Electrochemical oxygen reduction to hydrogen peroxide (H_{2}O_{2}) in acidic media, especially in proton exchange membrane (PEM) electrode assembly reactors, suffers from low selectivity and the lack of low-cost catalysts. Here we present a cation-regulated interfacial engineering approach to promote the H_{2}O_{2} selectivity (over 80%) under industrial-relevant generation rates (over 400 mA cm\(^{-2}\)) in strong acidic media using just carbon black catalyst and a small number of alkali metal cations, representing a 25-fold improvement compared to that without cation additives. Our density functional theory simulation suggests a “shielding effect” of alkali metal cations which squeeze away the catalyst/electrolyte interfacial protons and thus prevent further reduction of generated H_{2}O_{2} to water. A double-PEM solid electrolyte reactor was further developed to realize a continuous, selective (~90%) and stable (over 500 hours) generation of H_{2}O_{2} via implementing this cation effect for practical applications.
Hydrogen peroxide (H₂O₂) is ranked as one of the top 10 most energy-intensive chemicals in the chemical manufacturing bandwidth study by the Advanced Manufacturing Office in Department of Energy. It is currently manufactured industrially by the energy- and waste-intensive anthraquinone cycling process, which consumes a primary current typical of about ~13,000 Btu/lb (8.1 kWh/kg) without taking into account the H₂/O₂ feedstokes. Electrochemical synthesis of H₂O₂ via the 2e⁻ ORR, where the O₂ molecule is electrochemically reduced to H₂O₂ via a two-electron (2e⁻) pathway, provides a promising energy-efficient and low-waste alternative. Recent efforts have been mostly focused on developing catalysts in alkaline solutions, in which small overpotential and high selectivity of the 2e⁻ ORR toward H₂O₂ have been comparatively easy to achieve on low-cost materials such as carbon. However, in alkaline solutions, H₂O₂ is deprotonated (pKₐ > 11) and easily degraded. Moreover, for practical electrolyzers such as membrane electrode assembly (MEA), catalysts developed in alkaline solutions need to be applied on an anion exchange membrane (AEM), which is typically not as stable as its counterpart of proton exchange membrane (PEM), e.g., Nafion, especially operated under air. In addition, with stronger oxidation ability in acid, the acidic H₂O₂ solution shows a wider range of applications and greater demand, which strongly motivates studies in high-performance electrochemical generation of H₂O₂ in acidic media. To this end, there are only a few known noble metal catalysts, including Pt- and Pd-based catalysts, demonstrated to be selective and stable for the 2e⁻ ORR in strong acids, but their high cost and toxicity of heavy metals (in the case of PtHg alloys) could limit their applications in large-scale H₂O₂ generation. Some low-cost catalysts such as carbon materials may also show good H₂O₂ selectivity in acids within small overpotential and small current density regions (typically less than 10 mA cm⁻²). Their H₂O₂ selectivity and stability were dramatically dropped when an industrial-relevant current was reached. In acidic media, carbon catalysts present sluggish ORR kinetics and typically require a large overpotential (>300 mV) to initiate the ORR reaction, and consequently, a large negative cathodic overpotential is required to deliver a high current density. While the carbon surface might intrinsically prefer a 2e⁻ ORR pathway due to their relatively weak binding with oxygen intermediates as demonstrated by several previous studies, such negative overpotential could further push the ORR reaction all the way down to H₂O with significantly decreased H₂O₂ selectivity and production rate especially in acids. This is because under negative potentials in acids, the catalyst surface accumulates concentrated protons that are prone to further reduce the locally generated H₂O₂ molecules to H₂O (H₂O₂ + 2e⁻ + 2H⁺ = 2H₂O). Therefore, diluting the local proton concentration and minimizing the electrochemical dissociation of as-produced H₂O₂ to H₂O could be one promising strategy for resolving this H₂O₂ selectivity-activity dilemma, and delivering industrial-relevant H₂O₂ production rate in acidic solution while maintaining good H₂O₂ selectivity. Here we report a cation-regulated catalyst/electrolyte interface to promote electrochemical O₂ reduction to H₂O₂ in acids with high-selectivity and industrial-relevant production rates. By adding only a small amount of alkali metal ions into the acidic electrolyte, which barely affects the solution’s pH, we demonstrated a dramatic improvement in H₂O₂ selectivity and activity especially under large ORR current densities across different catalysts. Our molecular dynamic simulations suggest that the solvated alkali metal cations, compared to concentrated protons in acids, could preferentially be attracted to the catalyst/electrolyte interface and squeeze out local protons during the reaction, suppressing the further reduction of as-generated H₂O₂ to H₂O. Using commercial carbon black catalysts with 10 mM Na₂SO₄ as an additive, the H₂O₂ Faradaic efficiency (FE) can reach over 80% under a significant current of 400 mA cm⁻² in 0.1M H₂SO₄, representing a 25-fold improvement compared to the case without Na⁺ additive where negligible H₂O₂ was produced (<5% FE). Based on this cation promotion concept, a double-PEM-based solid electrolyte (SE) reactor was developed for a continuous generation of H₂O₂ with high FE (>90%) and good stability (over 500 h) for practical applications in the future.

Results

The alkali metal cation effect on acidic H₂O₂ generation in flow cell. We first employed a standard three-electrode flow cell reactor to investigate the cation effect towards H₂O₂ generation in acid (Fig. S1), allowing to evaluate our hypothesis in a more practical environment and produce H₂O₂ under higher current densities compared to the traditional RRDE setup (Supplementary Note 1, Fig. 2a). The commercially available carbon black catalyst (BP2000) with a high surface area was used as a model ORR catalyst in this study (Fig. S2). Its intrinsic H₂O₂ activity and selectivity were first evaluated in 0.1 M H₂SO₄ electrolyte (pH = 0.96) (Fig. 2b, c). We observed that while the H₂O₂ FE of carbon black catalyst in acid remained relatively good (~70%) under small current regions, it started to decrease dramatically once the current density is over 100 mA cm⁻² with very negative applied potentials (Fig. 2c). Under 200 mA cm⁻², the carbon black catalyst can only deliver a 35% H₂O₂ FE and the majority of electrons were directed towards H₂O instead (Fig. 2c). The decreased FE is as expected, because under such a negative potential of ~0.89 V versus reversible hydrogen electrode (vs. RHE) needed to drive this high current, even if the catalyst prefers to reduce O₂ to H₂O₂ in its first place, those generated H₂O₂ at the electrode surface could be easily further reduced to H₂O coupling two electrons and two local protons. Please be noted here that, under each current density, its corresponding H₂O₂ FE was measured within 8 min of operation. With a longer time of electrolysis, the H₂O₂ FE could be further dropped (as shown in the stability test in Fig. 3g). After introducing a trace amount of Na⁺ additive (5 mM Na₂SO₄) into the acidic electrolyte, while the ORR activity did not show that much difference (Fig. 2b), the H₂O₂ FE was significantly improved especially under high current densities. As shown in Fig. 2c, in the potential range of the ORR onset, the impact of Na⁺ (5 mM Na₂SO₄) toward H₂O₂ is negligible; while in the range of large overpotentials at high current densities, the small amount of Na⁺ helped the carbon black catalyst to hold a high H₂O₂ FE plateau of over 80% until 200 mA cm⁻², suggesting a more than doubled FE compared to that in pure acid (Fig. 2c).

The measured trends of H₂O₂ FE show that the promotion effect of Na⁺ is more pronounced at high current density toward H₂O₂ formation. We understand that Na⁺ and protons are both positively charged ions and will be attracted towards the ORR
catalyst surface to form the electrochemical double layer under negative potentials\textsuperscript{34}. We would assume that, Na\textsuperscript{+} ions could be more competitive than protons to be aligned along the electrochemical double layer, which dramatically reduces the local proton concentration and thus protects the generated H\textsubscript{2}O\textsubscript{2} from further reductions coupling protons and electrons (discussed in the following sections in detail). To further amplify the cation effect and drive the O\textsubscript{2}-to-H\textsubscript{2}O\textsubscript{2} production at even higher current densities in acid (>200 mA cm\textsuperscript{-2}), we gradually increased the Na\textsuperscript{+} cation concentration in the electrolyte. As shown in Fig. 3a, the overall current density, as well as the H\textsubscript{2}O\textsubscript{2} FE gradually increases with increased Na\textsuperscript{+} concentrations. In general, a higher concentration of Na\textsuperscript{+} can maintain larger 2e\textsuperscript{−}−ORR currents without sacrificing the H\textsubscript{2}O\textsubscript{2} selectivity. With only 0.01 M Na\textsubscript{2}SO\textsubscript{4} in 0.1 M H\textsubscript{2}SO\textsubscript{4}, the FE of H\textsubscript{2}O\textsubscript{2} can reach 83% at 400 mA cm\textsuperscript{-2} (Fig. 3b), representing a 25-fold improvement compared to that in pure acids without Na\textsuperscript{+} (H\textsubscript{2}O\textsubscript{2} FE only 3.3%). Along with the increased H\textsubscript{2}O\textsubscript{2} FE, the improvement of the H\textsubscript{2}O\textsubscript{2} production rate was also obvious at high current densities (Fig. 3c). For example, the production rate of 6.21 mmol cm\textsuperscript{-2} h\textsuperscript{-1} H\textsubscript{2}O\textsubscript{2} (partial current of 332 mA cm\textsuperscript{-2}) was achieved under the current density of 400 mA cm\textsuperscript{-2}, much higher than that in pure H\textsubscript{2}SO\textsubscript{4} acid (only 0.245 mmol cm\textsuperscript{-2} h\textsuperscript{-1}). The production rate can be further enhanced by providing more Na\textsuperscript{+} cations (the production rate of 6.52 mmol cm\textsuperscript{-2} h\textsuperscript{-1} was achieved at 400 mA cm\textsuperscript{-2} and the maximum FE can be up to 94% at 150 mA cm\textsuperscript{-2} by using 0.05 M Na\textsubscript{2}SO\textsubscript{4} as additive). Further increasing the concentration of Na\textsuperscript{+} cations could continually push up the H\textsubscript{2}O\textsubscript{2} FE to higher values at high current densities (Fig. S3). It is important to note here that the electrolyte pH did not show obvious change and stayed around pH 1 after these Na\textsubscript{2}SO\textsubscript{4} additives, ranging from 0.96 (0.1 M H\textsubscript{2}SO\textsubscript{4}), 0.96 (0.1 M H\textsubscript{2}SO\textsubscript{4} + 0.005 M Na\textsubscript{2}SO\textsubscript{4}), 0.98 (0.1 M H\textsubscript{2}SO\textsubscript{4} + 0.01 M Na\textsubscript{2}SO\textsubscript{4}) to 1.04 (0.1 M H\textsubscript{2}SO\textsubscript{4} + 0.05 M Na\textsubscript{2}SO\textsubscript{4}). To fully exclude the pH effect of the bulk solution (even though the change is quite small), the pH value of 0.1 M H\textsubscript{2}SO\textsubscript{4} (pH = 1.13) was adjusted to be the same as that of 0.1 M H\textsubscript{2}SO\textsubscript{4} (pH = 0.96) by adding more sulfuric acid. As shown in Fig. S4 and S5, the H\textsubscript{2}O\textsubscript{2} FE in both electrolytes with Na\textsuperscript{+} additives (before and after pH tuning) showed very similar trend in all current ranges, indicating the Na\textsuperscript{+} cations dominate the H\textsubscript{2}O\textsubscript{2} generation process and the small pH differences of electrolytes have negligible influence on the production rate or H\textsubscript{2}O\textsubscript{2} FE. With 0.1 M Na\textsubscript{2}SO\textsubscript{4} as an additive in 0.2 M H\textsubscript{2}SO\textsubscript{4} solution (pH = 0.76), we were able to produce H\textsubscript{2}O\textsubscript{2} at the current density of 1 A cm\textsuperscript{-2} with a FE of more than 65% (Fig. S6). The H\textsubscript{2}O\textsubscript{2} partial currents of up to 650 mA cm\textsuperscript{-2} were achieved, and high FEs were maintained, better than the highest O\textsubscript{2}-to-H\textsubscript{2}O\textsubscript{2} conversion rates reported. At even lower pH electrolyte, i.e., 1 M H\textsubscript{2}SO\textsubscript{4} solution (PH=0), similar trends were also observed (Fig. S7), indicating the general phenomenon of cation promotion effect toward H\textsubscript{2}O\textsubscript{2} production through ORR.
The low threshold of the alkali metal cation concentration towards promoting H$_2$O$_2$ generation puts forward new requirements for the purity of the electrolyte during ORR to H$_2$O$_2$ tests in acids. For the traditional electrolytic ORR process, the Na$_2$SO$_4$ is widely used as the anolyte to balance the electrochemical reaction. However, even far away from the cathode side and separated by ion exchange membranes, we found that the Na$^+$ in the anolyte can still penetrate the PEM and move to the cathode chamber, and thus significantly improve the H$_2$O$_2$ FE of ORR at the cathode (Fig. S8). Therefore, it is highly recommended to perform the ORR reaction using the same acidic electrolyte to avoid any cross-over cation contaminations which could significantly improve H$_2$O$_2$ performance in acids.

The promotion effect is not only limited to the Na$^+$. The H$_2$O$_2$ production rate can also be enhanced by using other alkali metal ions. Figure 3d shows the I-V curves for four different alkali metal cations in each sulfuric acid electrolyte with a concentration of 0.01 M (0.005 M X$_2$SO$_4, X = Li, Na, K, Cs). As compared with the pure H$_2$SO$_4$ electrolyte, while the ORR activities were slightly improved, significant improvements in H$_2$O$_2$ FE were observed for all the cations (Fig. 3d–f). The FE and production rates of H$_2$O$_2$ are relatively unaffected by the size of the alkali metal cations in the electrolyte. As differences in total current density exist for electrolytes containing different cations, the H$_2$O$_2$ production rate provides a better representation of trends in product formation rates than FE. As shown in Fig. 3f, with 0.005 M X$_2$SO$_4$ as the additive, all the alkali metal cations are able to drive the O$_2$-to-H$_2$O$_2$ reaction efficiently with high production rates, and the differences induced by different cations are relatively marginal. Nevertheless, we find that the promotion effect is only limited to IA alkali metal cations (such as Li$^+$, Na$^+$, K$^+$, Cs$^+$), while the other cations (including the IIA cations such as Mg$^{2+}$, Ca$^{2+}$ and IIIA cations such as Al$^{3+}$) decrease the H$_2$O$_2$ FE dramatically. This might due to the local environment change from acid to alkaline induced by the cation additives during ORR (will discuss the details in the simulation part). The alkaline local environment could induce the formation of solid metal hydroxide on the catalyst surface and block the ORR reaction, decreasing the H$_2$O$_2$ FE and production rate (Fig. S9).

It was also exciting to find out that the cation additives not only promote the H$_2$O$_2$ selectivity but also improve the long-term operation stability, which is another important target for practical
production of H2O2. Figure 3g shows the comparison of H2O2 FE at 200 mA/cm² ORR current as a function of operation time in the flow cell. In pure acidic electrolyte, the H2O2 FE rapidly dropped to less than 10% within 2 h. As a sharp contrast, with the presence of Na⁺ cations, the potential and H2O2 FE showed negligible changes for over 20 h. We suppose the improved activity and stability are induced by the alkalinization of the local environment induced by the cation additives during ORR. During the ORR process, the solvated alkali metal cations, compared to concentrated protons in acids, could preferentially be attracted to the catalyst/electrolyte interface, which gives rise to a local alkaline environment (will discuss the details in the simulation part). At alkaline conditions, the carbon-based catalyst typically shows higher activity and better stability compared to acidic conditions8–10. We then found this cation promotion effect has broad applicability to different catalysts and acidic electrolytes. With a small amount of Na₂SO₄ as the additive in 0.1 M H₂SO₄, the hydrogen evolution reaction was not considered because only a trace amount of H₂ byproduct (from H₂ evolution at large overpotentials) was detected from the cathode side (Fig. S15). We consider the acid condition and use pH = 0 in our simulations. Since alkali metal cations are not likely to directly participate in ORR, we explore two aspects of the cation effects: (1) how alkali metal cations affect the distribution of the protons, and (2) how the redistribution of protons will influence the selectivity of O₂ reduction to H₂O₂. For the first question, we adopted a model with relatively thick water layers (equivalent to 6 ice layers) on (6 × 6) periodic graphene (Fig. S16), and then put a certain number of cations/protons to represent the electrode environment under the lower potential like V_{RHE} = −1 V. For the second question, we use a thinner model (~4 ice layers) with single-vacancy to represent the reaction site, and then use slow-growth method36 to evaluate the reaction barrier under different conditions. The details of the simulations can be found in the experiment section in supporting information (SI).

As shown in Fig. 5a, b, both Na⁺ cations drift towards the surface in molecular dynamics. This is not unexpected considering that under the low potential V_{RHE} = −1 V, the surface is charged by −3e⁻. Such a fast drift may have two consequences: firstly, the local concentration of Na⁺ can be much higher than that in the bulk; secondly, as a charge carrier that compensates the net charge of the substrate, Na⁺ may compete with protons which is the major charge carrier in the acid electrolyte when Na⁺ cations are not added. Indeed, as shown in Fig. S17, when Na⁺ cations and protons co-exist near the interface, the cations compete with the protons by repelling the proton away from the surface. After 3 picoseconds of AIMD, both cations stay ~4.5 Å from the surface, while the protons end at ~8 Å from the surface. These results clearly suggest that the cations, which can be enriched by the attraction of the negatively charged surface, can strongly repel the local protons, and thus dramatically reduce the local proton concentrations.

Then we consider how the selectivity of the 2e⁻−ORR is affected by the presence of Na⁺ cations and the reduced local proton concentrations. We understand that carbon catalysts typically bind oxygen intermediates weakly and thus present an intrinsic selectivity towards H₂O₂, which can be seen from our above experimental results (high H₂O₂ selectivity under low currents in Fig. 2c) as well as
previous reports. The catalyst’s H2O2 selectivity starts to drop under significant overpotentials to deliver large currents in pure acids, where two possible reaction mechanisms could play a role in guiding the reaction towards the 4e− pathway of H2O. One possibility is that, while the catalyst still produced H2O2 selectively in the first place, those locally generated H2O2 under such negative potentials could be further reduced to H2O coupling electrons and protons (H2O2 + 2e− + 2H+ = 2H2O), resulting in a low apparent H2O2 selectivity. In this case, as the Na+ cation additives can effectively screen away local protons, the further dissociation of generated H2O2 can be depressed, resulting in better H2O2 selectivity. This “cation protection” of as-formed H2O2 can be validated by performing the electrochemical reduction of H2O2 in both pure and Na+−containing acidic electrolytes (Figs. S19–21, Fig. 5c). As shown in Fig. 5c, the H2O2 reduction activity was greatly suppressed, especially under large overpotentials, when Na+ was added, suggesting that the introduction of cations can greatly inhibit the H2O2 dissociation to H2O under reductive potential environments. Please be noted here that the only possible side reaction, the hydrogen evolution reaction, was also taken into consideration when measuring the H2O2 reduction currents (Fig. S15). This suppression effect can be further validated from our simulation results. Clearly, as shown in Fig. 5d, the absence of protons increases the H2O2 decomposition barrier to 0.519 eV, 0.156 eV higher than that when a proton is present. The initial state, transition state and eventual forms of H2O and H2O2 are shown in Fig. S16 and S17. As the O−O bond elongates, the proton attaches to one of the O in H2O2 and forms a HO−OH2 complex at transition state and eventually forms OH− and H2O. This process clearly shows how the proton promotes H2O2 decomposition, explaining the reason why cations could prevent the further reduction of as-synthesized H2O2 by screening out local protons. Another possible factor for improved H2O2 selectivity is that the cations could suppress the dissociation process of peroxide intermediate (‘OOH) during ORR due to local proton depletion. To explore this hypothesis, we further used a slow-growth approach based on AIMD to evaluate the reaction barriers of both 2e− and 4e− paths under different proton concentration conditions. As displayed in Fig. 5d, when a proton is present, both the 2e− and 4e− paths have an extremely low barrier and take place spontaneously at 300 K. In contrast, the absence of protons increases the “O−O breaking (2e− path) barrier to 0.136 eV, in comparison to 0.167 eV for O−OH breaking (4e− path), suggesting 2e− pathway being favorable by exp ((0.167−0.136)kBT) = 3.36 times than the 4e− pathway and thus enhanced H2O2 selectivity. Therefore, the local absence of protons, a result of cation accumulation near the surface, can strongly enhance the H2O2 selectivity in acids.

We also evaluate the effect of Mg2+ on the 2e−−ORR by replacing two Na+ by one Mg2+, and running the AIMD simulations similar to the case of Na+ (Fig. 5b). As shown in Fig. S27, Mg2+ does not show the same effect as Na+. This is likely due to two reasons: (1) Mg2+ is more efficiently screened as the Mg2+ bonds stronger with O of H2O than the case of Na+, which is evidenced by the significantly shorter distance between Mg and O (averaged distance dMg−O = 2.05 Å vs. dNa−O = 2.55 Å); (2) the mole concentration of Mg2+ is only half of that of Na+ in the electrical double layer and the electrostatic repelling decays in the form of 1/r, so there is more “screened” space for H+ in the electrical double layer.

**Practical generation of H2O2 using cation exchange membrane solid electrolyte reactor.** Obtaining good H2O2 selectivity and activity in acidic ORR is a prerequisite for practical implementations of membrane electrode assembly (MEA) reactor using
reliable and well-established PEM such as NaFon (sulfonated tetrafluoroethylene based fluoropolymer-copolymer membrane). However, till so far, only noble metal catalysts such as PtHg, PdHg or PtP2 nanocrystals could deliver reasonable H₂O₂ selectivity and stability in proton exchange MEA device. This observed notable promotion effect of cations on low-cost and non-toxic carbon catalysts in acidic H₂O₂ generation therefore provides us with a great opportunity to deliver practical H₂O₂ activity, selectivity, and stability. Our basic assumption is that, as the alkali metal cations can move across the PEM, they may help to regulate the local environment of the catalyst/membrane interface for better H₂O₂ activity and selectivity. To explore how to successfully make use of this cation tuning effect, we first evaluated its applicability in a traditional PEM-MEA cell configuration (Figs. S22–S24). First, it is well within our expectation that the traditional PEM-MEA cell using commercial carbon black catalyst with 0.1 M H₂SO₄ as the anolyte, presented negligible H₂O₂ selectivity, due to the high proton flux at the catalyst/membrane interface (Fig. S22). However, we found out that even with the addition of cations in acids (Fig. S23), or directly using Na₂SO₄ solution in the anolyte (Fig. S24), no obvious improvements were observed. This is because on the anode side, a significant number of protons will be generated locally at the catalyst/membrane interface during the oxygen evolution reaction and then immediately transported across the membrane to the cathode side, suppressing the possibility of Na⁺ ion transportation from the bulk anolyte towards the cathode to regulate the interfacial environment of improved 2e⁻–ORR. The low H₂O₂ selectivity in PEM-MEA drove us to design a new cell configuration to employ this cation effect for continuous production of H₂O₂ in a practical way. Instead of the traditional PEM-MEA cell design, here we developed a SE reactor with three chambers separated by two PEMs to fully implement this cation effect for high-performance H₂O₂ generation (Fig. 6a and Fig. S25). Specifically, the cathode (carbon black) and anode (IrO₂) of our device are catalyst-coated GDL electrodes, which were separated by a thin SE layer sandwiched by two identical PEMs (NaFon-117). The cathode side was continuously supplied with a mixture of O₂ stream and water flow for 2e⁻–ORR, while the anode side was circulated with H₂O for water oxidation. In the middle chamber, a SE layer consisting of porous polymer ion conductors was used to minimize the iR-drop between cathode and anode. A dilute cation solution flows through this SE layer to introduce the cation effects on the cathode side 2e⁻–ORR. Please be noted here that without this SE layer, the cell voltage was significantly increased due to the increased cell resistance between the cathode and anode (Fig. S26). Under a negative reduction potential, the cations in the middle SE chamber are driven by the electrical field to penetrate the PEM toward the cathode surface and thus regulate the local environment at the catalyst/PEM interface to promote H₂O₂ generation (Supplementary Note 2 and Fig. S27). The H₂O₂ molecules formed at the cathode side are then efficiently brought out via the oxygen and DI water flow stream. Meanwhile, protons generated from water oxidation at the anode penetrate the right-hand side PEM and move into the middle chamber to compensate for the charge.

The I–V curve of our 4-cm² three-chamber PEM SE cell flowing 0.03 M Na₃SO₄ solution in the middle layer is plotted in Fig. 6b. Of note that the concentration of Na₃SO₄ can be varied to higher values. Our target is to realize the high production rate of H₂O₂ while minimizing cations’ consumption for practical demonstrations. Therefore, a 0.03 M Na₃SO₄ solution is adopted to regulate the interfacial environment of improved 2e⁻–ORR in our SE cell. A mixture of O₂ gas flow (180 sccm) and DI water flow (1.8 mL min⁻¹) was supplied to the cathode. The flow of DI water is to efficiently bring out the generated H₂O₂. By ramping up the overall current density, the cell voltage of the SE reactor gradually increased. The H₂O₂ FE remained over 85% across the entire cell voltage range, with a maximum of 96% at 5 and 20 mA cm⁻² (Fig. 6b), much higher than the traditional MEA cell configuration. In comparison, the reactor without alkali metal cations requires a higher potential to deliver and shows much lower H₂O₂ FE, practically at high current densities (Fig. S28). The cros-s-over Na⁺ from the middle SE layer to the cathode plays a key role in determining the H₂O₂ FE (Fig. S27).

The electrolysis stability is always one of the most important but challenging parts in practical applications. Benefiting from the stable material properties in carbon black and PEM as well as reliable cation effects, our SE cell with the double-PEM configuration presents excellent long-term stability in producing H₂O₂. The SE reactor stability was evaluated by holding a 50 mA cm⁻² cell current density (200 mA total current). As shown in Fig. 6c and d, when supplying dilute Na⁺ ions in the SE layer, a continuous generation of H₂O₂ solution on the cathode side can be stably operated for over 500 h with no degradations in product FE (~90%). As a sharp contrast, in the absence of cations, the H₂O₂ FE started with less than 60% and rapidly dropped to less than 10% in 6 h, which can even be recovered to ~90% when cations were later introduced (Fig. S29), clearly suggesting this prominent cation effect. The observation indicates that the carbon catalyst still works well, and this is not the reason for FE degradation. We suppose the FE degradation is because of the accumulation of local H⁺ to high concentrations with the extension of reaction time, which accelerates the further reduction of H₂O₂ to H₂O and decrease the H₂O₂ selectivity.

A continuous supply of cation solutions in the SE layer could limit the device’s real applications due to the following two reasons. First, it could result in a significant consumption of cations as most of them are flowing out of the SE layer and only part of them crossed to the cathode chamber. Second, the generated H₂O₂ solution in the cathode would be slightly alkaline due to the Na⁺ ion crossover from the SE layer (resulting in slight acidity in the SE layer downstream flow). To further explore the high potential of our SE cell for practical uses, we operated the cell by circulating the cation solution from the SE layer into the cathode side, and then back to the SE layer for H₂O₂ accumulation. The outlet solution in the middle chamber was mixed with oxygen flow and supplied to the cathode to produce H₂O₂. Then the as-produced solution containing H₂O₂ and cations was cycled back into the middle chamber (Fig. 6c). By doing so we could continuously reuse the cations by circulating them back to the SE layer for a closed system without the need for a continuous cation stream supply. Also, the excessive OH⁻ groups generated from the cathode would be neutralized by exactly the same number of excessive protons in the SE layer. Our target is to accumulate the H₂O₂ concentration to ~5000 ppm in a 250 mL solution (containing only 60 mM of Na⁺) for each operation cycle via maintaining a 50 mA cm⁻² cell current. As shown in Fig. 6f, the H₂O₂ concentration continuously increased to ~5000 ppm in about 13 h. The cell can be operated for more than 200 h with negligible degradations. During this stability test, a total of 3.7 L 5000 ppm H₂O₂ solution was obtained. We also observed that, in each operation cycle the H₂O₂ FE slightly decreases with increased H₂O₂ concentration, which may be due to the H₂O₂ self-decomposition, further reductions on the cathode, and/or the crossover oxidation on the anode side. For each operation cycle, the H₂O₂ concentration can reach up to ~0.15 M, which is 5 times of the Na₂SO₄ additive in the final product. A higher concentration of H₂O₂ solutions can also be produced by extending the operation time while maintaining the current and FE. As a result, a high concentration of 20,000 ppm
H2O2 solution was achieved in 17 h by circulation of the 50 mL water at the cathode side (Fig. S30). Based on the above promising H2O2 activity, selectivity and especially the durability, and since all the reactor components, including catalysts, membrane, and the polymer SE are all commercially available, our PEM-based H2O2 SE cell with cation promotion effect has a great potential for future’s practical applications.

To conclude, we presented a cation-regulated interfacial engineering approach to improve the catalytic performance of O2 reduction to H2O2 at industrial-relevant rates in strong acidic media. By adding a small number of alkali metal cations in acid solutions, the selectivity and stability of H2O2 generation using commercial carbon black catalyst can be dramatically improved, especially under large ORR current densities (over 400 mA cm\(^{-2}\)). Modeling of reaction and local environment suggest that the cations could preferentially be attracted to the catalyst/electrolyte interface, showing a “shielding effect” to squeeze out the catalyst/electrolyte interfacial protons and thus prevent further reduction of generated H2O2 to water. A double-PEM-based reactor was further developed for continuous production of H2O2 solution. By using only 0.03 M Na2SO4 as the cation source, a promoted H2O2 FE (>90%) and stability (>500 h) were achieved. In light of this performance, this would be a promising demonstration of the use of renewable electricity for the continuous generation of H2O2 through O2 reduction at a more practical scale. This cation “shielding effect” could also be used in other electrocatalytic reactions such as selective CO2 reduction into fuels and chemicals or N2 reduction into ammonia.

**Experiment**

**Materials.** All chemicals including lithium sulfate (Li2SO4), sodium sulfate (Na2SO4), potassium sulfate (K2SO4), caesium

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**Fig. 6 Continuous production of H2O2 solution using carbon catalyst in a SE cell with a double-PEM configuration.** a Schematic illustration of reducing O2 to H2O2 in our SE cell with double-PEM configuration. The O2 + H2O/PEM//SE//PEM/H2O cell in which O2 is reduced at the cathode side to form H2O2 and flowed out by H2O flow. The cations in the middle chamber cross over the PEM under an applied reduction potential and move to the cathode, protecting the catalyst surface for the production of H2O2. b The I-V curve and corresponding FEs for producing H2O2 using the SE cell with double-PEM configuration through flowing 0.03 M Na2SO4 in the middle chamber. The concentration of Na2SO4 can be varied. c, d The schematic illustration and chronopotentiometry stability test of the SE cell with double-PEM configuration by directly flowing 0.03 M Na2SO4 solution in the middle chamber at 50 mA·cm\(^{-2}\) current density. The flow rate of Na2SO4 solution is 2.7 mL min\(^{-1}\). The oxygen gas (flow rate 180 sccm) and DI water (flow rate 10.8 mL min\(^{-1}\)) are mixed and flowed into the cathode to producing H2O2 solution. DI water with flow rate of 2.7 mL min\(^{-1}\) was circulated at the anode side. e, f The schematic illustration and chronopotentiometry stability test of the SE cell for practically producing 5000 ppm H2O2 solution. The volume of Na2SO4 stock solution in the first cycle is 200 mL, and the other 14 cycles hold 250 mL. The SE cell can produce around 3.7 L 5000 ppm H2O2 solution in 15 cycles for more than 200 h. The liquid flow rate is 4.5 mL min\(^{-1}\) and the O2 gas flow rate is 140 sccm. The total geometric area of the flow field in the cathode of our SE cell is 4 cm\(^2\).
sulfate (Cs2SO4), perchloric acid, sulfuric acid, and Nafion per-fluorinated resin solution (527084-25 mL) were purchased from Sigma Aldrich. H2O2 solution (35 wt%) was purchased from Merck & Co. Vulcan XC-72 were purchased from Fuel Cell Store. The conductive carbon black BP2000 was purchased from Cabot Corporation. Millipore water (18.2 MΩ·cm) was used throughout all experiments.

Preparation of electrodes. Typically, 40 mg conductive carbon black (BP2000) and 80 µL of Nafion (527084-25 mL) binder solution was mixed with 4 mL of 2-propanol (Sigma-Aldrich) and 1 ml methanol. After sonication in ice water for 30 min, the obtained homogeneous ink was air-brushed onto a 5 × 5-cm2 gas diffusion layer (GDL, Sigracet 28 BC, Fuel Cell Store) electrode at room temperature. Then the prepared electrode was dried in a vacuum at room temperature for 24 h before use. The procedure for preparing electrodes with other catalysts is same as that of carbon black BP2000. The reduced graphene oxide (rGO) catalyst was pretreated using HCl and acetone to remove impurities before making the catalyst ink.

Activation of the Nafion-117 membrane. The proton exchange membrane (PEM, Nafion-117) was purchased from Fuel Cell Store. The Nafion-117 membrane was pre-treated with 5% (v/v) H2O2 for 1 h at 80 °C and 10% (v/v) H2SO4 for 1 h at 80 °C before assembling a cell.

Materials characterization. The scanning electron microscopy (SEM) was performed on an FEI Quanta 400 field emission scanning electron microscope. BET surface area analysis was performed using Quantachrome Autosorb-iQMP/Kr BET Surface Analyzer.

Electrochemical test in flow cell. The electrochemical H2O2 generation was conducted at 25 °C by using a conventional flow cell with a typical three-electrode setup, and the electrochemical response was recorded by using a BioLogic VMP3 workstaton. The cathode and IrO2 anode (Fuel Cell Store) were placed on opposite sides of two 0.5 cm thick PTFE plates with 0.5 cm * 2 cm channels. The catalyst layers faced the flowing liquid electrolyte, and the geometric surface area of the catalytic was 1 cm2. A Nafion-117 film was sandwiched by the two PTFE plates to separate the chambers. At the cathode side, 30 sccm humidified O2 was supplied through a titanium gas flow chamber, and a catholyte containing 0.1 M H2SO4 and cations flowed into the cathode chamber. The catholyte flow rate of 1.8 mL min−1 was controlled by a syringe pump. The pH value of the catholyte was determined by an Orion 320 PerpHecT LogR Meter (Thermo Scientific). At the anode side, 0.1 M H2SO4 anolyte was circulated with a flow rate of 1.8 mL min−1 for O2 evolution reaction as the counter electrolyte. A saturated calomel electrode (SCE, CH Instruments) was employed as the reference electrode. All potentials measured against SCE were converted to the reversible hydrogen electrode (RHE) scale using ERHE = E_SCE + 0.241 V + 0.0591 × pH. The resistance (Rs) of the catalytic system was determined by potentiostatic electrochemical impedance spectroscopy (PEIS) at frequencies ranging from 0.1 Hz to 200 kHz. All the measured potentials using the three-electrode flow cell setup were manually 85% compensated unless stated otherwise.

Solid state electrolyte cell with double-PEM configuration. The continuous electrolysiss of H2O2 was conducted using a solid electrolyte (SE) cell with a sandwiched double-PEM configuration. The cell configurations and the production setup are illustrated in Fig. 6a and Fig. S25. The cathode side was supplied with an oxygen/water mixture of 180 sccm of O2 gas and 10.8 mL min−1 of DI water. The gas flow rate was controlled by a mass flow meter (MFC) and the water flow rate was controlled by a syringe pump. The flow rate of H2O2 product at the outlet was calibrated using a measuring cylinder. The fast water flow in the gas/liquid mixture through the cathode chamber is beneficial for bringing out the generated H2O2 molecules and decreasing the further electroreduction of H2O2. In the middle chamber, the styrene-divinylbenzene sulfonated copolymer Dowex 50WX8 hydrogen form (Sigma–Aldrich) cation conductor was employed as the SE. A solution containing H2SO4 and/or Na2SO4 flowed into the SE layer controlled by a syringe pump. The anode side was circulated with 0.1 M H2SO4 at 2.7 mL min−1. All the measured potentials using a two-electrode setup were manually 100% compensated unless stated otherwise.

Bath synthesis of 5000 ppm H2O2 Solution using double-PEM cell. The bath electrolysiss of 5000 ppm H2O2 was conducted using double-PEM cell configuration (as shown in Figs. 6a and S25). A certain volume of 0.03 M Na2SO4 solution (200 mL for the first cycle and 250 mL for other cycles) was supplied into the middle SE layer with flow rate of 4.5 mL min−1. The outlet of the middle chamber was mixed with 140 sccm O2 gas and then supplied to the cathode side for producing H2O2. The cathode outlet containing H2O2 and remaining Na2SO4 was then circulated back to the middle SE chamber for continually running of the cell. Once the accumulated H2O2 concentration reached around 5000 ppm, the cell was flushed with fresh 0.03 M Na2SO4 for 10 min to remove residue H2O2, and another bottle of fresh 0.03 M Na2SO4 (250 mL) was used to start a new batch.

Determination of the H2O2 concentration. The concentration of the generated H2O2 was determined through a titration process. After electrolysis, the as-produced H2O2 solution was collected and evaluated using the standard potassium permanganate (0.1 N KMnO4 solution, Sigma–Aldrich) titration process, according to the following equation:

\[
2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}
\] (1)

The sulfuric acid (1 M H2SO4) was used as the H+ source. The FE for H2O2 production is calculated using the following equation:

\[
\text{FE} = \frac{\text{generated H}_2\text{O}_2 (\text{mol L}^{-1}) \times 2 \times 96485 (\text{C mol}^{-1}) \times \text{flow rate (mL s}^{-1})}{i_{\text{total}} (\text{mA})} \times 100 \text{ (maximum 100%)}
\] (2)

Electrochemical H2O2 dissociation. The electrochemical H2O2 dissociation was conducted in a customized gas-tight H-type glass cell at 25 °C. Before the experiment, the glass cell was carefully cleaned by boiling the cell in a mixture of H2SO4: H2O2 (3:1) for 1 h. After being thoroughly cleaned by DI at room temperature, the cell was further boiled in DI water for another 1 h to totally remove H2O2 residual.

The electrochemical H2O2 dissociation was conducted with a BioLogic VMP3 workstation. The cathode electrode was prepared by spray coating carbon black (BP2000) on a GDL (Sigracet 28 BC, Fuel Cell Store), and the anode electrode was a carbon rod. The cathode electrode was fixed using a gold-coated clip and the exposed geometric surface area of each electrode was 1 cm2. Since the traditional clip made of iron can be easily dissolved to Fe2+ by acid and may contribute to the H2O2 dissociation, the gold-coated clip is necessary to avoid the dissolution of the iron clip during the process. The working and counter electrodes were parallel and separated by a clean PEM. The mixture of 0.2 M H2O2 + 0.1 M H2SO4 was used as catholyte, 0.1 M H2SO4 was used as anolyte, and
each volume of the electrolyte was 25 mL. A gas dispersion frit was used at the cathode chamber to provide vigorous electrolyte mixing. The cathode chamber was supplied with Ar gas (99.9999% Praxair) at a rate of 20 sccm for 30 min before the electrochemical measurements. During electrolysis, continuous Ar flow was supplied throughout the experiment and the gas outlet was connected to a gas chromatograph (GC, Shimadzu GC-2014 GC) for detection of the H₂ gas. The H₂ amount was quantified by a thermal conductivity detector. After the electrochemical decomposition, the amount of H₂O₂ remaining was determined by using the standard potassium permanganate titration process.

**Theoretical simulation.** The Vienna Ab initio Simulation Package (VASP)⁴⁰,⁴¹, together with the VASPsol patch⁴², was employed to perform slow-growth calculation. The constant potential along the MD track is realized by adjusting the number of electrons on-the-fly, as described in our previous work⁴⁵. Perdew-Burke-Ernzerhof (PBE) functional⁴³ together with D3 van der Waals correction⁴⁴ were employed in most of the calculations. The cutoff energy of the plane-wave basis is 400 eV in the relaxation while 300 eV was used in the MD simulations. Gamma-only MD calculations were done for the thick model in Fig.5a, b (water layers equivalent to 6 ice layers), while 3 x 3 x 1 Gamma-centered k-mesh was used in MD simulations using the thinner defect-graphene model shown in Fig. S17. One proton is added into the 45 H₂O molecules to simulate the pH = 0 condition. We choose the bond length (–O–O or O–OH) to be the reaction coordinate (ε). Time step in MD was set to be 0.5 femtoseconds, and the slow-growth method³⁵ was set to be 0.0004 Å. A Nose-Hoover thermostat⁴⁵ was used to keep temperature (statistically) constant at 300 K. The proton is determined as the H that is farthest from the central O among two other H atoms of a H₂O⁺ for snapshots that are evenly distributed along the AIMD track.

**Data availability**

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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**Author contributions**

X.Z. and X.H.Z. contributed equally. X.Z. and H.W. conceived the project and designed the experiments. X.Z., P.Z., Z.A., and Z.W. perform the experimental study. X.H.Z. and Y.L. performed the theoretical study. X.Z., X.H.Z., Y.L., and H.W. wrote the manuscript with support from all authors.

**Competing interests**

A patent application has been filed based on this study.

**Additional information**

**Supplementary information** The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-30337-0.

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