conduction decreases considerably as PSE microsphere diameters decreases (Fig. S11c), which in turn decreases the cell voltage and EC of H_2O_2 production (Fig. 2c and Fig. S11d).

With decreasing the PSE microsphere diameter, higher pressures were required to drive the water to pass through the PSE reactor. Nevertheless, the increase of pressures did not considerably influence the performance of H_2O_2 electrosynthesis. For example, Figs. S11e and f show that FEs and H_2O_2 concentrations were generally the same under the different pressures. However, when the smallest PSE microspheres (35–75 μm) were used, the outlet of the reactor would be gradually clogged by microspheres washed away from the PSE chamber. Consequently, the flow rate decreased considerably during H_2O_2 electrosynthesis with the smallest PSE microspheres (Fig. S11e), which in turn increased H_2O_2 concentrations in the reactor effluent considerably, while FEs remained almost unchanged (Fig. S11f).

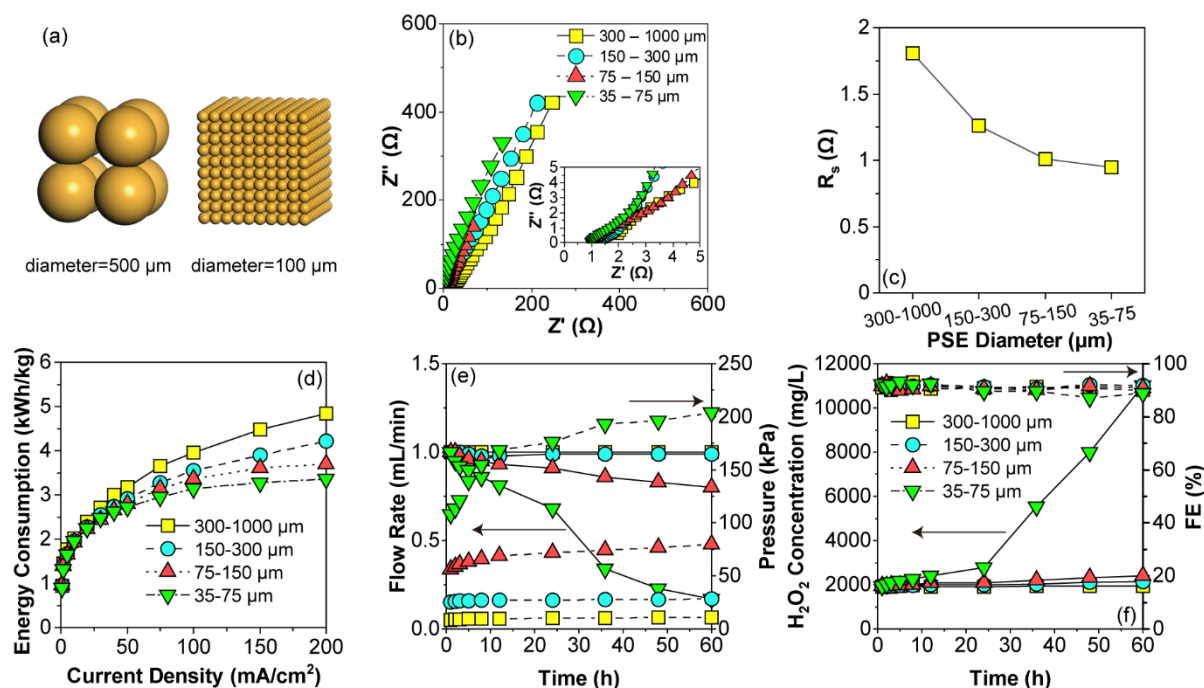


Fig. S11. The effects of PSE microsphere diameter on H_2O_2 production. (a) The number of contact points, (b) Nyquist plots, (c) R_s of PSE microspheres of various diameters; (d) the energy consumption, (e) water flow rate (solid lines) and pressure (dash lines) in the PSE reactor, and (f) H_2O_2 concentrations (solid lines) and Faradaic efficiency (FE, dash lines) during H_2O_2 electrosynthesis with PSE microspheres of various diameters. Source data for Fig. S11b–f are provided as a Source Data file.

With increasing PSE packing densities, the GDE is more likely to fracture at the edge of serpentine channel of GDE due to stress concentration (Fig. S12d upper). Therefore, we used a porous titanium plate to cover the serpentine channel of GDE (Fig. S12e). This configuration avoided the stress concentration effect and thus effectively prevented the GDE fracture even with a PSE packing density of $\sim 1400 \text{ mg/mL}$ (Fig. S12d lower).

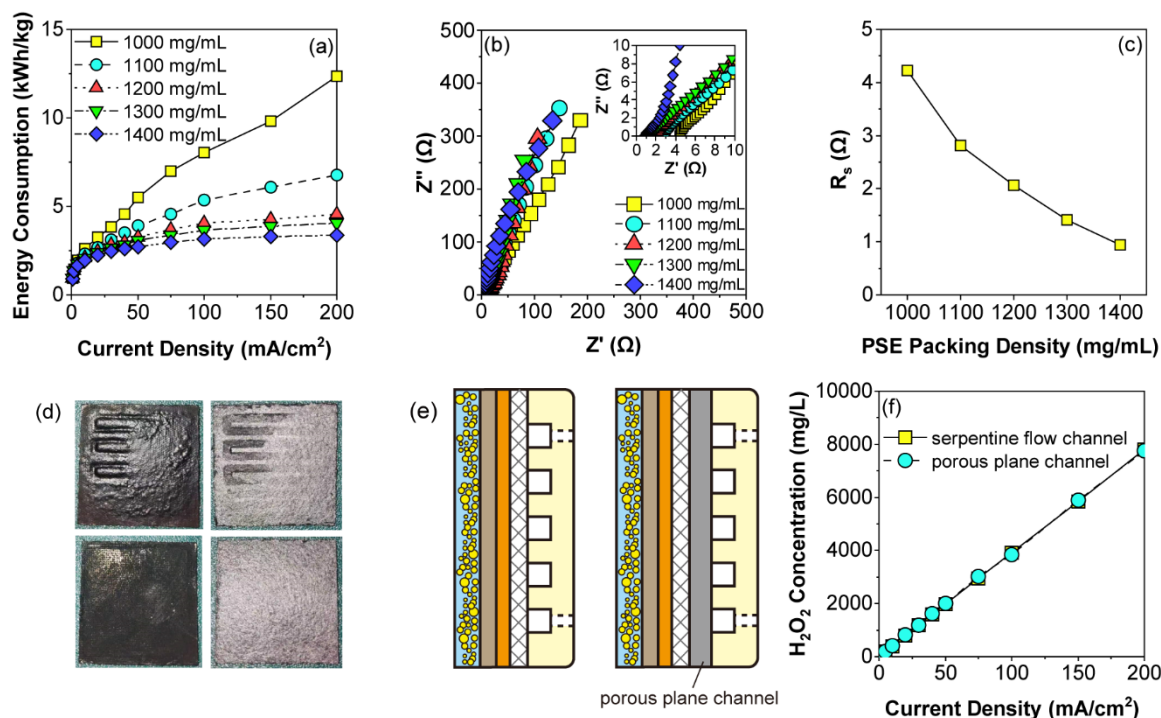


Fig. S12. Effects of PSE packing densities on (a) EC of H₂O₂ production, (b) Nyquist plots and (c) R_s of PSE; (d) photos of fractured (upper) and well-preserved (bottom) cathode, (e) schematic of the cathodic half-cell, and (f) H₂O₂ concentration in the absence and presence of the porous titanium plate. Source data for Fig. S12a–c and f are provided as a Source Data file.

We also evaluated the feasibility of using anion exchange PSE for H₂O₂ electrosynthesis with the PSE reactor. The anion exchange PSE is designed to conduct HO₂[−] ions produced by the cathode. As shown in Figs. S13a–c, the performance of H₂O₂ electrosynthesis with anion PSE (Dowex 1×8) was significantly inferior to that with cation exchange PSE (Dowex 50W×8) because the HO₂[−] conductivity of anion exchange PSE is considerably lower than the H⁺ conductivity of cation exchange PSE.

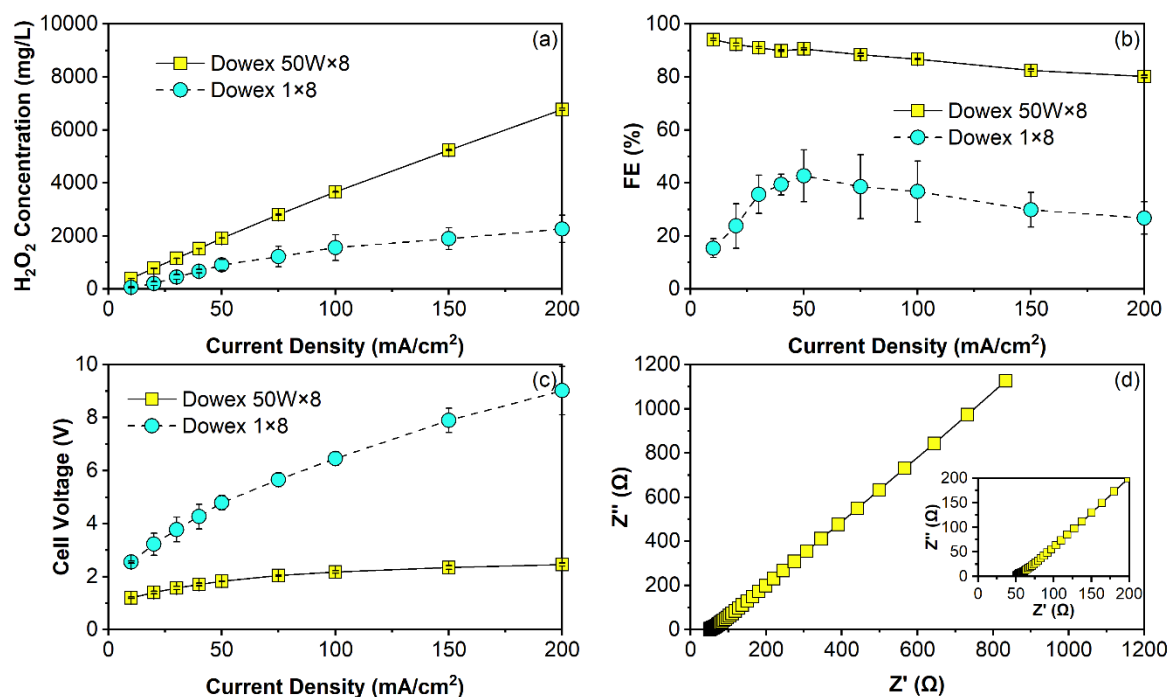


Fig. S13. The effects of anion exchange PSE on H_2O_2 production. (a) H_2O_2 concentrations, (b) Faradaic efficiency (FE), and (c) cell voltages as a function of current density during H_2O_2 electrosynthesis with anion exchange PSE, (d) Nyquist plots of the anion exchange PSE. The resistance of PSEs used in this figure is $\sim 5.88 \Omega$. All the voltages are reported without iR -correction. Each experiment has been repeated at least three times. The error line represents the standard deviation. Source data for Fig. S13 are provided as a Source Data file.

S4. Effects of AEM on H₂O₂ electrosynthesis

In the absence of an AEM, the PSE reactor exhibited excellent H₂O₂ production performance and very low cell voltage at the beginning (Fig. S14a-c). However, the GDE then experienced rapid deterioration within 12 h, as manifested by the quick decrease of H₂O₂ concentrations and increase of cell voltages and GDE backpressure (Fig. S14d-f). The deterioration of H₂O₂ electrosynthesis performance can be mainly attributed to the flooding of GDE pores by water.² Due to the electrocapillary effect and high water pressure inside the PSE reactor, water can easily intrude progressively into the GDE pores if there is not an AEM to separate the water and GDE, thus causing the electrode flooding and failure (Fig. S14g). By natural air drying the flooded GDE, the performance of H₂O₂ electrosynthesis could be temporarily restored (Fig. S14h). Nevertheless, the GDE would be quickly flooded again (Fig. S14h). These results indicate that it is impractical to operate the PSE reactor without an AEM to separate the GDE and water.

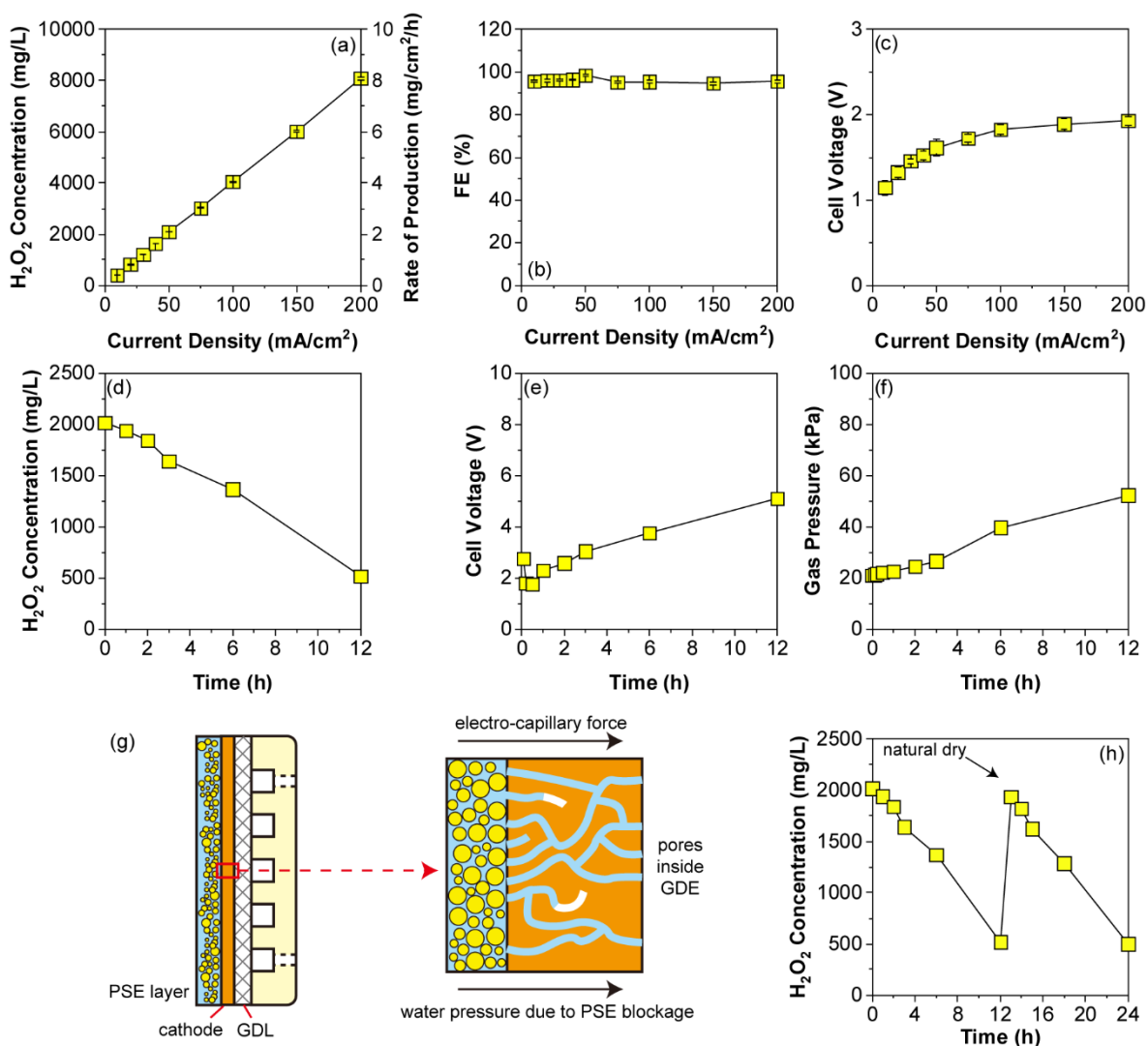


Fig. S14. H_2O_2 electrosynthesis performance of the PSE reactor without AEM. (a) H_2O_2 concentration, (b) Faradaic efficiency (FE), and (c) cell voltage as a function of applied current density; (d) H_2O_2 concentration, (e) cell voltage, and (f) GDE backpressure as a function of operating time; (g) schematic of GDE flooding by water, and (h) effect of natural drying of flooded GDE on H_2O_2 electrosynthesis. The resistance of PSEs used in this test is $\sim 0.01 \, \Omega$. All the voltages are reported without iR -correction. Each experiment was repeated at least three times except for stability test. Error bars represent the standard deviation. Source data for Fig. S14a–f and h are provided as a Source Data file.

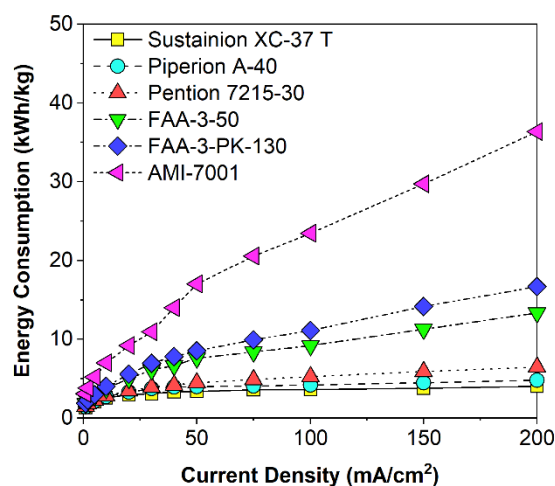


Fig. S15. EC of H_2O_2 production as a function of applied current densities during H_2O_2 electrosynthesis with various AEMs. Source data for Fig. S15 are provided as a Source Data file.

The resistance of HO_2^- conduction of the AEMs was measured using the EIS technique (Fig. S16). Prior to the measurement, the AEMs were soaked in 1% H_2O_2 solutions at pH 13 for 1 h to adsorb HO_2^- at the QA groups. The AEMs were then placed between two Pt sheet electrodes to measure their resistance of HO_2^- conduction in a similar way as described previously for the PSEs (see Fig. S8).

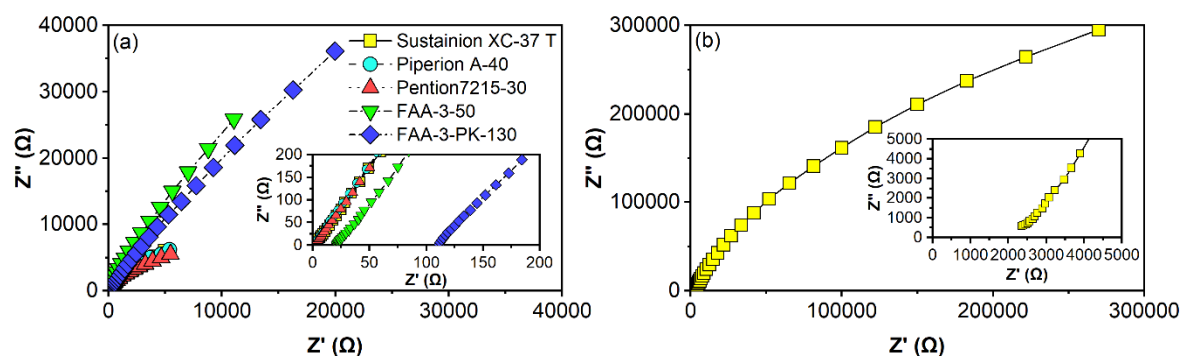


Fig. S16. Nyquist plots of the AEMs tested in this study: (a) Piperion A-40, Pention 7215-30, FAA-3-50, and FAA-3-PK-130, (b) Sustainion XC-37T. Source data for Fig. S16 are provided as a Source Data file.

Before molecular dynamics (MD) simulation, the water uptakes of Sustainion XC-37T, Piperion A-40, Pention 7215-30, and AMI-7001 were measured using a method described previously.³ Briefly, the AEM samples were hydrated in DI water for at least 3 days. The samples were subsequently weighed after cleaning by the delicate wipers (KimTech Co., Ltd., Canada). Later, the samples were dried at 60 °C for 24 h and then weighted again. The water uptakes are calculated using Eqs. S3 and S4, and are shown in Table S1.

$$\lambda = \frac{\varphi}{IEC \times M_W} \quad (S3)$$

$$\varphi = \frac{m_h - m_d}{m_d} \times 100\% \quad (S4)$$

where φ is the water content, IEC is the ion exchange capacity of AEMs (eq/g), M_W is the molecular weight of water (18.02 g/mol), m_h and m_d are the weight of hydrated and dried AEM (g).

Table S1. Measured water uptake (λ) of various AEMs.

	m_h (g)	m_d (g)	water content (%)	IEC (meq/g)	water uptake
Sustainion XC-37T	0.0456	0.0287	58.9	1.05	31.2
Piperion A-40	0.1328	0.093	42.8	1.89	12.6
Pention 7215-30	0.3384	0.2135	58.5	1.51	21.5
AMI-7001	0.7896	0.5415	45.8	1.3	19.6

The molecular polarity index (MPI) of neighboring groups of the QA group of in the AEMs are calculated by the Multiwfn software and shown in Fig. S17. MPI has been taken as an indicator of the inter- and intra-molecular polarity,⁴ with a greater MPI typically meaning a higher polarity and thus a higher hydrophilicity. As shown in Fig. S17, the groups near QA group in Sustainion XC-37 T, Piperion A-40, and Pention 7215-30 have MPIs that are generally larger than 4. In contrast, the MPI of the benzene-C adjacent to QA group in AMI-7001 is only

3.195, which means a lower hydrophilicity of this site. Therefore, water molecules will be pushed away from the benzene ring to the QA group of AMI-7001, resulting in a greater hydration of QA group. Consequently, HO_2^- ion is more likely to bond with QA group in AMI-7001 because of the hydrophilicity of HO_2^- .

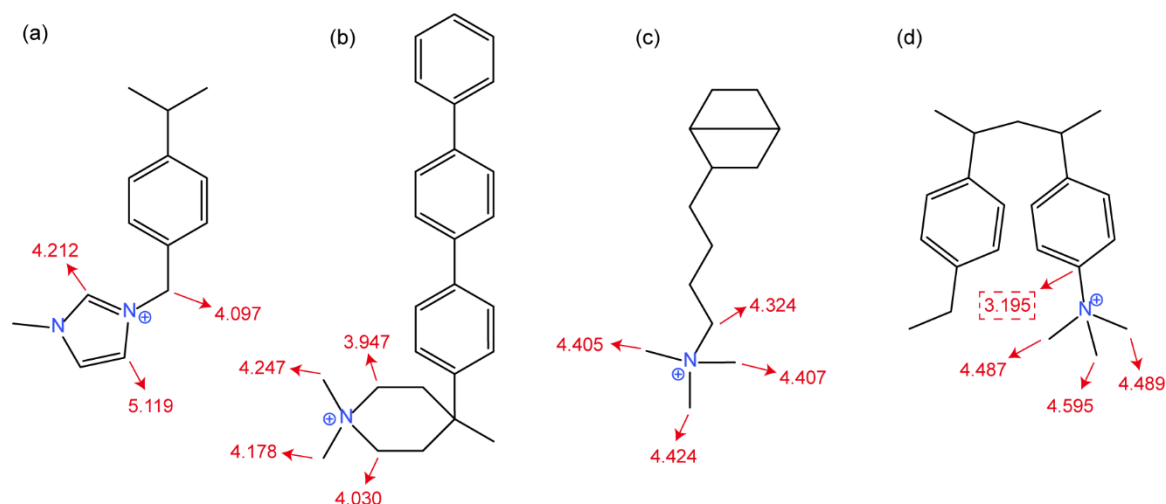


Fig. S17. The molecular structure and calculated MPI of (a) Sustainion XC-37 T, (b) Piperion A-40, (c) Penton 7215-30, and (d) AMI-7001.

For the four AEMs, the radial distribution function (RDF, defined as the probability of finding a particle at a distance r from another tagged particle) between various particles were simulated, and the corresponding coordination number (CN, defined as the number of molecules that are found in the range of each coordination sphere) were calculated using Eqs. S1 and S2.

$$g(r) = \frac{dN}{4\pi r^2 \rho dr} \quad (\text{S1})$$

$$\text{CN} = \int_0^r 4\pi r^2 \rho g(r) dr \quad (\text{S2})$$

where $g(r)$ is RDF, N is number of particles, r is a given distance ($\text{\AA}$), ρ is the average number density of atoms in the simulation cell.

The results in Fig. S18e indicate that the CNs of QA group to HO_2^- increase in the order of Sustainion XC-37 T, Piperion A-40, Pention 7215-30, and AMI-7001 within the range of 12 Å. This suggests that in AMI-7001, the number of HO_2^- ions around QA groups is greater than that in other three AEMs. According to the Coulomb's law, the lower distance between the opposite-charged ions means an increased electrostatic attraction, as shown in Eq. S3.

$$F = \frac{kq_1q_2}{r^2} \quad (\text{S3})$$

Beyond a certain threshold, the greater the electrostatic attraction of functional groups to ions, the more difficult the ion transfer becomes.⁵ Hence, this result can explain the lower HO_2^- conductivity of AMI-7001 (Fig. 3d) than other three AEMs.

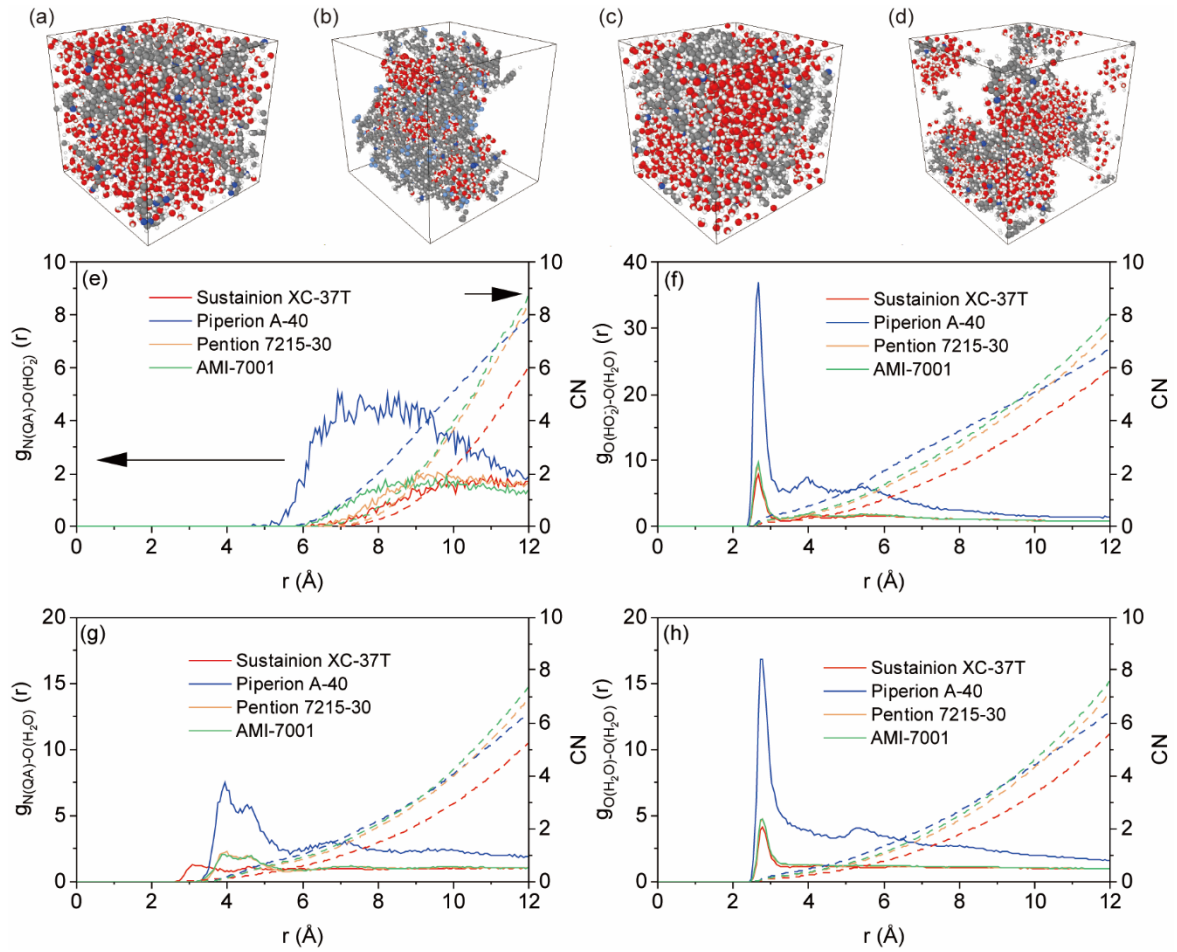


Fig. S18. Pictures of the unit cells used in MD after equilibrium calculations. (a) Sustainion XC-37 T, (b) Piperion A-40, (c) Pention 7215-30, (d) AMI-7001; The RDF and coordination number (CN) of (e) N(QA)-O(HO₂⁻), (f) O(HO₂⁻)-O(H₂O), (g) N(QA)-O(H₂O), (h) O(H₂O)-O(H₂O) of four AEMs. Source data for Fig. S18e–h are provided as a Source Data file.

To elucidate fundamental mechanism of the differences in RDF between HO₂⁻ and QA groups in these two AEMs, RDF analysis was performed for other particles. Fig. S18 shows the RDF between HO₂⁻ and water. Obviously, the higher CN of AMI-7001 within 12 Å than other three AEMs indicates that there are more water molecules around HO₂⁻ in AMI-7001 than other AEMs. Fig. S18g presents the RDF between HO₂⁻ and water. The higher CN of AMI-7001 within 12 Å than other three AEMs demonstrates the most hydration of QA group in AMI-7001. Similarly, the highest CN of AMI-7001 in Fig. S18g suggests a closer interaction between water molecules in AMI-7001 compared to other AEMs, possibly due to the water is more likely to aggregate in AMI-7001. All these results indicate that the water molecules are prone to move towards the QA group in AMI-7001, resulting in the larger hydration of QA group and thus lead to the tight bonding with HO₂⁻ due to hydrophilic interaction (e.g., hydrogen bond). Consequently, HO₂⁻ is more difficult to be transport alongside the polymer chain of AMI-7001 than other AEMs.

To simulate the HO₂⁻ conductivity of the AEMs by MD, we collected the mean square displacement (MSD) of HO₂⁻ within 10000 fs simulation (Fig. S19). Based on the slope obtained by fitting the quasi-linear region (0–4000 fs) of the MSD curve, the diffusion coefficients of HO₂⁻ in the AEMs were calculated according to the Stokes-Einstein equation (Eq. S4). The HO₂⁻ conductivity of Sustainion XC-37T, Piperion A-40, Pention 7215-30, and AMI-7001, is then calculated to be 5.29, 3.86, 1.58, and 0.85 mS/cm, according to the Nernst-Einstein equation (Eq. S5).

$$D = \frac{1}{6N_a} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_a} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (S4)$$

$$\sigma = \frac{z^2 D F^2}{RT} \quad (S5)$$

where D is the HO_2^- diffusion coefficient (m^2/s), N_a the number of HO_2^- in the simulation box, $r_i(t)$ and $r_i(0)$ are the displacement of ion i after and before diffusion time t , σ is the conductivity (S/m), z is the charged number of HO_2^- , R is the ideal gas constant ($8.314 \text{ J}/(\text{mol K})$), T is the temperature (K).

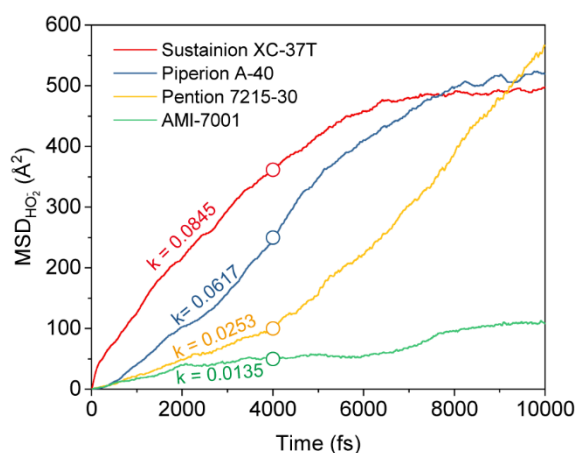


Fig. S19. MSD results and corresponding slopes of various AEMs. Source data for Fig. S19 are provided as a Source Data file.

Fig. S20 shows that the PSE microspheres exhibited insignificant changes in the appearance and ion conductivity after 500 h of H_2O_2 electrosynthesis. In addition, the GDE also maintained similar ORR activity after the experiments.

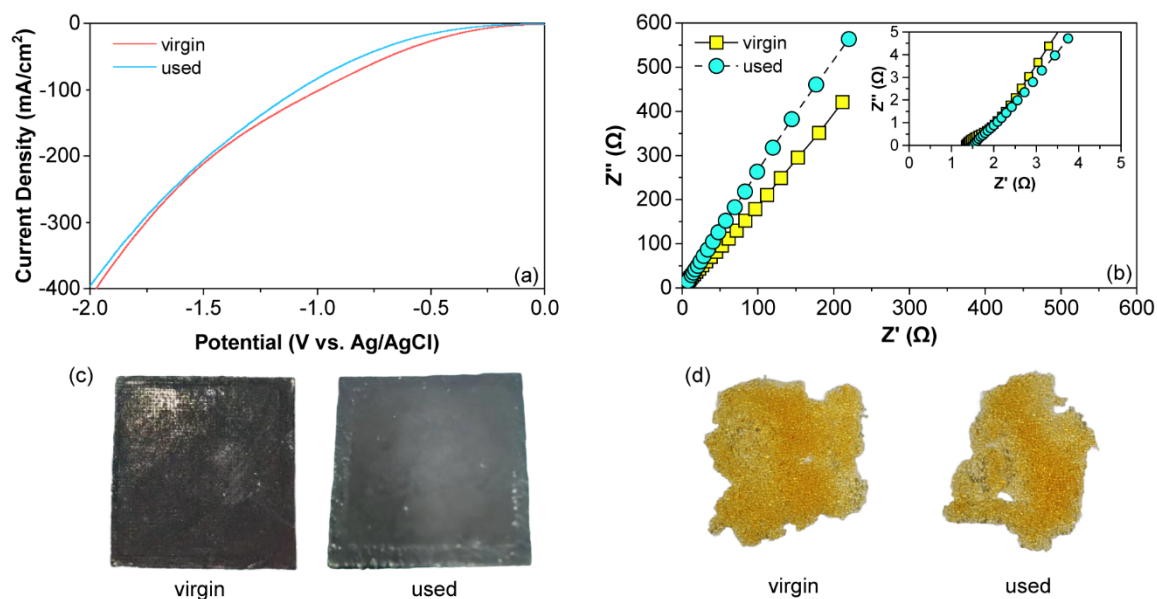


Fig. S20. Stability of GDE and PSE during H₂O₂ production. (a) LSV curves of GDE cathode, (b) EIS plot of PSE (Dowex 50W×8), photos of (c) GDE cathode and (d) PSE (Dowex 50W×8) before and after 500 h of H₂O₂ electrosynthesis experiments. Source data for Fig. S20a and b are provided as a Source Data file.

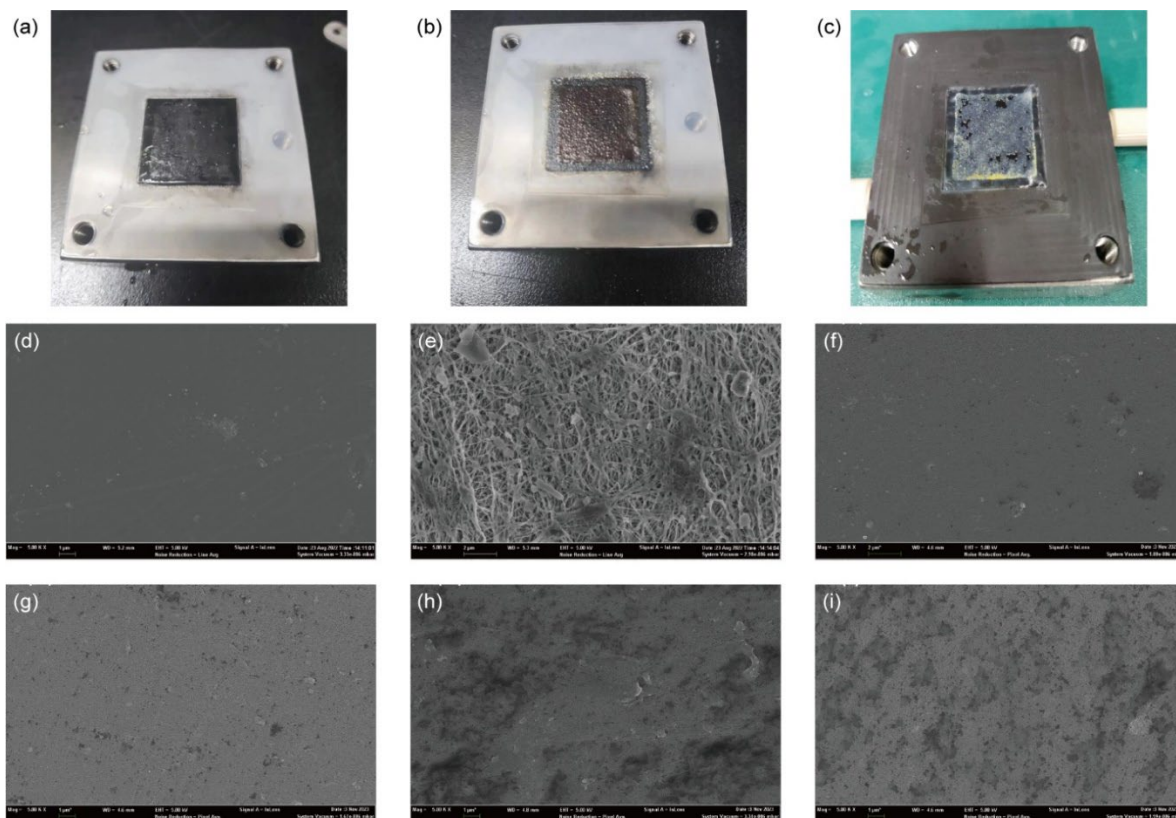


Fig. S21. Digital photos of Sustainion XC-37T at (a) 0 h, (b) ~300 h, and (c) ~500 h during H₂O₂ electrosynthesis with 75 mA/cm², and SEM images of Sustainion XC-37T at (d) 0 h, (e) 500 h, (f) NaOH pH = 13 treated, (g) 1% H₂O₂ pH = 7 treated, (h) 1% H₂O₂ pH = 13 treated, (i) 1% H₂O₂ UV treated.

The calculated highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) of HO₂⁻ and AEMs are shown in Fig. S22, and their energies are shown in Table. S3. For all AEMs, the energy differences between HOMO of HO₂⁻ and LUMO of AEMs are essentially smaller than the energy difference between HOMO of AEM and LUMO of HO₂⁻. This means electrons are preferably transferred from the HOMO of HO₂⁻ to LUMO of AEMs. In other words, the HO₂⁻ can react with the AEM by nucleophilic attack.

Fig. S23 present the nucleophilic Fukui function (f^+) isosurfaces of various AEMs. Notably, f^+ is essentially larger around the QA group than other sites. This indicates that the HO₂⁻ nucleophilic attack sites of these AEMs are all QA groups, which is the functional groups for HO₂⁻ transfer.

Table S2. The ATR-IR peaks and their chemical meanings.

Wavenumber (cm ⁻¹)	group	vibration	REFs
925	-CH ₃	rocking vibration	6
982	N-O	stretching vibration	7
1004	-CH ₃	rocking vibration	8
1036	C-N	stretching vibration	9
1074	C-OH	asymmetry vibration	10
1150	benzene	ring vibration	11
1223	zigzag planar sequence of polystyrene		12
1260	C-N	stretching vibration	13
1300	-CH ₂ -	twisting vibration	14
1345	-COO-	asymmetry vibration	15

1378	benzene	ring vibration	11
1461	-CH ₃	asymmetry vibration	16
1491	benzene	ring vibration	17
1640	C=N	stretching vibration	18
2850	-CH ₃	stretching vibration	19
2920	-CH ₃	asymmetry vibration	19
2960	-COOH	bending vibration	20
3032	N-H	stretching vibration	21

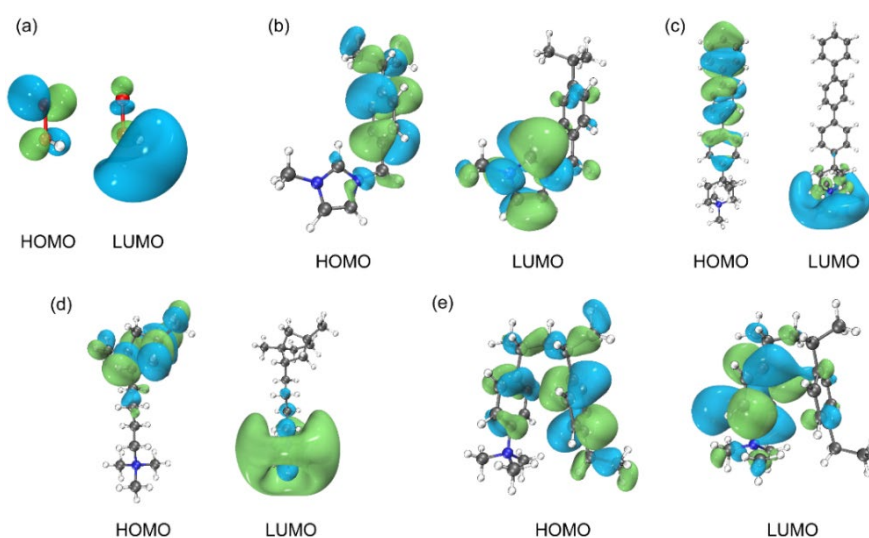


Fig. S22. The HOMO-LUMO of (a) HO₂⁻, (b) Sustainion XC-37T, (c) Piperion A-40, (d) Penton 7215-30, and (e) AMI-7001. The isosurface value is 0.02 a.u.

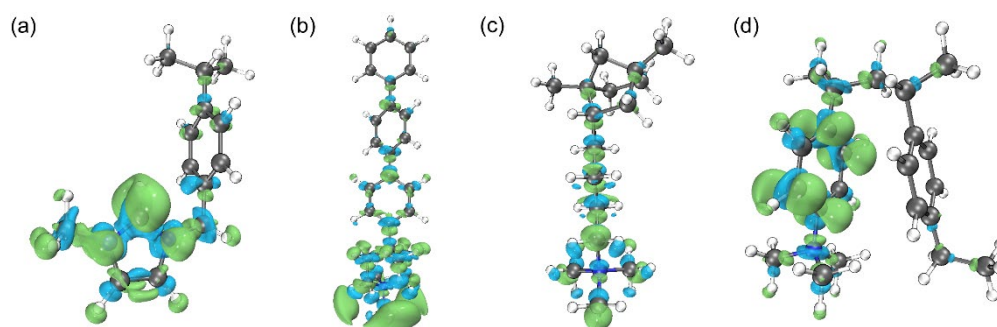


Fig. S23. The f^+ of (a) Sustainion XC-37T, (b) Piperion A-40, (c) Penton 7215-30, and (d) AMI-7001. The isosurface value is 0.005 a.u.

Table S3. The HOMO-LUMO energy of HO_2^- and various AEMs. (eV)

	HOMO	LUMO	AEM LUMO – HO_2^- HOMO	HO_2^- LUMO – AEM HOMO
HO_2^-	−0.20	7.36		
Sustainion XC-37T	−11.27	−3.68	−3.48	18.63
Piperion A-40	−9.01	−3.23	−3.03	16.37
Pention 7215-30	−11.15	−3.34	−3.14	18.51
AMI-7001	−10.29	−3.22	−3.02	17.65

The six designed pathways of nucleophilic attack of HO_2^- to QA-N of Sustainion XC-37T and four designed pathways of nucleophilic attack of OH^- to QA-N of Sustainion XC-37T are shown in Fig. S24, and the calculated reaction free energies ($\Delta G_{\text{reaction}}$) are shown in Table S4. The average $\Delta G_{\text{reaction}}$ of HO_2^- and OH^- nucleophilic attack to QA-N is −7.52 and −5.73 eV, respectively, demonstrating a thermodynamic preference of HO_2^- nucleophilic attack to QA-N compared to OH^- nucleophilic attack.

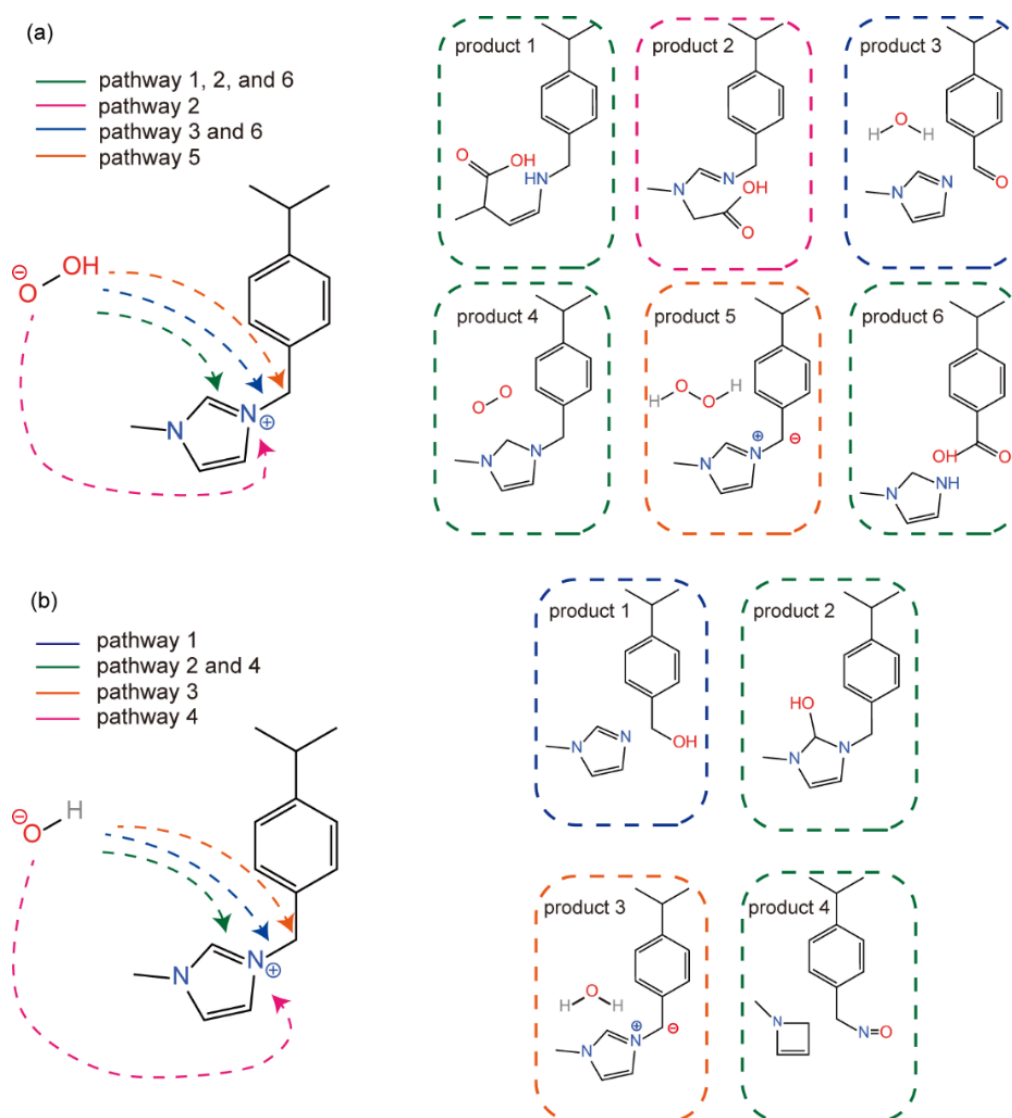


Fig. S24. The designed attacking pathways of ORR products to QA-N of Sustainion XC-37T.

(a) six designed pathways of nucleophilic attack of HO_2^- to QA-N of Sustainion XC-37T and
 (b) four designed pathways of nucleophilic attack of OH^- to QA-N of Sustainion XC-37T.

Table S4. The $\Delta G_{\text{reaction}}$ of HO_2^- and QA-N in various AEMs. (eV)

items	E_{total}	$G_{\text{total},298.15\text{ K}}$	E_{corr}	$\Delta G_{\text{reaction}}$
virgin	-18890.40	7.25	-18883.20	
HO_2^-	-4328.15	-0.25	-4328.39	
H_2O	-2172.04	-0.17	-2172.21	
reaction with HO_2^-				
pathway 1	-23227.86	7.58	-23220.28	-8.69
pathway 2	-23228.08	7.58	-23220.50	-8.91

pathway 3	-23227.65	6.15	-23,221.32	-9.73
pathway 4	-23,223.38	7.04	-23,216.34	-4.75
pathway 5	-23,223.13	6.94	-23,216.19	-4.60
pathway 6	-23227.05	7.05	-23220.01	-8.42
reaction with OH ⁻				
pathway 1	-21069.73	6.87	-21062.86	-7.45
pathway 2	-21068.94	7.55	-21061.39	-5.98
pathway 3	-21,068.09	6.69	-21,061.40	-5.99
pathway 4	-21065.68	6.76	-21058.91	-3.50

S5. Effects of feeding materials on H₂O₂ electrosynthesis

Fig. S25 illustrates the blockage of proton transfer chain on the PSE by monovalent ion (Na⁺) and divalent ion (Ca²⁺). As shown in Fig. S25a, the proton transfer chain can be blocked by the adsorption of the Na⁺ on the SA group. Because Na⁺ has one positive charge and can be adsorbed by only one SA group, the electrostatic force is relatively low. Hence, Na⁺ can easily to desorb from the SA group with the continuously produced and transferred proton. Hence, the proton transfer chains can be easily regenerated. However, Ca²⁺ has two positive charges and can be adsorbed by two SA groups (Fig. S25b). Therefore, the electrostatic force between Ca²⁺ and PSE is relatively strong, causing Ca²⁺ desorption from the SA group to be difficult. Hence, the proton transfer chains on the PSE microspheres are hard to be regenerated (Fig. S25b). Similarly, it can be inferred that divalent cations can be adsorbed by AEM stronger compared with monovalent cations.

To further prove this mechanism, we determined the water quality for all the water samples, and are shown in Table S5. Obviously, the divalent ion-containing water sample effluents (CaCl₂ containing water, Na₂SO₄ containing water, and tap water) have substantially lower divalent ion concentration compared to the influents, proving the strong adsorption of the divalent ions by the PSE and AEM. However, water samples that only contain monovalent ion or even no ion (DI water, NaCl containing water, sodium humate containing water, and divalent-ion removed water) have little ion difference in the influents and effluents, suggesting an ignorable adsorption of the monovalent ions by the PSE and AEM. According to Fig. 4, PSE reactor with divalent ion-containing influents show poor stability, whereas PSE reactor with monovalent ion or no ion-containing water influents exhibit great stability. Hence, divalent ion-containing water samples have a much larger influence on the proton transfer than water samples that only contain monovalent ion.

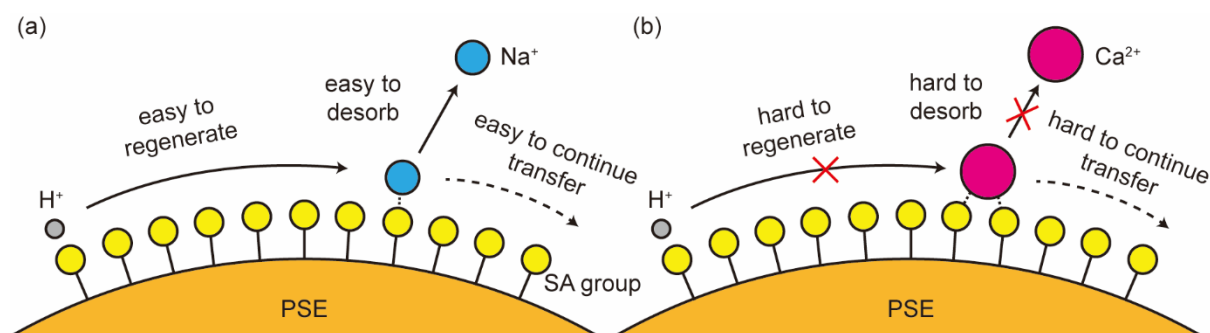


Fig. S25. The mechanism of proton transfer chain blockage by (a) Na⁺ and (b) Ca²⁺.

Table S5. The ion concentrations in the influents/effluents of the PSE reactor. (mg/L)

	Na ⁺	Cl ⁻	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	TOC
DI water	—/—	—/—	—/—	—/—	—/—	—/—
CaCl ₂ containing water	—/—	73.4/73.2	46.9/20.3	—/—	—/—	—/—
Na ₂ SO ₄ containing water	44.5/43.7	—/—	—/—	—/—	100.1/89.3	—/—
NaCl containing water	46.3/44.5	72.6/73.1	—/—	—/—	—/—	—/—
sodium humate containing water	1.9/1.9	—/—	—/—	—/—	—/—	3.4/3.3
tap water	25.8/25.6	52.1/53.3	73.7/51.9	37.9/25.2	86.5/74.8	1.1/1.2
divalent ion-removed water	186.5/183.1	156.9/151.9	—/—	—/—	—/—	1.2/1.1

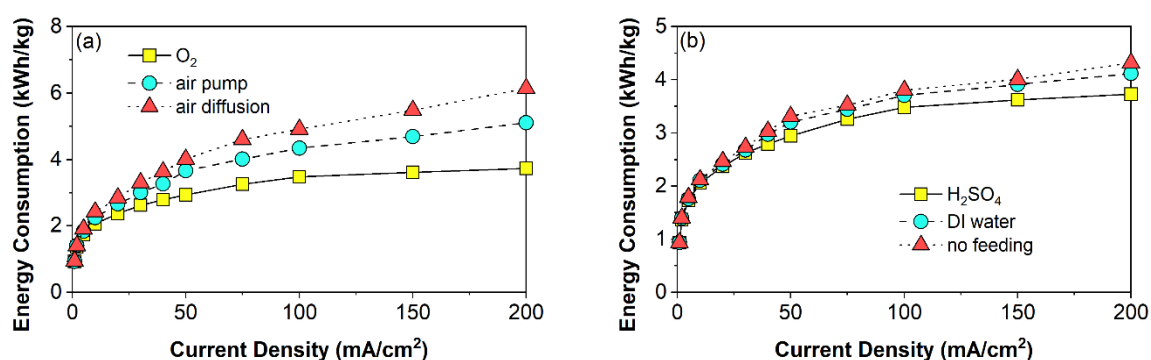


Fig. S26. EC during H₂O₂ electrosynthesis with various (a) cathode feeding materials and (b) anode feeding materials. Source data for Fig. S26 are provided as a Source Data file.

Water in a PEM undergoes four transfer modes: concentration diffusion, electro-osmotic drag, hydraulic permeation, and thermal osmotic drag, as depicted in Fig. S27.

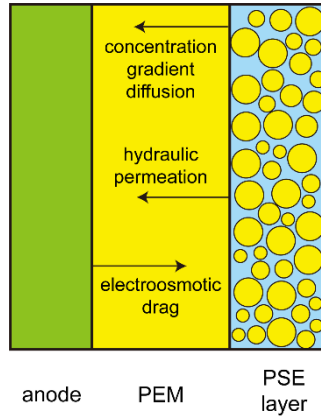


Fig. S27. Illustration of water transfer in PEM.

Due to the relatively lower temperature in a PSE reactor compared to the conventional PEM fuel cells, thermal osmotic drag can be neglected. Under the influence of concentration diffusion and hydraulic permeation, water in the PSE reactor migrates from the PSE layer to the anode side. Meanwhile, under the impact of electro-osmotic drag, it follows protons migrating from the anode to the PSE layer. Therefore, the total flux of water migrating from the PSE layer through the PEM to the anode and the maximum current density it can satisfy are expressed as Eq. S6:

$$N = N_{\text{conc}} + N_{\text{pres}} - N_{\text{drag}} \quad (\text{S6})$$

where N represents the total flux of water transfer within the PEM, N_{conc} denotes the concentration diffusion flux, N_{pres} signifies the hydraulic permeation flux, and N_{drag} represents the electro-osmotic drag flux. All units are expressed in $\text{mmol}/(\text{cm}^2 \text{ s})$.

The N_{conc} adheres to Fick's First Law,²² as Eq. S7.

$$N_{\text{conc}} = -D_{\text{conc}} \frac{dc_w}{dz} \quad (\text{S7})$$

where N_{conc} represents the concentration diffusion flux ($\text{mmol}/(\text{cm}^2 \text{ s})$), D_{conc} is the concentration diffusion coefficient of water in the PEM (cm^2/s), c_w denotes the concentration of water (mmol/cm^3), and z is the thickness of the PEM (cm).

Assuming c_w varies uniformly along the z -direction, the above equation can be expressed as Eq. S8.

$$N_{\text{conc}} = D_{\text{conc}} \frac{c_w(\delta) - c_w(0)}{\delta} \quad (\text{S8})$$

where c_w can be determined by the saturation vapor pressure of water and a proportionality constant between the water concentration in the membrane channels and the water concentration at the membrane surface, independent of the phase of water (Eq. S9).

$$c_w(\xi) = k p_s RH(\xi) \quad (\text{S9})$$

where k is the proportionality constant between the water concentration in the membrane channels and the water concentration at the membrane surface ($\text{mol}/(\text{m}^3 \text{ Pa})$), p_s denotes the saturation vapor pressure of water ($3.16 \times 10^3 \text{ Pa}$ at 25°C), RH represents the relative humidity.

The calculation of k is determined as Eq. (S10).

$$k = \frac{\bar{\lambda}}{p_s M} \left(\frac{1.98 + 0.0324\bar{\lambda}}{1 + 0.0648\bar{\lambda}} \right) \rho \quad (\text{S10})$$

where M is the molar mass of the membrane (0.554 kg/mol , based on the technical sheet), $\bar{\lambda}$ represents the water uptake (chosen as 15 with a broad range typically around 10-20),^{23,24} ρ denotes the membrane dry density (1050 kg/m^3 , according to the technical sheet). Thus, the calculated value of k is $11.25 \text{ mol}/(\text{m}^3 \text{ Pa})$.

The D_{conc} is calculated using an empirical formula (Eq. S11 and S12).

$$D_{\text{conc}} = 0.0031\lambda [\exp(0.28\lambda) - 1] \exp\left(\frac{-2436}{T}\right) \quad (\text{for } 0 < \lambda \leq 3) \quad (\text{S11})$$

$$D_{\text{conc}} = 0.000417\lambda [161\exp(-\lambda) + 1] \exp\left(\frac{-2436}{T}\right) \quad (\text{for } 3 < \lambda \leq 17) \quad (\text{S12})$$

Therefore, the average D_{conc} can be calculated using Eq. S13.

$$\overline{D_{\text{conc}}} = \exp\left(-\frac{2436}{T}\right) / \lambda \left[\int_0^3 0.0031x [\exp(0.28x) - 1] dx + \int_3^\lambda 0.000417x [161\exp(-x) + 1] dx \right] \quad (\text{S13})$$

Therefore, when $\bar{\lambda} = 15$, the D_{conc} can be calculated as $1.963 \times 10^{-5} \text{ cm}^2/\text{s}$, or 1.963×10^{-9}

m²/s.

Considering an air *RH* of 30%, the N_{conc} can be calculated as 4.88×10^{-3} mmol/(cm² s).

The N_{drag} is given by Eq. S14.

$$N_{\text{drag}} = n_d \frac{j}{F} \quad (\text{S14})$$

where N_{drag} represents the electro-osmotic drag flux (mmol/(cm² s)), n_d is the electro-osmotic drag coefficient, representing the number of water molecules migrated for every proton, j is the current density (mA/cm²), and F is Faraday's constant (96,486 C/mol).

According to Sellin et al.,²⁸ the n_d for Nafion N115 PEM is approximately in the range of 0.6 to 0.8 at 50°C and current densities ranging from 0 to 1000 mA/cm². For the PSE reactor, a reasonable value is chosen as $n_d = 0.7$.

The N_{pres} is given by Eq. S15.

$$N_{\text{pres}} = -D_{\text{pres}} \frac{dp}{dz} \quad (\text{S15})$$

where N_{pres} is the hydraulic permeation flux (mmol/(cm² s)), D_{pres} is the hydraulic permeation coefficient of water in PEM (cm²/s), p is the static hydraulic pressure (Pa), z is the thickness of the membrane (cm).

Assuming that p varies uniformly along the z -direction, the above expression can be written as Eq. S16.

$$N_{\text{pres}} = D_{\text{pres}} \frac{p(\delta) - p(0)}{\delta} \quad (\text{S16})$$

In the liquid water system, D_{pres} can be expressed by Eq. S17.

$$D_{\text{pres}} = \frac{k_m}{\mu} \quad (\text{S17})$$

where k_m is the effective hydraulic permeation coefficient (mmol/cm), and μ is the viscosity of water, which is 1.01×10^{-3} Pa s.

According to Husar et al.,²⁶ it can be speculated that $k_m = 6.5 \times 10^{-15}$ mmol/cm for N115 at 25°C. Therefore, when the internal pressure in the PSE electrolysis cell is 100 kPa, the

pressure diffusion flux at 25°C can be calculated as $5.07 \times 10^{-5} \text{ mmol}/(\text{cm}^2 \text{ s})$.

When N_{drag} equals the sum of N_{conc} and N_{pres} , the total water flux (N) is zero. At this point, the maximum current density can be obtained without any anode influent. According to the calculations, the maximum N_{drag} is $4.93 \times 10^{-3} \text{ mmol}/(\text{cm}^2 \text{ s})$. Therefore, the water transfer rate can fully meet current densities up to 680 mA/cm². The transfer rate is sufficient for applied current densities in the range of 1–200 mA/cm², allowing the anode to be adequately supplied with water through the self-permeability of PEM without the need for additional reactants at the anode.

S6. Scaling up the PSE reactor for H₂O₂ electrosynthesis

Based on the optimized reactor configurations determined with the small PSE reactor (4 cm²), a modular electrode stack with a total electrode area of 1200 cm² was manufactured (see Fig. S28a). The electrode stack consisted of 12 modular units connected in parallel, and each unit has an effective electrode area of 100 cm². PSE microspheres (Dowex 50W×8, 150–300 μm) were packed with a layer thickness of 2 mm and packing density of ~1100 mg/mL in the serpentine channels between the AEM and PEM (see the video of reactor assembly for more detail). During H₂O₂ electrosynthesis, an oxygen gas (3000 mL/min) and water (25 mL/min) were fed to the cathode and anode of the units, respectively, and DI water (25 or 60 mL/min) was passed through the serpentine channels to collect produced H₂O₂. To prevent overheating of the electrode stack by the Joule heating effect, cooling water (~4 °C) was recirculated through the reactor at a flow rate of ~1000 mL/min using a peristaltic pump (see the video of reactor operation).

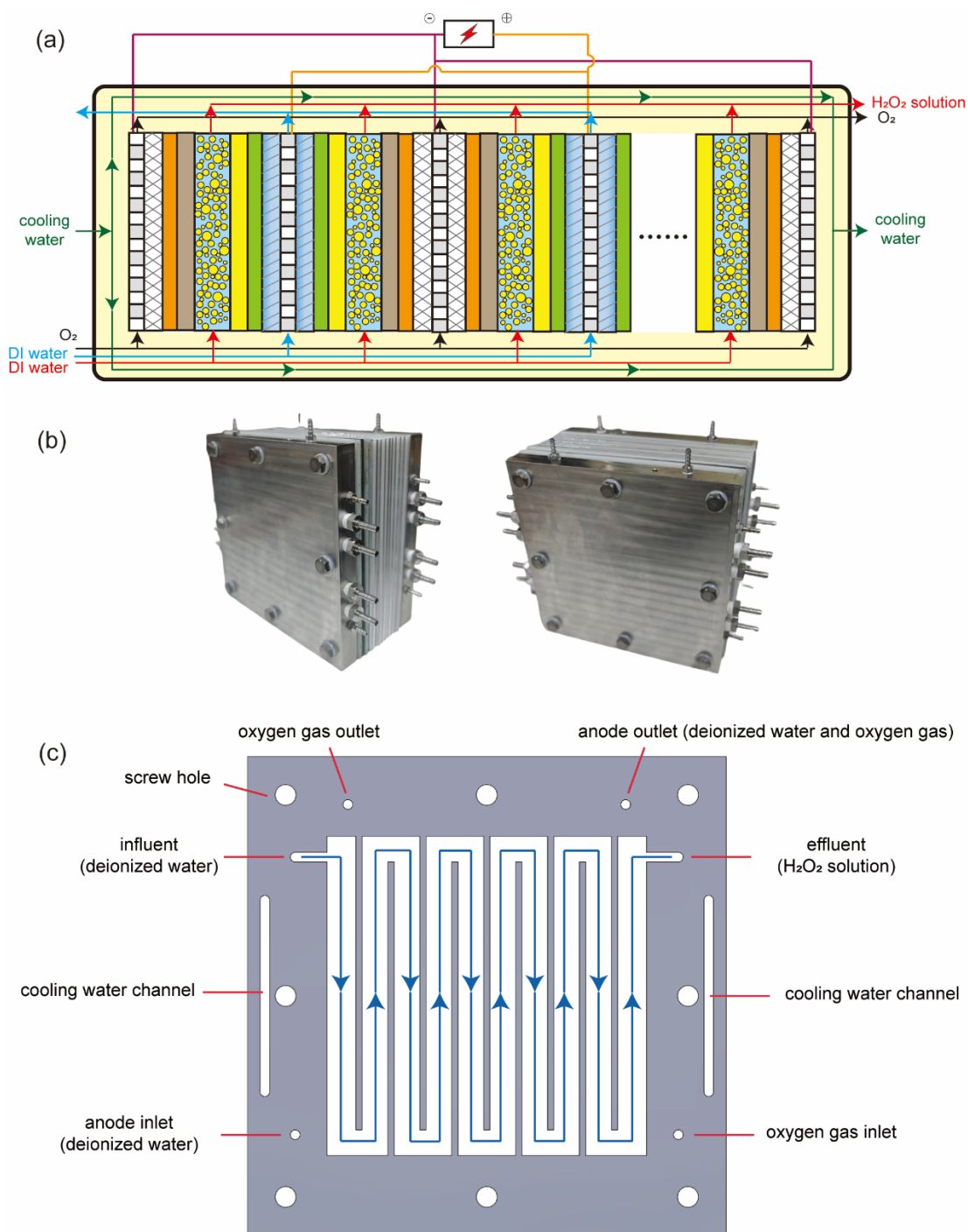


Fig. S28. The (a) schematic and (b) photos of the 12-unit modular electrode stack, (c) the design of flow channel of PSE chamber.

As shown by the infrared thermal image (Fig. S10d), the temperature field inside the small PSE reactor (4 cm^2) was generally uniform during H_2O_2 electrosynthesis. However, the

temperature field became uneven when the PSE reactor was scaled up to 1200 cm² (Fig. S29b), which may result in damages to some components of the reactor (e.g., the AEM) due to local overheating. Therefore, a cooling system was designed for the scaled-up reactor (see Fig. S28a and Fig. S29a for the reactor schematic). By recirculating cooling water (~4 °C) through the PSE reactor, a uniform temperature field was obtained during H₂O₂ electrosynthesis (Fig. S29c).

Note that during the experiments conducted with the 4 cm² PSE reactor (June–September, 2023), the room temperatures were $\sim 25 \pm 2$ °C. In comparison, the experiments with the 1200 cm² stack reactor were conducted in November 2023–February 2024, when the room temperatures were about 10 ± 2 °C. In addition, cooling water (4 °C) was recirculated during the experiments with the stack reactor. Therefore, the temperatures measured by the infrared thermal imaging were higher for the small reactor than the stack reactor (Figs. S10d and S29c). In general, the PSE reactors worked normally under the test temperature range of this study.

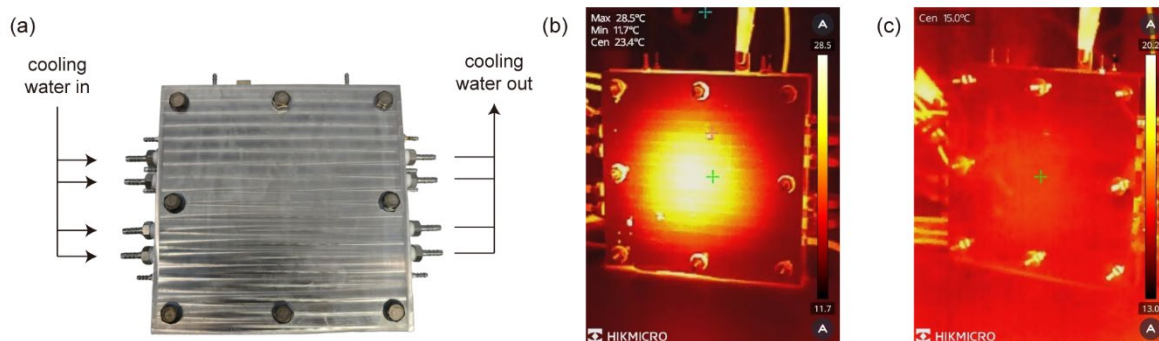


Fig. S29. Water cooling strategy of scaled up PSE reactor. (a) The inlet and outlet of cooling water of the electrode stack, infrared thermal imaging of the PSE reactor, (b) without and (c) with cooling water recirculation.

Cell voltages during H₂O₂ electrosynthesis with the PSE stack reactor are shown in Fig. S30a. For a given applied current densities, the cell voltage of the 1200 cm² stack reactor is higher than that of the 4 cm² reactor and 25 cm² reactor with the serpentine channel, but lower

than those of the 25 cm² without the serpentine channel. Increases of cell voltage with increasing electrode sizes in the cell are commonly observed in various electrochemical processes and can be mainly attributed to the increasingly uneven distribution of current on the larger electrode surface.^{27,28} For example, it has been reported that as the electrode area of the PSE reactor was enlarged from 4 to 80 cm², the cell voltage during H₂O₂ electrosynthesis increased significantly from ~2.1 to 5.7 V at the same applied current density of 200 mA/cm². Many factors can influence the distribution of current and thus the cell voltage during H₂O₂ electrosynthesis, such as the flow patterns, mass transport of oxygen gas, and bubble formation and detachment on the electrode surface.^{29,30} As shown in Fig. 6d, the introduction of serpentine channel considerably improved the uniformity of flow field in the PSE layer, which helped decrease the cell voltage (Fig. S30a). Additional studies are needed to optimize other factors that can influence the current distribution, and thus further reduce the cell voltage of H₂O₂ electrosynthesis with large electrodes.

Based on the applied currents and observed cell voltages during H₂O₂ electrosynthesis, the EC of H₂O₂ production can be calculated using Eq. S18. Meanwhile, the FE of H₂O₂ production can be calculated using Eq. S19.

$$EC = \frac{10^6 UI}{60cv} = \frac{16666.7UI}{cv} \quad (S18)$$

$$FE (\%) = \frac{nFcv}{M \times 6 \times 10^7} \times 100\% = \frac{cv}{10575I} \times 100\% \quad (S19)$$

where EC is energy consumption of H₂O₂ production (kWh/kg H₂O₂), U is the cell voltage (V), I is the applied current (A), c is the measured H₂O₂ concentration (mg/L), v is the flow rate (mL/min), n is the electron transfer number for one O₂ molecule reduction to H₂O₂ ($n = 2$), F is the Faraday constant (96,485 C/mol), and M is the molar mass of H₂O₂ (34.01 g/mol).

By substituting Eq. S19 to S18, the EC of H₂O₂ production can be expressed as Eq. S20 (i.e., Eq. 5 in the manuscript) based on the cell voltage and FE observed during H₂O₂ electrosynthesis.

$$EC = \frac{1.576U}{FE} \quad (S20)$$

The EC of H₂O₂ production during H₂O₂ electrosynthesis with the PSE reactors of different sizes are shown in Fig. S30b. The energy cost of H₂O₂ electrosynthesis is then calculated based on the electricity cost of 0.066 USD/kWh.²⁹

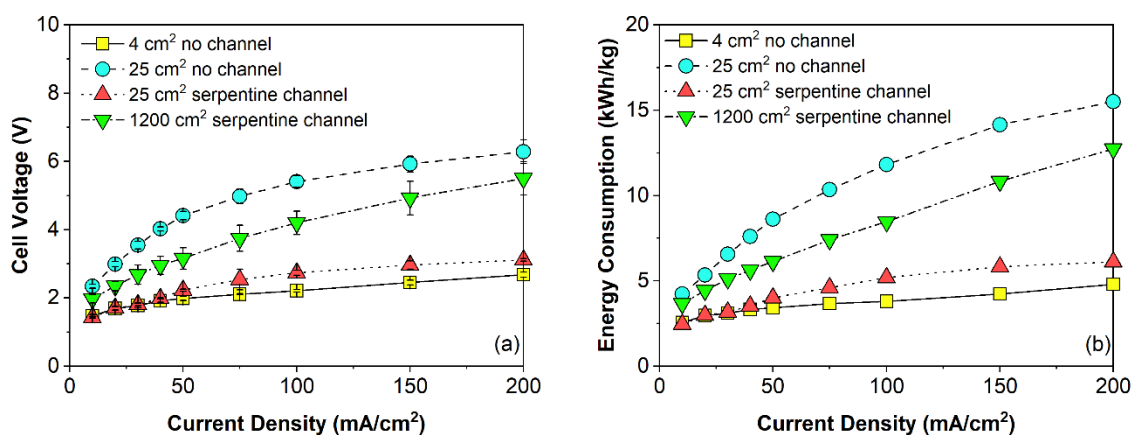
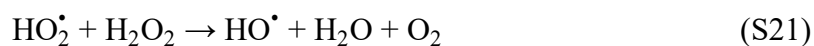


Fig. S30. The (a) cell voltage and (b) EC of H₂O₂ production as a function of applied current densities during H₂O₂ electrosynthesis with the PSE reactors of different sizes. Source data for Fig. S30 are provided as a Source Data file.

Fig. S31a shows the inactivation of *E. coli* with the electrosynthesized H₂O₂ solutions. With H₂O₂ concentrations of 5000–10000 mg/L, *E. coli* can be abated by >7 log within 10–15 min, which confirms that the electrosynthesized H₂O₂ solutions can be directly used for disinfection. According to the standard of peroxide disinfectants of China,³¹ the decomposition of H₂O₂ in qualified disinfectant products at 54 °C should not exceed 15% within 14 d (see Table S6). Fig. S30b shows that H₂O₂ solutions produced with the PSE reactor satisfy this requirement and decomposed less than 10% at 54 °C within 14 days. Nevertheless, H₂O₂ decomposition then accelerated because some decomposition products (e.g., HO₂[•] and [•]OH) can react with H₂O₂ and thus promote its further decomposition.³²



In case the electrosynthesized H_2O_2 solutions need to be stored for long time before use, small quantities of organic acids can be added in the H_2O_2 solutions to trap $^\bullet\text{OH}$ and $\text{HO}_2^\bullet$ and thus prevent these detrimental cascade reactions.^{32,33}

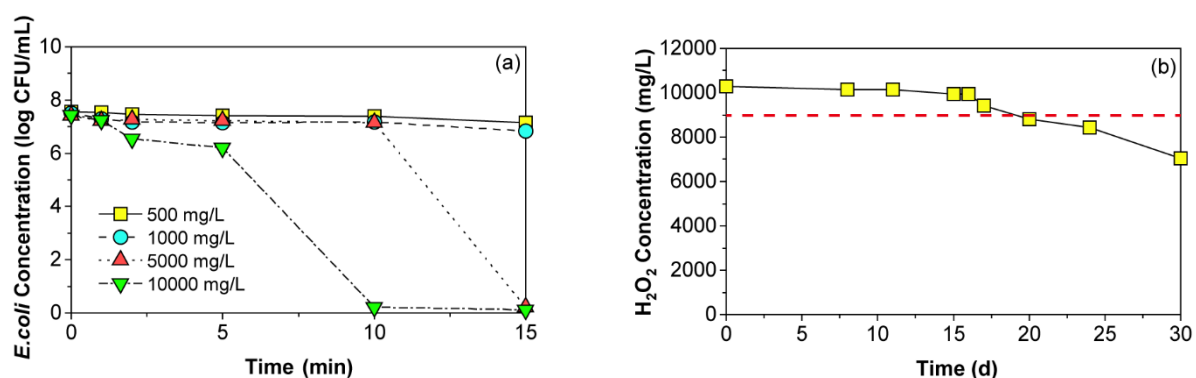


Fig. S31. The effect and quality of produced H_2O_2 by PSE reactor. (a) Inactivation of *E. coli* by electrosynthesized H_2O_2 solution, (b) stability of electrosynthesized H_2O_2 at 54 °C. Source data for Fig. S31 are provided as a Source Data file.

Table S6. The quality of electrosynthesized H_2O_2 by PSE reactor

	Value	GB/T 26371-2020 Standard threshold
pH	6.9 ± 0.1	indicated value ± 1.0
As	0.015 mg/kg	< 3 mg/kg
Pb	0.020 mg/kg	< 5 mg/kg
stability	< 15% loss (54 °C) within 20 d	< 15% loss (54 °C) within 14 d

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