Supporting Information

Experimental Section

Materials: Tween 20, tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate, titanium (IV) butoxide, and isopropyl alcohol were purchased from MilliporeSigma. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) 6HCl, nitric acid was purchased from Shanghai kaiyulin pharmaceutical technology Co. Ltd. Magnesium acetate (Mg(CH₃COO)₂·4H₂O), and aqueous ammonia (NH₄OH, 14 mol L⁻¹), isopropyl alcohol, dibasic sodium phosphate (Na₂HPO₄), sodium dihydrogen phosphate (NaH₂PO₄), Nafion (5 wt.%) solution, hexamethylenetetramine (HMT; C₆H₁₂N₄), Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, alkene substrates, KAc, KCl and the chloride and nitrate of rare earth metals, and the olefins, phenol and benzyl alcohol were purchased from Aladdin Chemical Reagent Co., Ltd. H₃PW₁₂O₄₀ (≥99.0%), Cs₂CO₃, cetyltrimethylammonium bromide (CTAB, ≥99.0%), tetrabutylammonium bromide (TBAB, ≥99.0%) and H₂O₂ (30 % aqueous solution) were purchased from sinopharm. All reagents were used as purchased without further purification.

Characterizations: XRD patterns were obtained from a Shimadzu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were obtained using a Quanta FEG 250 field-emission SEM. TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. The surface areas and pore size distribution were measured with Brunauer–Emmett–Teller analyzer (ASAP 2460, Micromeritics, Co. USA). XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were acquired on SHIMADZU UV-1800 UV-Vis spectrophotometer. In situ Raman measurements were performed using a Horiba-Xplora Plus confocal microscope with 638 nm laser (1–20 mW). In situ spectroelectrochemistry was performed using an electrochemical workstation (CHI760E, CH Instruments), a Pt counter electrode (Alfa Aesar; Pt mesh) and a Hg/HgO reference electrode in ~20 mL of 0.1 M O₂-saturated PBS. In situ ATR-

FTIR measurements were taken on a BRUKER-EQUINOX-55 IR spectrophotometer, a diamond-like carbon was coated onto a Si wafer $(5 \times 8 \times 1 \text{ mm}^3)$ to prepare the internal reflection element (IRE). The coated IRE was ultrasonicated for 2 min with 30 wt.% concentrated H_2SO_4 followed by rinsing with DI water before experiments. A 50 μ L of 2 mg mL⁻¹ catalyst ink (no Nafion binder) was dropcast on the IRE and dried under air at room temperature. A glassy carbon paper was placed on top of the catalyst layer for good electrical contact. Glassy carbon rod connected to the IRE, Pt gauze, and Ag/AgCl in 3 M KCl were used as the working electrode, counter electrode, and reference electrode, respectively. An FTIR spectrometer with a mercury cadmium telluride (MCT) detector was used for the in situ ATR-FTIR measurements. 0.1 M PBS were saturated with O2 for ORR. Gamry Reference 600 potentiostat is employed during recording of the IR spectra. The products were examined by 1H NMR spectra on a Varian 600 MHz NMR spectrometer (Bruker AVANCE AV III 600) and chromatograph (Shimadzu, GC-2014C). Chloroform was used as an internal standard and excess water was removed with anhydrous sodium sulfate before testing. The product was filtered and dehydrated, and deuterated chloroform was used as an internal to calibrate the chemical shifts in the spectra.

Sample preparation. The synthesis of $Mg_3(HHTP)_2$ was conducted via a modified method according to the previous reported.¹ First, the 2,3,6,7,10,11-hexahydroxytriphenylene (33 mg) was dissolved in 2.5 mL N,N-dimethylformamide (DMF) and heated to 80°C, then $Mg(CH_3COO)_2$ (11 mg) was dissolved in the 2.5 mL H₂O and added dropwise to the above solution, and stirred at 80 °C for 12h. The resulting black powder was centrifuged, filtered, and then washed in water under reflux for a total of 36 hours (the water was refreshed 2 times during this washing step, for a total of 3 steps, 12 hours each), and dried under vacuum at 60 °C.

 $Mg_{2/3}$ - $Al_{1/3}$ - CO_3^{2-} LDH hexagonal platelets were synthesized as previously reported.² $Mg(NO_3)_2 \cdot 6H_2O$ (0.02 mol), $Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol), and hexamethylenetetramine (0.026 mol) were mixed in 80 mL of water and kept at 140°C for 24 h. The obtained solid powder was washed with water, centrifuged and dried in air. The samples were further treated with 500 mL of an aqueous solution containing NaNO₃ (0.75 mol) and

 HNO_3 (0.0025 mol) to expel additional carbonate ions between the layers.

 $Cs_xH_{3-x}PW_{12}O_{40}$ were synthesized as previously reported.³ An aqueous solution of Cs_2CO_3 (0.10 mol·dm⁻³) was added dropwise to $H_3PW_{12}O_{40}$ (0.08 mol·dm⁻³, 20 cm³, room temperature) with vigorous stirring for 12 h. The Cs content can be adjusted according to the Cs_2CO_3 precursor content. After centrifugation and drying, a white powder was obtained.

We synthesized TS-1 as previously reported in the literature.⁴ 32 mL of deionized water containing 2 g of Tween 20 (s.d. FINE CHEM.) was added to 19.2 g of TPAOH (32% in water) with gentle stirring to form a clear and transparent solution. Then, 36 g of tetraethoxyethyl silicate (TEOS, Aldrich) were added dropwise with vigorous stirring and stirred for 1 hour. Then, a solution of 1.808 g of tetrabutyl titanate (TNBT, Aldrich) in 9.12 g of isopropanol (IPA, s.d. FINE CHEM.) was added dropwise with vigorous stirring to the above clear solution. Stirring was continued for 1 hour and the resulting mixture was still clear. The mixture was crystallized at ambient pressure of 433K for 18 hours. Centrifugal recovery, washed with distilled water, and dried (383 K 12h).

Surface oxidation of carbon materials. First, multi-walled carbon nanotubes (200 mg) are pretreated with concentrated hydrochloric acid (HCl, 12 M, 100mL) to remove excess iron oxide species, centrifuged and washed with deionized water until neutral. Then dissolved in 16 M concentrated nitric acid (HNO₃, 100mL), stirred at 80°C for 12h, washed with deionized water by centrifugation until neutral, and dried to obtain black powder.

Synthesis of NdPW₁₁ multilayer clusterphenes. $H_3PW_{12}O_{40}$ (288 mg, 100 µmol) and 42 mg (100 µmol) of Nd(NO₃)₃·5H₂O were dissolved in 20 ml of deionized water, and 43 mg of cetyltrimethyl ammonium bromide (CTAB) and 38 mg of tetrabutyl ammonium bromide (TBAB) were dissolved in 30 ml of chloroform. The organic phase was added dropwise into the POM solution under vigorous stirring. The organic phase was separated and centrifuged at 10,000 r.p.m. for 5 min after 10 h. The precipitate was collected and dried under air. The product was obtained as some powder.

Electrochemical measurements. Electrochemical measurements using an electrochemical workstation based on our previous work⁵⁻⁷ (CHI760E, CH

Instruments). For rotating ring disk electrode (RRDE) measurements (disk area: 0.2475 cm², ring area: 0.1866 cm²), a three-electrode system was built with an RRDE (glassy carbon (GC) disk + Pt ring), a Hg/HgO reference electrode, and a graphite rod counter electrode. The H_2O_2 production activity was assessed by LSV in O_2 -saturated 0.1 M PBS at a scan rate of 20 mV s⁻¹ and a rotation speed of 1,600 rpm. During the LSV, the Pt ring potential was held at 1.2 V.

The H₂O₂ selectivity was calculated using the following relation:

$$H_2O_2$$
 (%) = 200 × I_r / N / (I_d + I_r / N)

where I_r is the ring current, I_d is the disk current and N is the collection efficiency (0.325 after calibration). The collection efficiency (N) was determined using the $[Fe(CN)_6]^{3-/4-}$ redox system. The catalyst-deposited RRDE was soaked in N₂-saturated 0.1 M KNO₃ + 10 mM K₃[Fe(CN)₆], and chronoamperometry was performed at -0.3 V (vs. Hg/HgO) while the ring potential was fixed at 0.5 V (vs. Hg/HgO) for 50 s. The background response was also obtained similarly, but the applied disk potential was 0.5 V (vs. Hg/HgO). The collection efficiency could be calculated as follows:

$$N = (|i_r - i_{r,bg}|) / i_d$$

where $i_{r, bg}$ stands for the background ring current. The result yields that the collection efficiency is 32.5%.

The electrogeneration of H_2O_2 and olefin epoxidation. For the two-electrode solid electrolyte cell of electrosynthesized pure H_2O_2 , the method is proposed in this paper.^[8] Sustaninion X37-50 Grade 60 and Nafion 117 membranes were used for anion and cation exchange, respectively (Dioxide Materials). About 0.1 mg cm⁻² of Mg₃(HHTP)₂ and RuO₂ were loaded on a hydrophobic carbon paper (AvCarb) gas diffusion electrode (electrode area of about 1 cm²) as cathode and anode, respectively. The cathode side provided an O₂ feed rate of 30 sccm and the anode side was circulated with 1 M H₂SO₄. O₂ generated at the anode can be collected and used for O₂ reduction at the cathode for better product recycling. Anion/cation conductors (polymer from Dowex) were filled in the intermediate chamber, and the epoxidation catalyst was mixed with solid ionic conductors at a density of 5 mg cm⁻³. Flow cells were first stabilized for 30 minutes before collecting the liquid product. Solution resistance was determined by potentiostatic electrochemical impedance spectroscopy at frequencies ranging from 0.1 Hz to 100 kHz. All the measured potentials using three-electrode setup were manually 70% compensated.

To quantify the H_2O_2 produced, the samples was collected at certain time and mixed with same volume of titanium oxysulfate solution (6 g L⁻¹). The H_2O_2 yield was measured by using the indicator of titanium oxysulfate. The generated complex compound solution was detected with UV-vis spectrophotometer at the maximum absorption wavelength $\lambda = 406$ nm.

The FE and possibly generated H_2O_2 of OER was also explored by RRDE, where the ring voltage was set to 1.5 V to oxidize the possibly generated H_2O_2 . At a fixed current of 180 μ A and 470 μ A, oxygen was generated, respectively, and then swept across the surrounding Pt ring electrode for complete oxygen reduction at 0.45 V.⁹

The system energy conversion efficiency is calculated according to the following formula.

System energy conversion efficiency (%) = $FE_{(O2 to H2O2)}$ % * $FE_{(H2O to O2)}$ % * Selectivity_{epoxide}%

The H₂O₂ utilization efficiency was calculated as follows:

$$\mathrm{H_2O_2} \text{ utilization efficiency (\%)} = \frac{\mathrm{r_{PO}}}{\mathrm{r_{H2O2}} - \mathrm{r^r_{H2O2}}} \times 100$$

where r_{PO} , r_{H2O2} and r^r_{H2O2} indicate produced PO, and H_2O_2 and remaining H_2O_2 (mmol), respectively.

Calculation details: The spin-polarized density functional theory (DFT) calculations were performed via Vienna ab initio simulation package (VASP).¹⁰ The interaction between valence electrons and ion cores was dealt with projected augment wave (PAW) pseudopotential.¹¹ and the exchange-correlation effect dealt with Perdew, Burke, and Ernzerhof (PBE) functional.¹² DFT+D3 scheme was used to treat the van der Waals (vdW) interaction.¹³ The plane-wave basis with kinetic energy cutoff of 450 eV was adopted. The optimizations of total energy and Hellmann-Feynman force are stopped when they are less than 10⁻⁴ eV and 0.05 eVÅ⁻¹, respectively. Mg₃(HHTP)₂ monolayer was simulated with a vacuum layer of ~ 22 Å to decouple the interaction of the system

with its image. The Monkhorst-Pack grid¹⁴ was used to sample the first Brillouin zone, and $1 \times 1 \times 1$ and $3 \times 3 \times 1$ meshes are for the structural optimization and densities of states calculation, respectively.

The computational hydrogen electrode model was adopted to simulate the ORR processes on the Mg₃(HHTP)₂ monolayer,¹⁵ according to the following equation,

$$\Delta \mathbf{G} = \Delta E + \Delta E_{\rm ZPE} - T\Delta S$$

In the equation, ΔE , ΔE_{ZPE} , and $T\Delta S$ denote the free energy changes contributed by the total electronic energy (*E*), zero-point energy (E_{ZPE}), and entropy (*S*), respectively, and the temperature (*T*) equals to 298.15 K. E_{ZPE} and *S* of the free molecules were taken from the NIST database,¹⁶ and those of the reaction intermediates obtained from DFT calculations. The vibrational frequencies and corresponding energy corrections are presented in Table S6, S7, and S8. Solvation effect may slightly stabilize OOH* (* denotes the adsorption site). However, we note that the DFT calculation without solvation correction¹⁷⁻²⁰ can well reproduce the experimental 2e⁻ ORR activity and selectivity trend. Therefore, following previous works,¹⁷⁻²⁰ solvation effect has not been considered in determining the value of ΔG_{HOO*} , which in turn makes the direct comparison fair with the reported results.

The $2e^-$ and $4e^-$ ORR leads to production of H_2O_2 and H_2O , respectively, both of which were considered to occur through the associative mechanism.

The 2e⁻ ORR consists of two elementary steps (a and b):

$$* + O_2(g) + H^+ + e^- \rightarrow OOH^*$$
 (a)

$$OOH^* + H^+ + e^- \to H_2O_2(l) + *$$
 (b)

The 4e⁻ ORR consists of four elementary steps (c, d, e, and f):

$$* + O_2(g) + H^+ + e^- \rightarrow OOH^*$$
 (c)

$$OOH^* + H^+ + e^- \to O^* + H_2O(l)$$
 (d)

$$O^* + H^+ + e^- \rightarrow OH^*$$
 (e)

$$OH^* + H^+ + e^- \rightarrow H_2O(1) + *$$
 (f)



Fig. S1. N₂ adsorption-desorption isotherms of Mg₃(HHTP)₂.



Fig. S2. (a) STEM image and (b-e) corresponding EDX elemental mapping images of Mg, O and C of Mg₃(HHTP)₂. (f-g) EDX result of Mg₃(HHTP)₂.



Fig. S3. (a) Mg 1s and (b) O 1s spectra of $Mg_3(HHTP)_2$. The Mg-O bond exists clearly and independently, accompanied by the adsorption of OH⁻ species on the surface due to the inter-plane hydrogen bond network.^{21,22}



Fig. S4. (a) SEM image and (b) low magnification TEM image of TS-1.



Fig. S5. N_2 adsorption-desorption isotherms of TS-1.



Fig. S6. (a) XPS survey and (b) Si 2p and (c) O 1s spectra of TS-1.



Fig. S7. (a,b) TEM images and (c) O 1s spectra of O-CNTs. TEM images and XPS analysis demonstrated that we successfully synthesized O-CNTs with rich C=O and good morphology.



Fig. S8. (a) LSV curves of $Mg_3(HHTP)_2$ and O-CNTs recorded at 1600 rpm in 0.1 M PBS, with ORR and detected H_2O_2 current densities on disk and ring electrodes, respectively. (b) The calculated H_2O_2 selectivity and (c) Tafel plots from a. Electrochemical tests show that $Mg_3(HHTP)_2$ is an excellent electrocatalyst for the reduction of O_2 to H_2O_2 in neutral media.



Fig. S9. In situ ATR-IR spectra under applied potentials of $Mg_3(HHTP)_2$ in the range of (a) 3200–3700 cm⁻¹ and (b) 1200–1500 cm⁻¹ (OOH_{ad}: adsorbed OOH). (c) In situ Raman spectra of $Mg_3(HHTP)_2$ electrocatalysts at selected potentials in O₂-saturated 0.1 M PBS.

First, in situ infrared spectroscopy observed that the OOH* key intermediate was directly adsorbed on Mg^{2+} to form Mg-OOH at 3648 cm⁻¹ (Fig. S9a and Table S6 and S7), accompanied by the adsorbed water at 3400–3450 cm⁻¹, acting as a proton source for H₂O₂ formation (Table S6 and S7).⁷ Simultaneously, the final product HOOH and the adsorbed OOH* were also detected, together confirming that Mg acts as the real active center to catalyze O₂ to H₂O₂ (Fig. S9b). Subsequently, an in situ Raman spectroscopic technique was employed to investigate the atomic-level structural details of the catalyst surface during reactions (Fig. S9c). The obtained Raman peaks are consistent with the previous literature, proving that Mg₃(HHTP)₂ was successfully synthesized with good crystalilinity.⁷ Then, the Raman spectrum is divided into three main peaks, D (defects), G (graphene), and 2D (second order of the D peak) peaks at 1380, 1550, and 2150 cm⁻¹, respectively. The ratio of I_{2D}/I_G is widely accepted to

evaluate the number of layers in 2D materials, and the larger the ratio, the fewer the layers. It can be observed from Fig. S9c that the 2D peak is obviously raised during the reaction (From 0.7-0.2 V, the G peak remains unchanged, and the 2D peak becomes larger), indicating that it tends to a monolayer state, which is conducive to accelerating the diffusion of reactants and enhancing the reaction kinetics. At the same time, due to the adsorption and desorption of oxygen intermediates and the construction of the interlayer hydrogen bond network in the aqueous solution during the reaction, the D peak changed erratically from 0.9 to 0.6 V and remained stable at 0.6 to 0 V. When the overpotential continues to increase, it leads to a more violent reaction environment, which seriously interferes with the Raman scattering signal.



Fig. S10. (a) The geometric configuration of the Mg₃(HHTP)₂ monolayer. Besides Mg, C1 and C2 sites are also considered for the $2e^-$ ORR. Yellow, grey, red, and pink spheres represent Mg, C, O, and H atoms, respectively. (b) The densities of states (DOS) of the Mg₃(HHTP)₂ system and those of the C, N, and Mg atoms in the system. DOS of the Mg atom is magnified by 20 times for clarity. (c) The electronic state distribution for the energy interval between -0.1 and 0.1 eV relative to Fermi level. The isosurface is taken as 0.0005 e/bohr^[3]. (d) The distribution of electron localization function for the Mg₃(HHTP)₂ monolayer. The isosurface is taken as 0.21.

DFT calculations were conducted to unravel the nature of the active site and explore the intrinsic activity and selectivity for $2e^-$ ORR on Mg₃(HHTP)₂ [see Computational Details in Supporting Information]. The atomic model of the Mg₃(HHTP)₂ monolayer is presented in Fig. S10a. Its densities of states (DOS) presented in Fig. S10b show that there are rich electronic states crossing Fermi level (E_f), indicating the metallic conductivity feature. This can be further confirmed with the electronic state distribution around E_f (Fig. S10c), which distribute over the whole plane of the Mg₃(HHTP)₂ monolayer. More importantly, as shown in Fig. S10d, the values of electron localization function around the Mg atom are almost zero, indicating the strong ionic bonding characteristics of Mg-N bonds and Mg in the 2+ valence state. In fact, Bader analysis²³ shows that almost all the valence electrons are lost for the Mg atom. It is expected that the highly positively charged Mg cation is in favor for the adsorption of oxygenated species, such as OOH* herein (* denotes the adsorption site).



Fig. S11. Free energy diagrams for the 2e⁻ (red line) and 4e⁻ (blue line) ORR at the Mg site under zero potential versus RHE, and the optimized configuration of OOH*.

The 2e⁻ ORR to H₂O₂ is composed of two proton-coupled electron transfer steps with OOH* as the only intermediate. In contrary, 4e⁻ ORR usually proceeds through four proton-coupled electron transfer steps, for which O₂ is successively hydrogenated to OOH*, O*, OH*, and H₂O. The free energy diagrams for 2e⁻ and 4e⁻ ORR at the Mg site are displayed in Fig. S11. Significantly, OOH* binds to Mg properly with the binding free energy (ΔG_{OOH*}) of 4.29 eV, close to the optimum value of 4.22 eV,^{5,17,19} which gives a theoretical overpotential of 0.07 V for 2e⁻ ORR. Moreover, the Mg site also exhibits 4e⁻ ORR activity. However, the 2e⁻ ORR towards H₂O₂ will be dominated due to the weak binding of O* on the Mg site (see Fig. S12 for OH*). The calculated binding free energy of O* (ΔG_{O*}) (3.86 eV) is not only much higher than that for PtHg₄ (2.75 eV)¹⁷ and MoTe₂ (2.33 eV),¹⁹ but only unfavorable compared with the production of H_2O_2 . These results further confirm the experimental observation that Mg^{2+} serves as the catalytically active site for 2e⁻ ORR on Mg₃(HHTP)₂. In addition, we also studied the 2e⁻ ORR of the C sites (C1 and C2 in Fig. S10a). From Fig. S13, for both sites, OOH* binds very weakly (4.91 and 5.28 eV for C1 and C2 sites, respectively) and show negligible 2e⁻ ORR activity.



Fig. S12. The top and side views of O^* (a) and OH^* (b) at the Mg site of $Mg_3(HHTP)_2$ monolayer.



Fig. S13. Free energy diagrams for the $2e^-$ ORR at the C1 and C2 sites of Mg₃(HHTP)₂ under zero potential versus RHE, and the optimized configuration of OOH*.



Fig. S14. (a) The disk and ring current of RuO_2/C electrocatalyst on the RRDE equipment (1600 rpm) with the ring potential applied at 1.50 V in 1.0 mol L⁻¹ H₂SO₄ solution. (b) Ring currents of the RuO₂/C on the RRDE (1600 rpm) with the ring potential applied at 0.45 V at different disk currents (180 and 470 µA). The ring voltage was set to 1.5 V and 0.45 V for the oxidation of H₂O₂ and the reduction of O₂, respectively.



Fig. S15. (a) Mg 1s (b) and O 1s spectra of $Mg_3(HHTP)_2$ before and after the durability tests.



Fig. S16. PO concentration changes upon adsorption on TS-1 ($C_0 = 10 \text{ mM}$, 5 mg_{TS-1/solid ion conductor}/mL).



Fig. S17. (a) The XRD pattern and (b,c) SEM images of Mg-Al LDH. (d) The XRD pattern and (e,f) SEM images of $Cs_xH_{0.5}PW_{12}O_{40}$ (see Table S3 for element distribution).



Fig. S18. Effects of organic polymer ionic conductors and inorganic ionic conductors on yield.



Fig. S19. (a-c) TEM images of NdPW $_{11}$ clusterphenes at different scales.

Solvent	H^{+} conductor	HO_2^- conductor	
Aqueous (pure DI water/	styrene–divinylbenzene copolymer consisting of	styrene-divinylbenzene copolymer consisting of	
tert-butanol-water/	sulfonic acid functional	quaternary amino functional	
Organic	groups	groups	
(Acetonitrile/ Dichloromethane/ Trichloromethane)	$Cs_xH_{3^{-x}}PW_{12}O_{40}$	$Mg_{2/3}\text{-}Al_{1/3}\text{-}CO_{3}{}^{2-}LDH$	

Table S1. The preferred type of ionic conductor depends on the reaction environment.

The selection of ionic conductors should follow three points in order: higher ionic conductivity, weak adsorption to reactants, low cost and stability.

Electrocatalyst	Electrolyte	Selectivity [%]	Onset potential vs RHE	Stability	Productivity	Reference
	0.1 M PBS	92.5	0.7		2450 11 0	
Mg ₃ (HHTP) ₂	Solid-electrolyte	~97	1.9 V _{cell}	100 h @ 100 mA cm ⁻²	pure 2450 ppm H ₂ O ₂ 75 mmol L ⁻¹ h ⁻¹	This work
O-CNTs	0.1 M PBS	82	0.5	10 h by RRDE		18
Co1-NG(O)	0.1 M PBS	80	0.68	110 h by H-cell	242 ppm	24
Co-N-C	0.1 M K ₂ SO ₄	55	0.6			25
Hierarchically porous carbon	0.1 M PBS	70.8	0.65			26
Activated carbon/carbon fiber	solid polymer electrolyte	26.5	0.31			27
Carbon fiber	solid polymer electrolyte	52	0.51			28
NCMK3IL50_800T	0.1 M K ₂ SO ₄	75	0.2	8 h by H-cell	900 mmol g _{cat.} ⁻¹ h ⁻¹	29
MCHS-9:1	0.1 M PBS	>90	0.57			30
B-C	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	75	0.4	30 h by flow cell	pure 1100 ppm H ₂ O ₂	31
NADE	0.05 M Na ₂ SO ₄	66.8	0.7	2 h by H-cell	56 mg cm ⁻²	32
g-N-CNH	0.1 M PBS	~90	0.45	25 h by H-cell		33
PtP ₂ -Al ₂ O ₃	membrane fuel cell (H ₂ anode)	78.8%		110 h by PEMFC	$2.26 \text{ mmol } h^{-1} \text{ cm}^{-2}$	34

Table S2. Comparing the performance of recently reported electrocatalysts for O_2 reduction to H_2O_2 .

		$Cs_xH_{0.5}PW_{12}O_{40} \\$		
Element	0	Р	Cs	W
Atomic %	68.57	1.51	1.78	28.14
		Mg-Al LDH		
Element	0	Mg	Al	
Atomic %	67.27	16.98	15.76	

Table S3. The EDX element ratio distribution of $Cs_xH_{0.5}PW_{12}O_{40}$ and Mg-Al LDH.

				Stratam		
			V : 1	System		
Substrate	Selectivit	Conversio	Y lei	energy .	G 1 4	Catalyst
S	y (%)	n (%)	d	conversio	Solvent	S
	• • •		(%)	n		
				efficiency		
1	>99	>99	>99	92.9	H ₂ O	TS-1
2	87.2	79.4	69.2	81.7	CH ₃ CN	TS-1
3	90.1	91.5	82.4	84.5	CH ₃ CN	TS-1
4	>99	>99	>99	92.9	CH ₃ CN	TS-1
5	>99	>99	>99	92.9	CH ₃ CN	NdPW ₁₁
6	98.0	79.1	77.5	91.9	CH ₃ CN	NdPW ₁₁
7	>99	94.7	93.7	92.9	CH ₃ CN	NdPW ₁₁
8	>99	93.1	92.2	92.9	CH ₃ CN	NdPW ₁₁
9	98.6	95.3	94	92.5	CH ₃ CN	NdPW ₁₁
10	>99	95.0	94.1	92.9	CH ₃ CN	NdPW ₁₁
11	>99	98.3	97.3	92.9	CH ₃ CN/CH ₂ Cl ₂	NdPW ₁₁
12	84.0	60.4	50.7	78.8	CH ₃ CN/CH ₂ Cl ₂	NdPW ₁₁
13	>99	90.1	89.2	92.8	CH ₃ CN/CH ₂ Cl ₂	NdPW ₁₁
14	97.9	91.6	89.7	91.8	CH ₃ CN/CH ₂ Cl ₂	NdPW ₁₁
15	95.5	92.6	88.4	89.6	CH ₃ CN/CH ₂ Cl ₂ /CHCl	NdPW ₁₁
16	95.7	97.2	93.0	89.8	CH ₃ CN/CH ₂ Cl ₂ /CHCl 3	NdPW ₁₁
17	98.4	80.1	78.8	92.3	CH ₃ CN/CH ₂ Cl ₂ /CHCl 3	NdPW ₁₁

Table S4. Preferred solvents and catalysts depend on different substrate properties where the solvent flow rate is 5 mL h^{-1} , the constant current is 40 mA cm⁻², and the olefin concentration is 100 μ mol mL⁻¹. CH₂Cl₂ as solvent for performance test of **9-15**.

 $Selectivity (\%) = \frac{epocide (\mu mol)}{total \ products \ observed \ (\mu mol)}$

 $Conversion (\%) = \frac{initial \ substrate \ (\mu mol) - \ final \ substrate \ (\mu mol)}{initial \ substrate \ (\mu mol)}$

 $Yield (\%) = \frac{epocide (\mu mol)}{initial \ substrate (\mu mol) - final \ substrate (\mu mol)}$

Substrates	Products	Selectivity (%)	Conversion (%)	Yield (%)	Solvent	Catalysts
benzene	phenol	93.2	14.5	13.5	CH ₃ CN	TS-1
benzyl alcohol	benzaldehyde	94.6	24.7	23.4	CH ₃ CN	TS-1

 Table S5. Preferred solvents and catalysts depend on different substrate properties.

Tables S6. The calculated vibrational frequencies for the intermediates on the Mg site. Asterisk (*) denotes the adsorption site.

Vibrational frequencies (cm ⁻¹)			
O*	402.95, 103.07, 70.11		
OH*	3795.69, 482.72, 385.99, 174.17, 108.73, 49.95		
OOH*	3645.47, 1312.94, 882.64, 349.48, 298.97, 180.87, 126.44, 88.89, 41.145		

Table S7. The calculated vibrational frequencies for the intermediates on the C1 site.

	Vibrational frequencies (cm ⁻¹)
OOH*	3546.33, 1313.65, 913.46, 405.69, 309.14, 150.46, 114.14, 36.37, 34.36

Tables S8. The zero-point energy (EZPE) and the product (TS) of temperature (T = 298.15 K) and entropy (S) of the intermediates, where asterisk (*) denotes the adsorption site.

Species	EZPE (eV)	TS (eV)
H ₂ O	0.56	0.67
H_2	0.27	0.41
O* (Mg)	0.04	0.11
OH* (Mg)	0.30	0.12
OOH* (Mg)	0.43	0.21
OOH* (C1)	0.42	0.17
*	0.00	0.00

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