

Supplementary Information

Nd Doping Enables Efficient and Durable Manganese-based Water Oxidation Catalysts under Acidic Conditions

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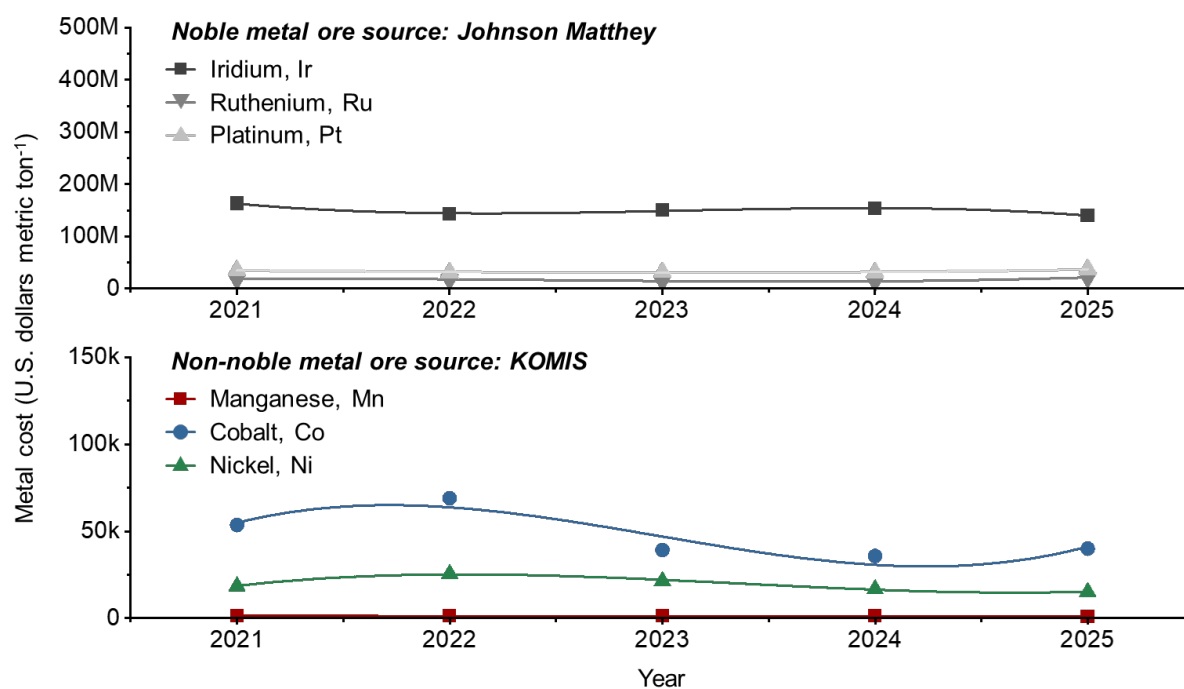
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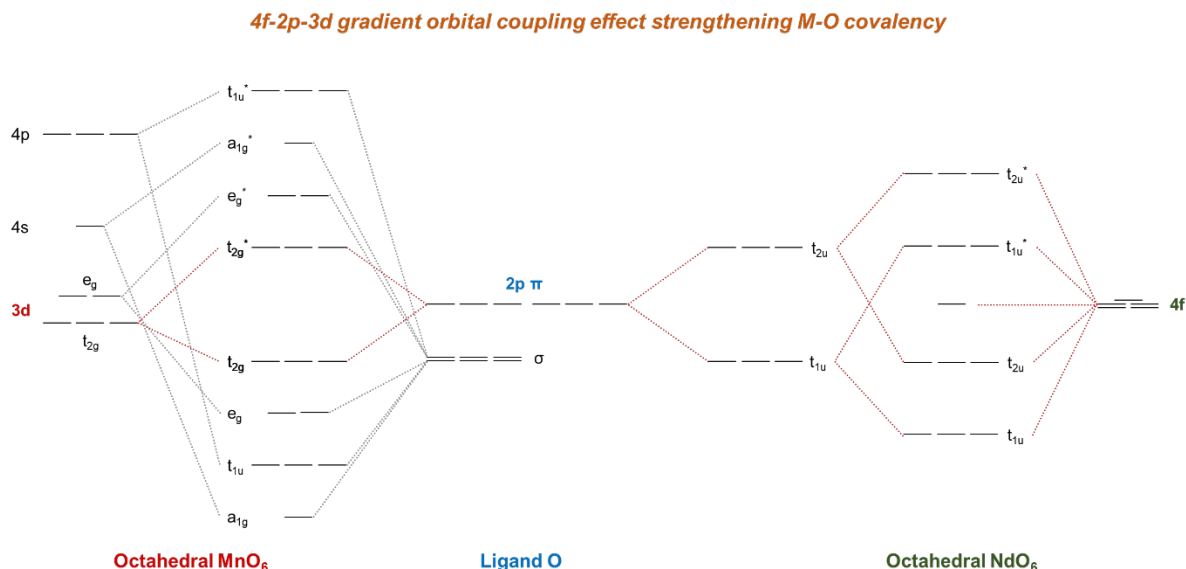
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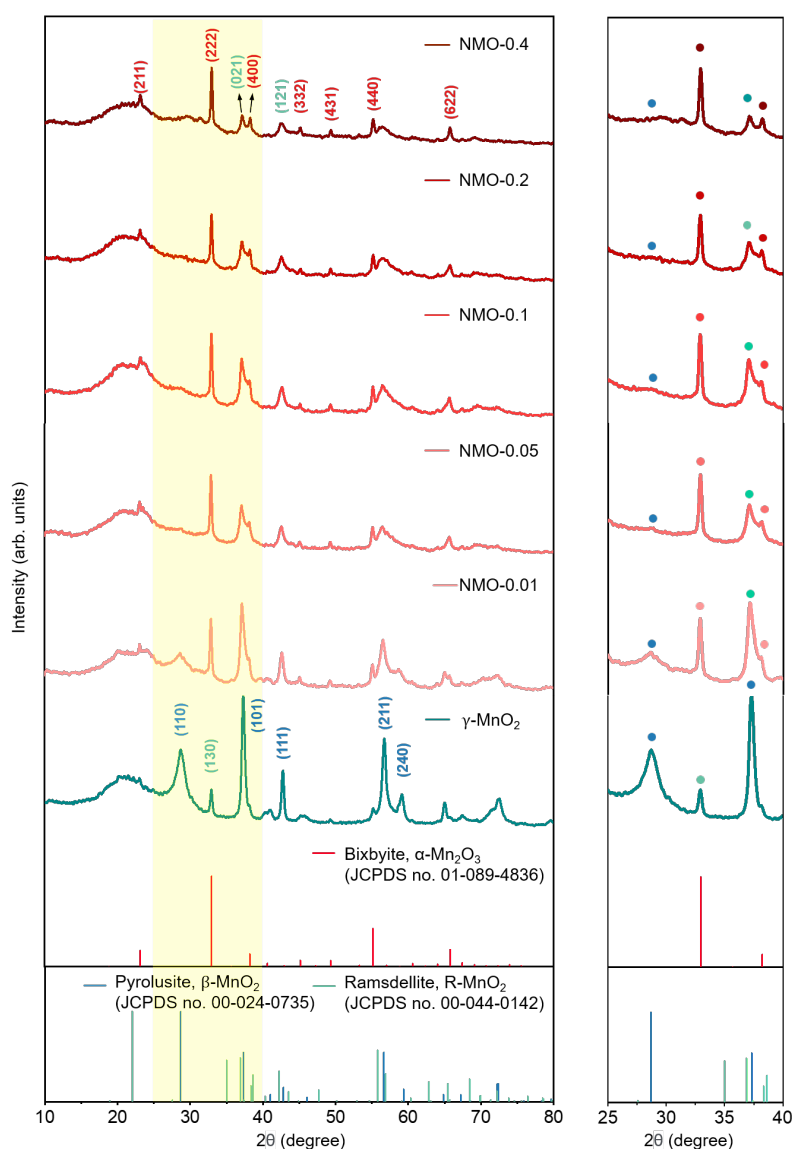


Supplementary Fig. 1 Year-by-year price trends of (top) noble metal ores (Ir, Ru, and Pt) and (bottom panel) non-noble metal ores (Mn, Co, and Ni).^{1,2}



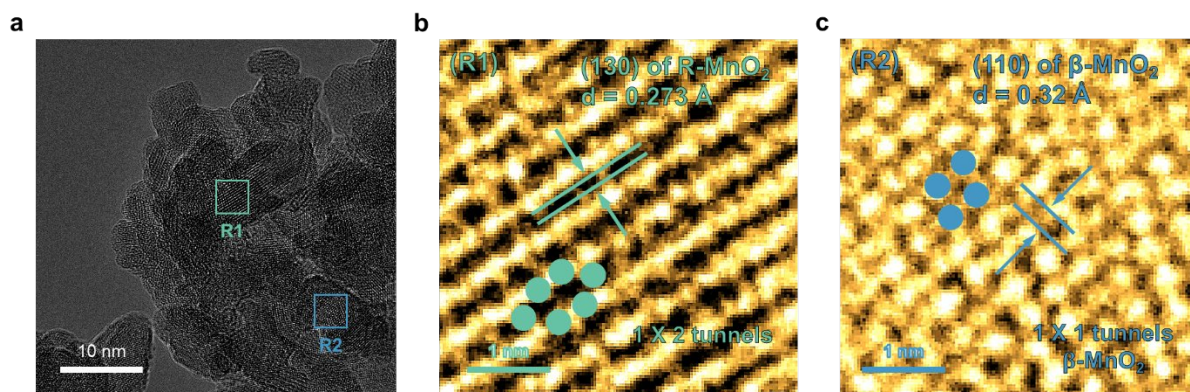
Supplementary Fig. 2 Schematic illustration of $4f$ - $2p$ - $3d$ gradient orbital coupling within the Mn-O-Nd framework.

Supplementary Note 1 Lanthanide elements, possessing highly degenerate yet spatially localized $4f$ orbitals that are shielded by valence $5d$ and $6s$ electrons, can serve as functional dopants in transition metal–oxide (TM–O) coordination systems.³ Through $4f$ - $2p$ - $3d$ gradient orbital coupling, the valence electronic structure can be modulated, thereby optimizing electrocatalytic performances.^{4,5} During the OER, the unique valence electron configuration arising from $4f$ - $2p$ - $3d$ orbital hybridization serves as an electron buffer, compensating for electron loss and suppressing over-oxidation of the active metal sites.^{4,6-8} The p - d hybridized $4f$ band, located above antibonding $(\text{M-O})^*$ states and closer to the Fermi level (E_f), buffers electron depletion from the $(\text{M-O})^*$, thereby preserving the covalency of the TM–O bond during the OER process. Moreover, electronic redistribution at the $3d$ TM active centers, induced by gradient orbital coupling, introduces additional electron and state perturbations, enhancing the intrinsic catalytic activity. Therefore, doping lanthanide elements into Mn–O framework may provide dual advantages; modulating the electronic structure of active sites and stabilizing the active metal centers.

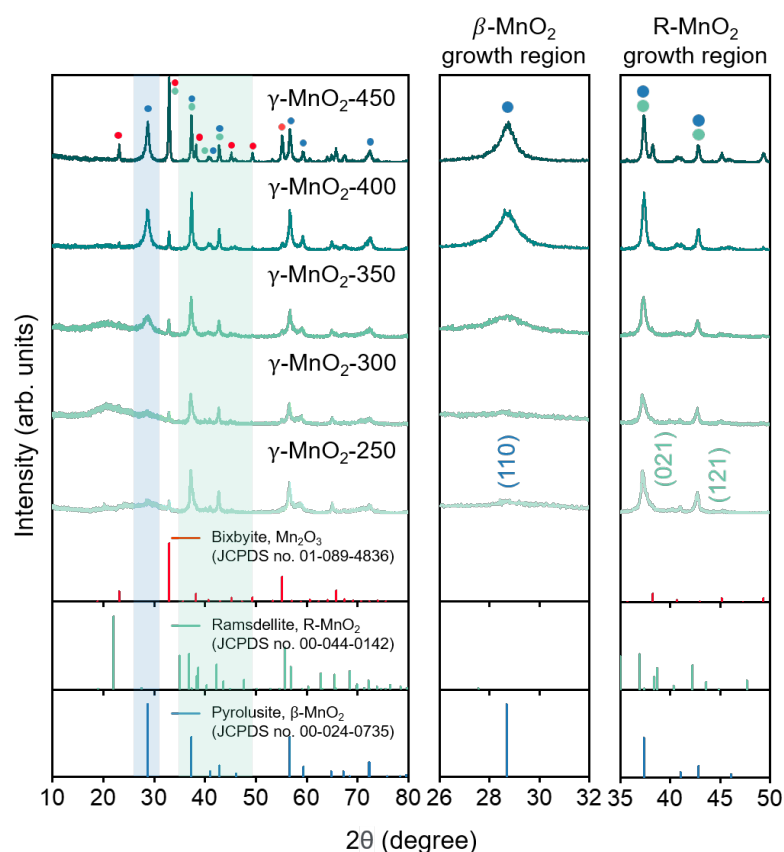


Supplementary Fig. 3 PXRD patterns of γ - MnO_2 and NMO- x series (where x denotes the Nd molarity in the precursor solution). The pale-yellow regions in the left panel are magnified in the right panel, highlighting a decrease in the intensity of the (110) and (101) peaks associated with β - MnO_2 and the (130) peak corresponding to R- MnO_2 after Nd doping.

Supplementary Note 2 With increase of Nd doping, the characteristic diffraction peaks of γ - MnO_2 corresponding to the (110), (130), and (101) planes were progressively diminished, while new peaks of α - Mn_2O_3 , assigned to the (211), (222), and (400) planes, gradually emerged and intensified. This evolution indicates a phase transformation toward α - Mn_2O_3 , particularly evidenced by the pronounced growth of the (222) and (400) peaks.

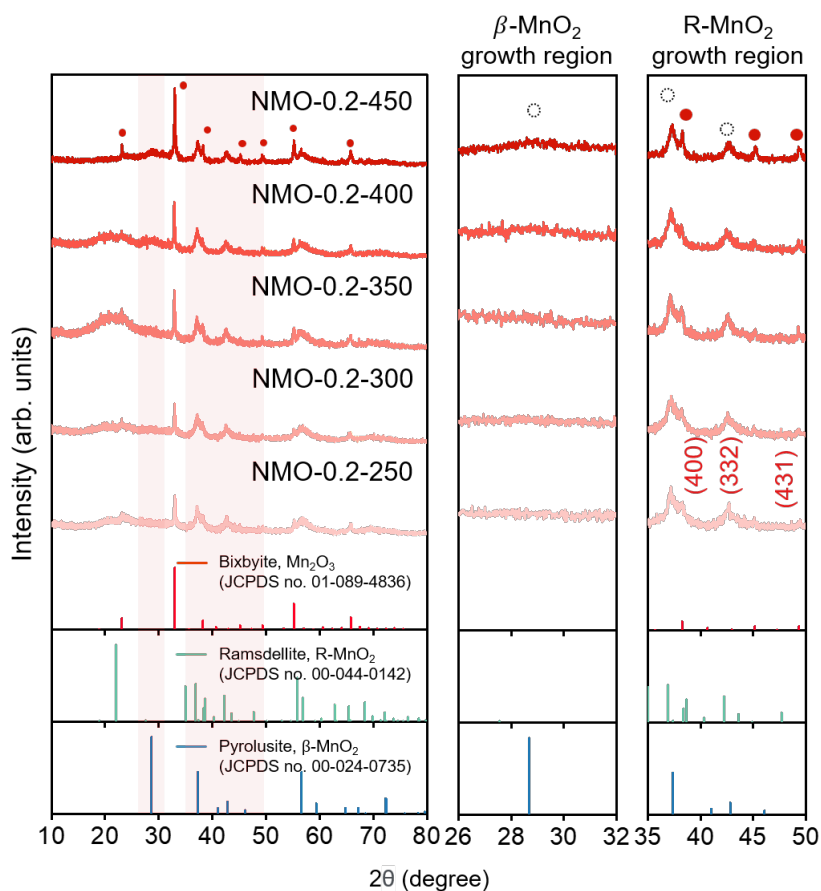


Supplementary Fig. 4 HRTEM image of γ - MnO_2 . (a) Overall structure of the γ - MnO_2 composed of R- MnO_2 and β - MnO_2 . (b) R1 region showing the R- MnO_2 phase with a “1 × 2” tunnel structure. (c) Region R2 showing the β - MnO_2 with a “1 × 1” tunnel structure.



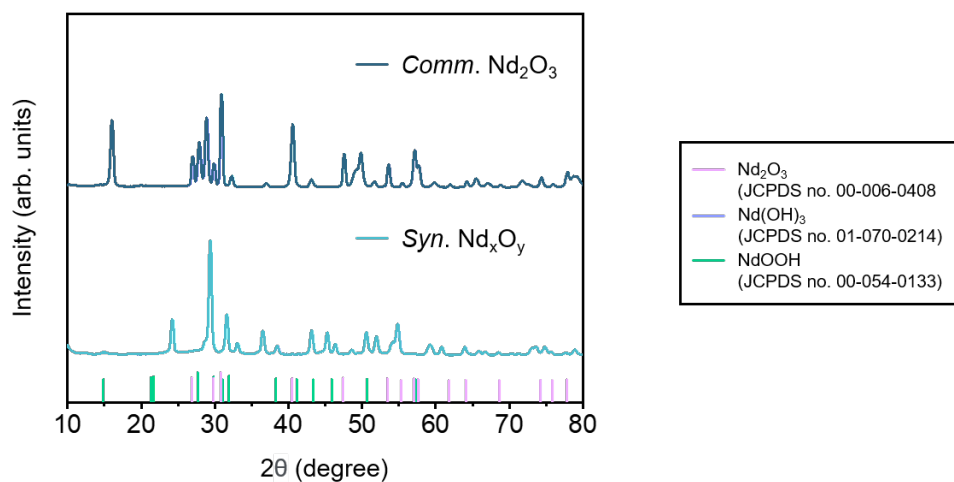
Supplementary Fig. 5 PXRD patterns of $\gamma\text{-MnO}_2\text{-}x$ samples (x denotes thermal decomposition temperature, varied between 250 and 450 °C), showing the full patterns (left panel) and enlarged region (middle and right panels).

Supplementary Note 3 With the temperature increased, a gradual enhancement in the intensity of the $\beta\text{-MnO}_2$ (110) peak, shown in the second panel from the right, as well as the R-MnO_2 (021) and (121) peaks in the rightmost panel, was observed.

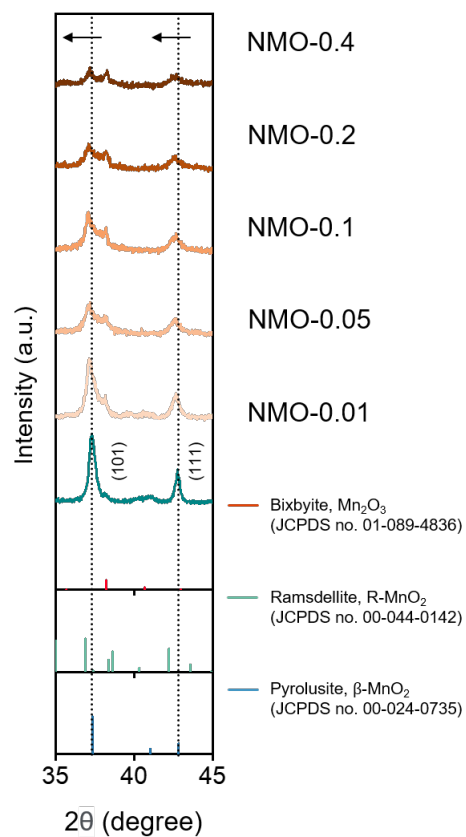


Supplementary Fig. 6 PXRD patterns of NMO-0.2-*x* samples (*x* denotes thermal decomposition temperature, varied between 250 and 450 °C), showing the full patterns (left panel) and enlarged region (middle and right panels).

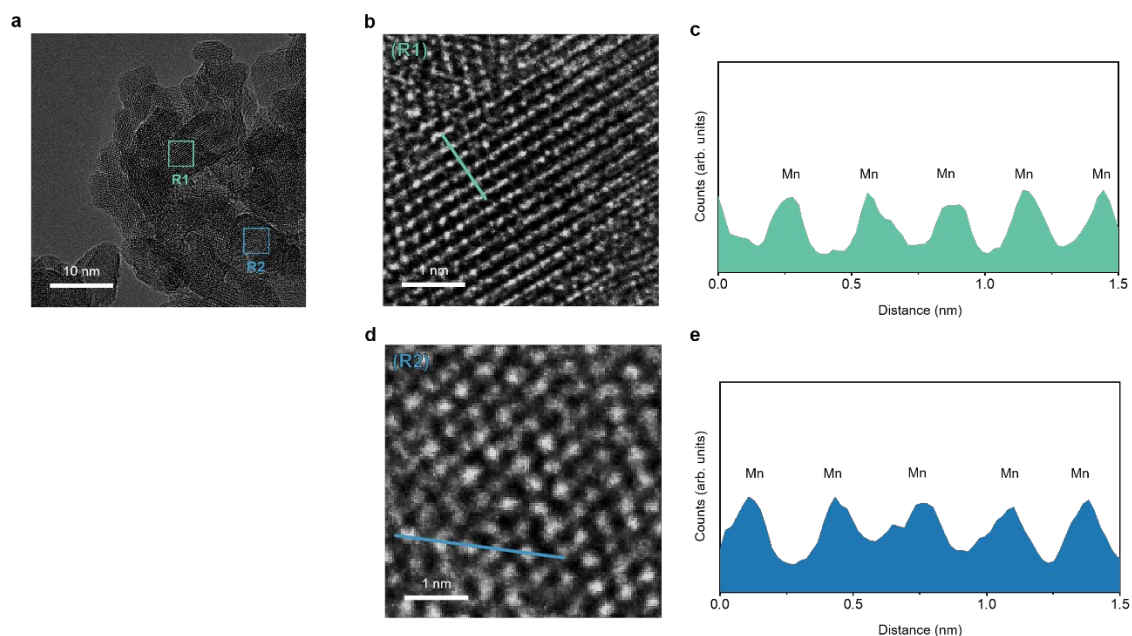
Supplementary Note 4 As the temperature increased, the intensities of the (440), (332), and (431) peaks corresponding to α -Mn₂O₃ gradually increased, as shown in the rightmost panel. In contrast, the (100) peak corresponding to β -MnO₂ showed no noticeable change in the second panel, suggesting that Nd doping promotes the formation of the α -Mn₂O₃ phase.



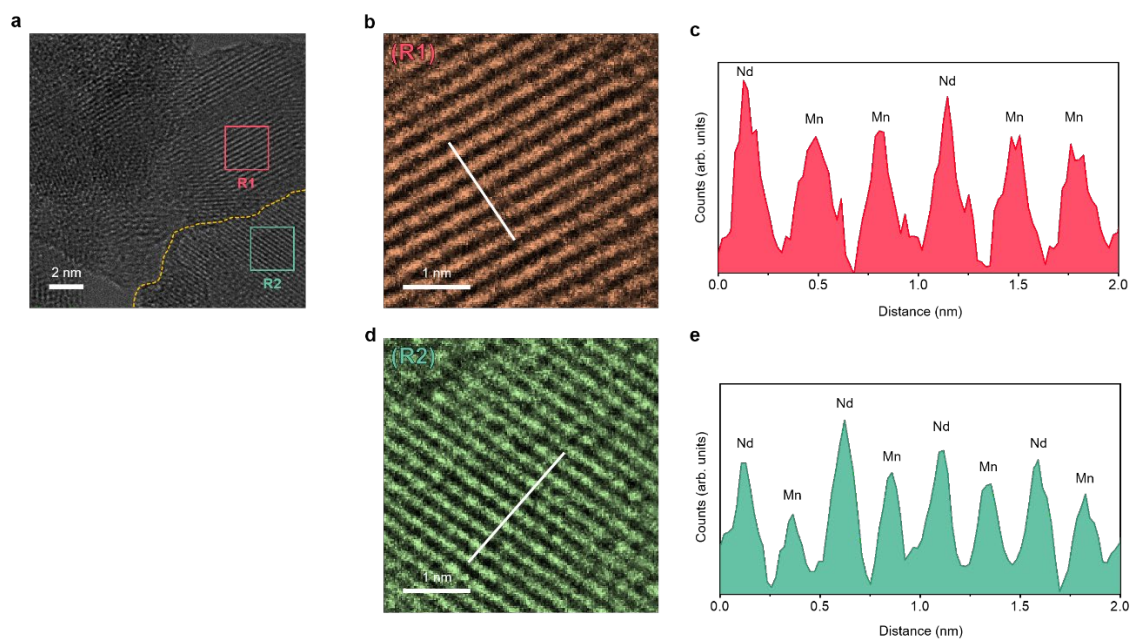
Supplementary Fig. 7 PXR D patterns of commercial Nd_2O_3 (Comm. Nd_2O_3) and synthesized Nd_xO_y (Syn. Nd_2O_3). Based on the JCPDS reference cards, the Syn. Nd_xO_y , obtained via thermal decomposition of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, is identified as a mixed-phase compound containing Nd^{3+} , composed of Nd_2O_3 and NdOOH .



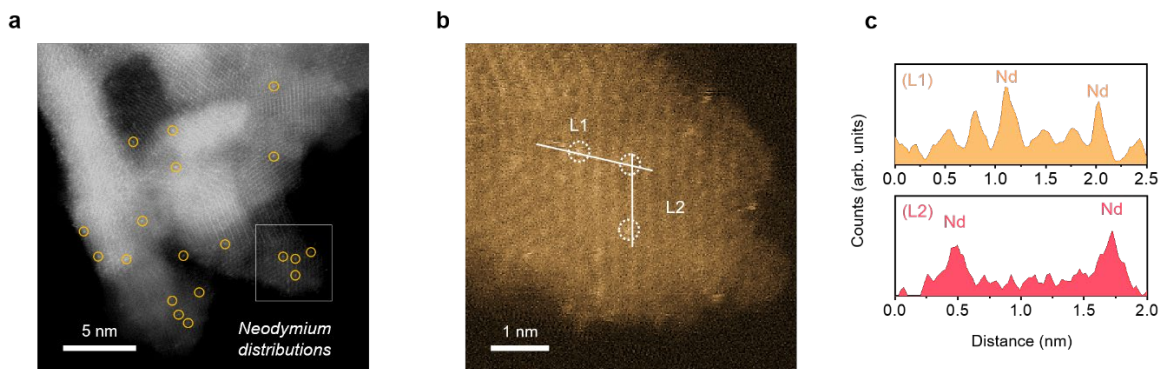
Supplementary Fig. 8 PXRD patterns showing the peak shifts of $\gamma\text{-MnO}_2$ induced by Nd doping.



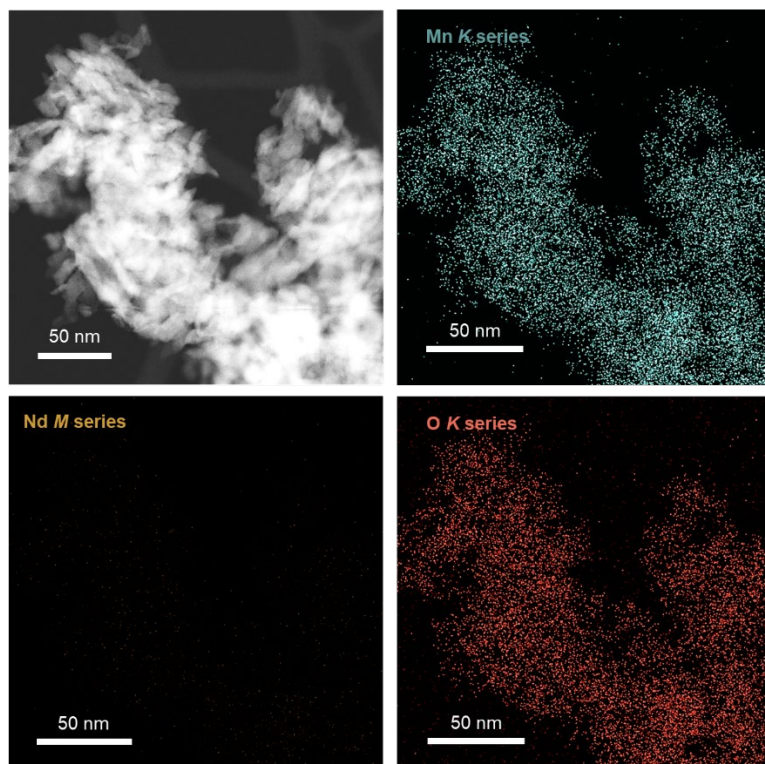
Supplementary Fig. 9 HRTEM image of γ -MnO₂ and corresponding line-scan profiles. (a) Overall structure of γ -MnO₂. (b, c) Region R1 showing the line-scan profile for R-MnO₂. (d, e) Region R2 showing the line-scan profile of β -MnO₂. The line-scan profiles of R1 and R2 indicate that Mn atoms are arranged in a regular pattern with uniform intensity, suggesting an ordered atomic distribution.



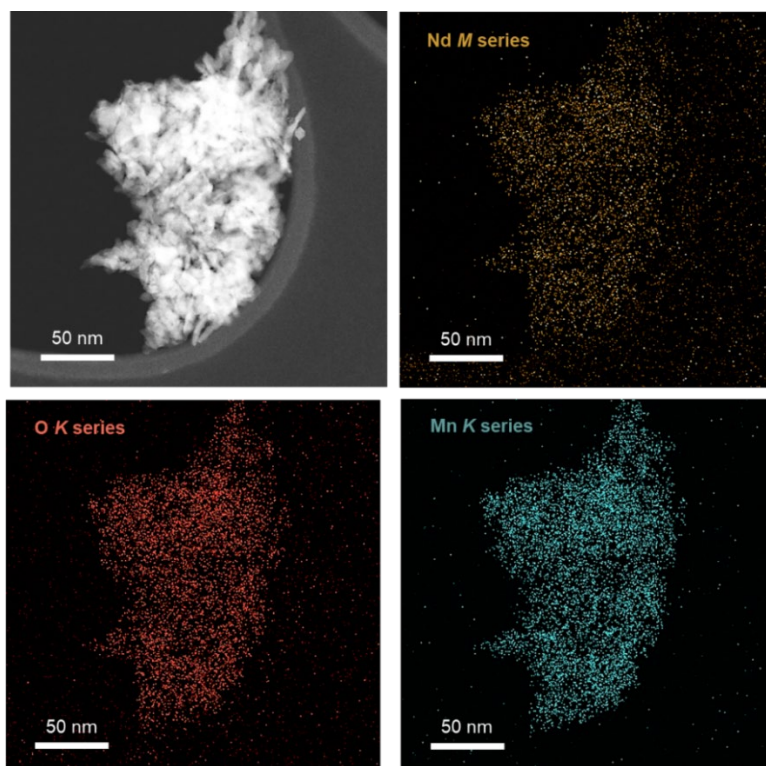
Supplementary Fig. 10 HRTEM image of NMO-0.2 and corresponding line-scan profiles. Regions R1 and R2 correspond to Nd-doped α - Mn_2O_3 and R- MnO_2 phases, respectively. The protruding peaks in the line-scan profiles indicate the presence of Nd. (a) Overall structure of NMO-0.2. (b, c) Region R1, suggesting incorporation of Nd within the α - Mn_2O_3 lattice. (d, e) Region R2, indicating incorporation of Nd within the R- MnO_2 lattice.



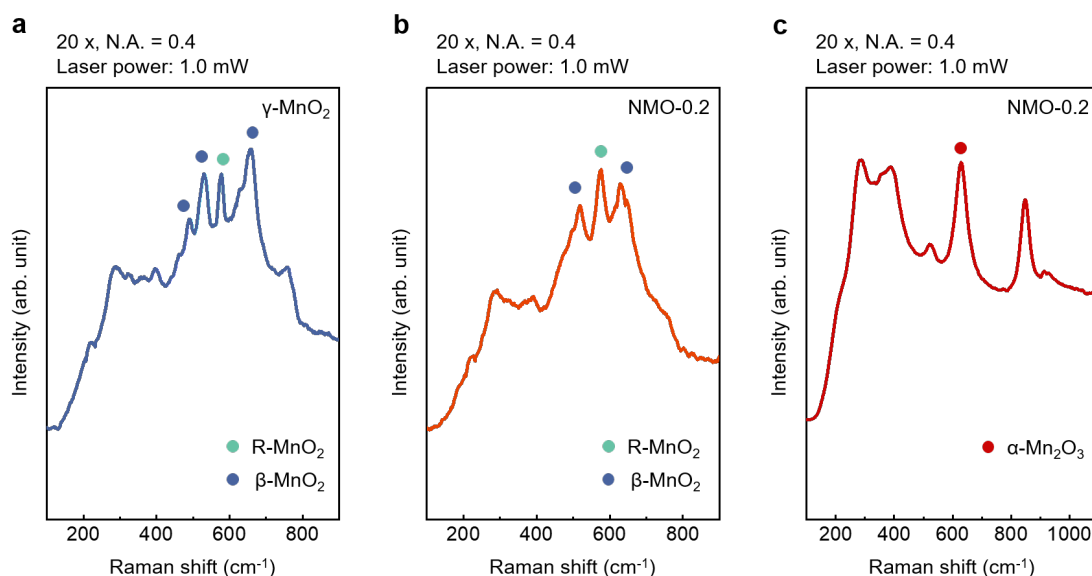
Supplementary Fig. 11 AC-HAADF-STEM image of NMO-0.2. The bright atomic columns, whose signal intensity is proportional to the square of the atomic number (Z^2), indicate the presence of heavier Nd atoms incorporated into the Mn–O framework.⁹ (a) The bright spots correspond to Nd elements within the NMO-0.2 structure. (b, c) Line-scan analyses along L1 and L2 across these regions reveal distinct Nd peaks, confirming the localization of Nd at the bright spots.



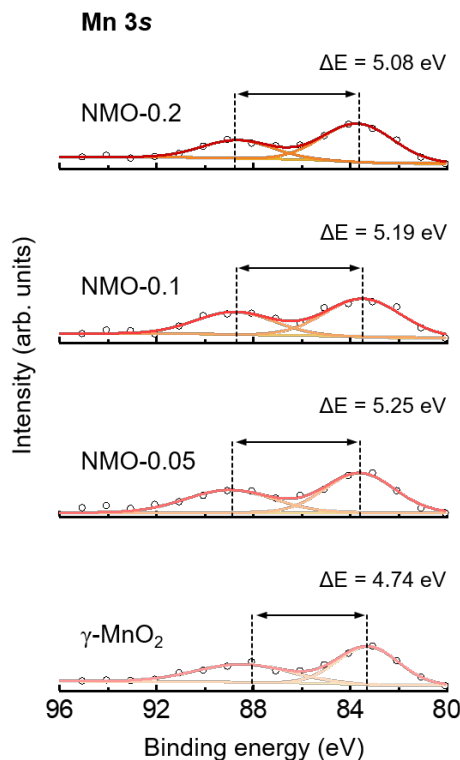
Supplementary Fig. 12 AC-HAADF-STEM image of γ -MnO₂ and corresponding EDS elemental mappings of Mn, Nd, and O.



Supplementary Fig. 13 AC-HAADF-STEM image of NMO-0.2 and corresponding EDS elemental mappings of Mn, Nd, and O.



Supplementary Fig. 14 Optimized confocal Raman analysis of Mn oxide phases. Raman spectra of (a) $\gamma\text{-MnO}_2$, (b) the MnO_2 -rich region of NMO-0.2, and (c) the Mn_2O_3 -rich region of NMO-0.2. The $\gamma\text{-MnO}_2$ -derived MnO_2 framework showed Raman features near ~ 570 and $\sim 650 \text{ cm}^{-1}$, corresponding to R- MnO_2 - and $\beta\text{-MnO}_2$ -related vibrations, respectively, and the increased I_{570}/I_{650} ratio after Nd incorporation indicates an increased contribution of the R- MnO_2 component within the MnO_2 -rich framework.¹⁰⁻¹² In addition, the NMO-0.2 surface exhibited an $\alpha\text{-Mn}_2\text{O}_3$ -related Raman band near $\sim 630 \text{ cm}^{-1}$, supporting the coexistence of MnO_2 and minority $\alpha\text{-Mn}_2\text{O}_3$ phases.



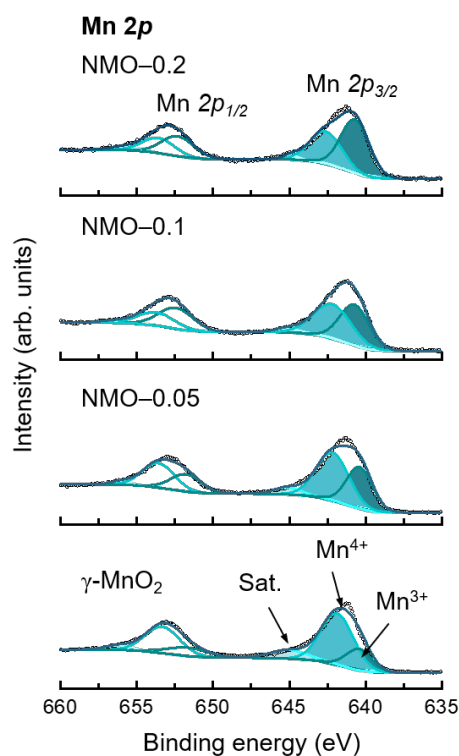
Supplementary Fig. 15 Valence state of Mn determined from the high-resolution Mn 3s XPS spectra of γ -MnO₂ and a series of NMO samples used to determine the Mn valence state.

Supplementary Note 5 Determination of Mn valence state from Mn 3s XPS spectra

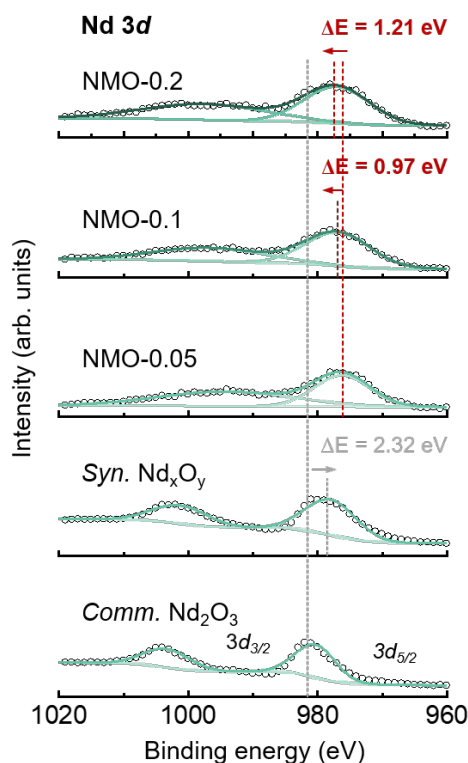
The average Mn valence state was calculated from the binding energy difference (ΔE) between the multiplet-split Mn 3s photoelectron peaks. The magnitude of the Mn 3s splitting energy increases linearly with decreasing Mn valence states, arising from the exchange interaction between the 3s core hole and unpaired 3d electrons. The relationship is given by the following empirical equation:¹³

$$V_{\text{Mn}} = 7.88 - 0.85\Delta E_{3s}/\text{eV}$$

High-resolution Mn 3s XPS spectra were collected for γ -MnO₂ and NMO-x samples to evaluate changes in Mn oxidation states upon Nd incorporation. Compared with γ -MnO₂, the NMO sample exhibited reduced Mn valence states: 3.852, 3.417, 3.468, and 3.562 for γ -MnO₂, NMO-0.05, NMO-0.1, and NMO-0.2, respectively, indicating a gradual increase in the Mn³⁺ fraction, likely associated with the formation of α -Mn₂O₃ phase.

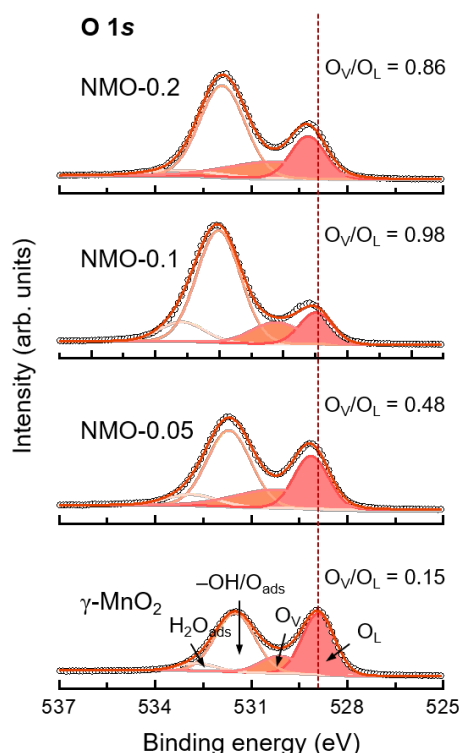


Supplementary Fig. 16 High-resolution Mn 2p XPS spectra of γ -MnO₂ and a series of NMO samples. The deconvoluted Mn 2p spectra show peaks at 641.3 and 642.5 eV corresponding to Mn³⁺ 2p_{3/2} and Mn⁴⁺ 2p_{3/2}, respectively, confirming the predominance of Mn³⁺ species following Nd doping.



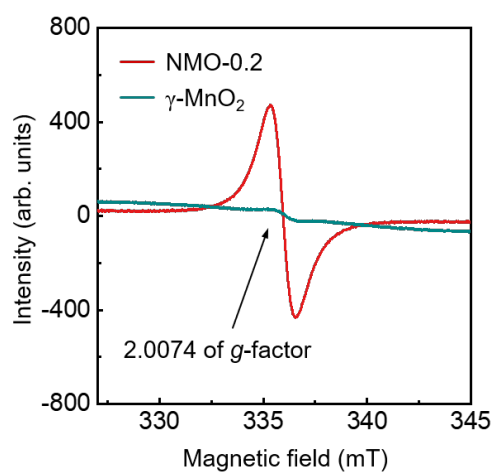
Supplementary Fig. 17 High-resolution Nd 3d XPS spectra of commercial Nd₂O₃, synthesized Nd_xO_y, and a series of NMO samples.

Supplementary Note 6 In the Nd 3d XPS spectra, the NMO-x samples exhibited lower binding energies than both synthesized Nd_xO_y and commercial Nd₂O₃ samples, indicating a red shift that reflects the presence of Nd in a valence state lower than +3 when doped into the Mn–O lattice. This shift can be attributed to the role of Nd dopants as electron donors, transferring charges through the lattice oxygen to Mn due to the electronegativity difference between Mn⁴⁺ (1.912) and Nd³⁺ (1.382).¹⁴ Importantly, with increasing Nd dopants (NMO-0.05, NMO-0.1, and NMO-0.2), a gradual blue shift was observed, providing direct evidence that higher dopant concentrations enhance electron donation from Nd to the Mn–O lattice.

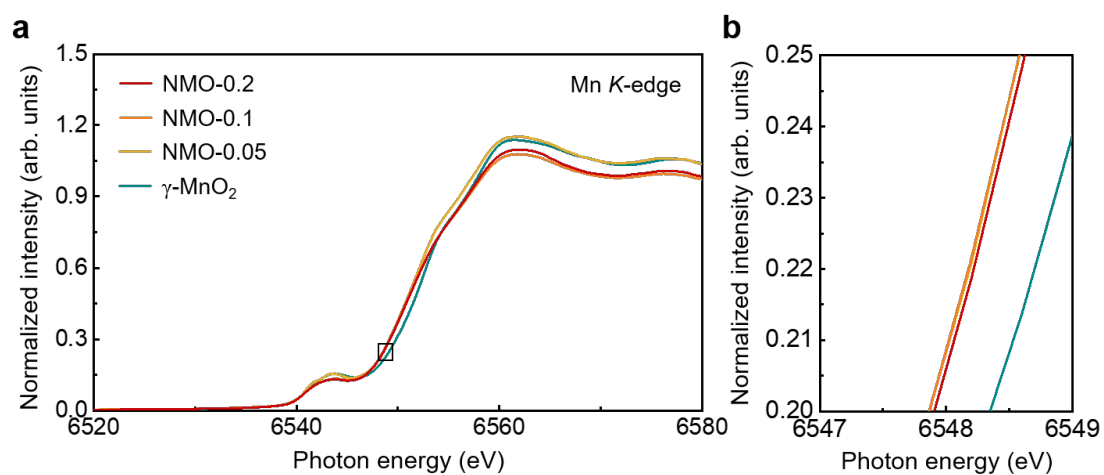


Supplementary Fig. 18 High-resolution O 1s XPS spectra of γ -MnO₂ and a series of NMO samples. Four distinct peaks at around 528.88, 530.16, 531.47, and 532.97 eV correspond to lattice oxygen (O_L), oxygen vacancy (O_V), chemisorbed hydroxyl groups or oxygen species (–OH/O_{ads}), and surface-adsorbed water molecules (H₂O_{ads}), respectively.

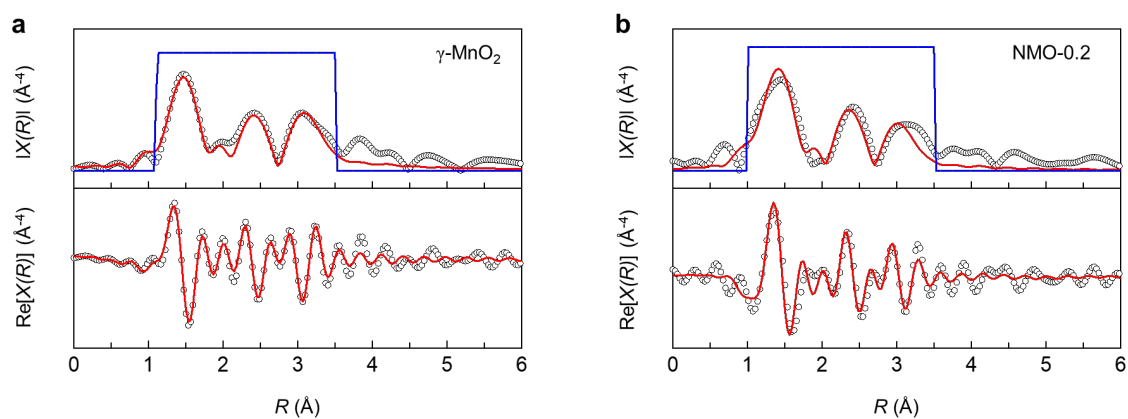
Supplementary Note 7: The O_L peak in NMO-*x* samples (NMO-0.05, NMO-0.1, and NMO-0.2) exhibited a discernible shift toward higher binding energies relative to γ -MnO₂, indicating charge transfer from Nd³⁺ to Mn⁴⁺. Upon Nd doping, a pronounced increase in the O_V/O_L ratio was observed, signifying the formation of additional O_V. This behavior can be rationalized by the charge-neutrality principle, where partial incorporation of host lattice sites (Mn⁴⁺–O) by low-valent cation (Nd³⁺) requires the formation of O_V to maintain electrostatic balance. In addition, the larger ionic radius of Nd³⁺ induces lattice distortion and perturbs the local oxygen coordination environment, thereby promoting O_V formation. Consistent with this rationale, the O_V/O_L ratio in NMO-*x* was markedly higher than that in γ -MnO₂. The increased population of O_V sites provides a higher density of electrophilic sites, which strongly interact with nucleophilic adsorbates such as water molecules and hydroxide ions, thus enhancing catalytic surface reactivity.



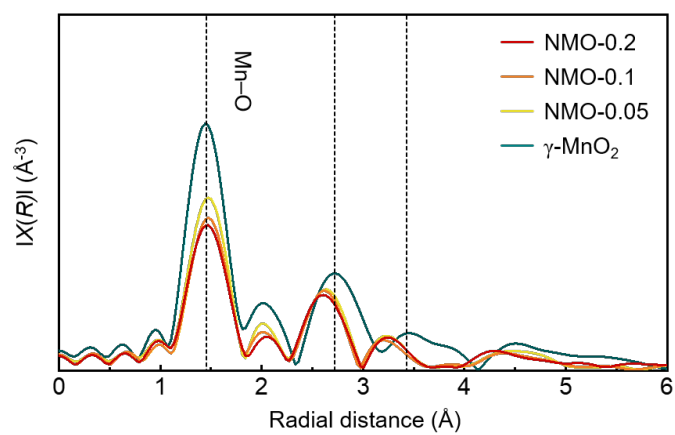
Supplementary Fig. 19 EPR spectra of γ -MnO₂ and NMO-0.2 samples. A distinct signal at $g = 2.0074$ in NMO-0.2 corresponds to unpaired electrons, likely localized at oxygen vacancy sites.



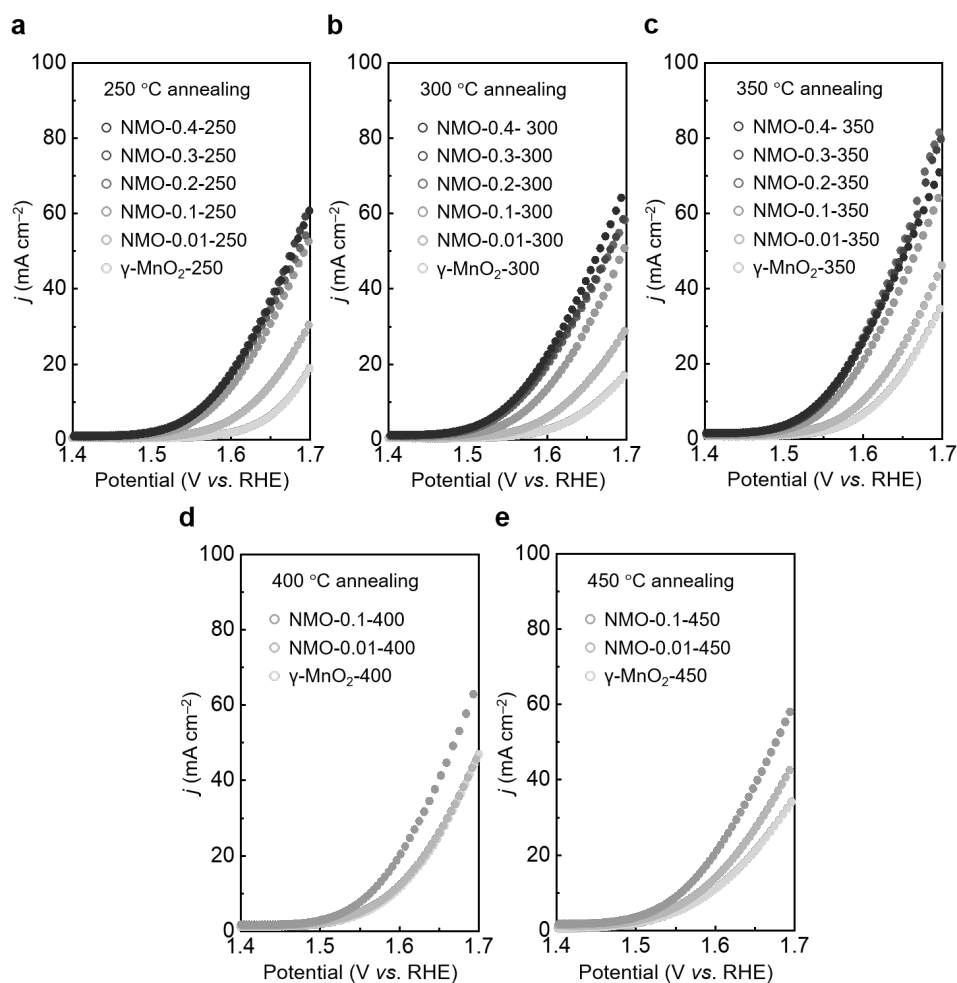
Supplementary Fig. 20 XANES spectra of γ -MnO₂ and various NMO samples. (a) Full-range XANES spectra. (b) Magnified view of the absorption-edge region extracted from Supplementary Fig. 20a.



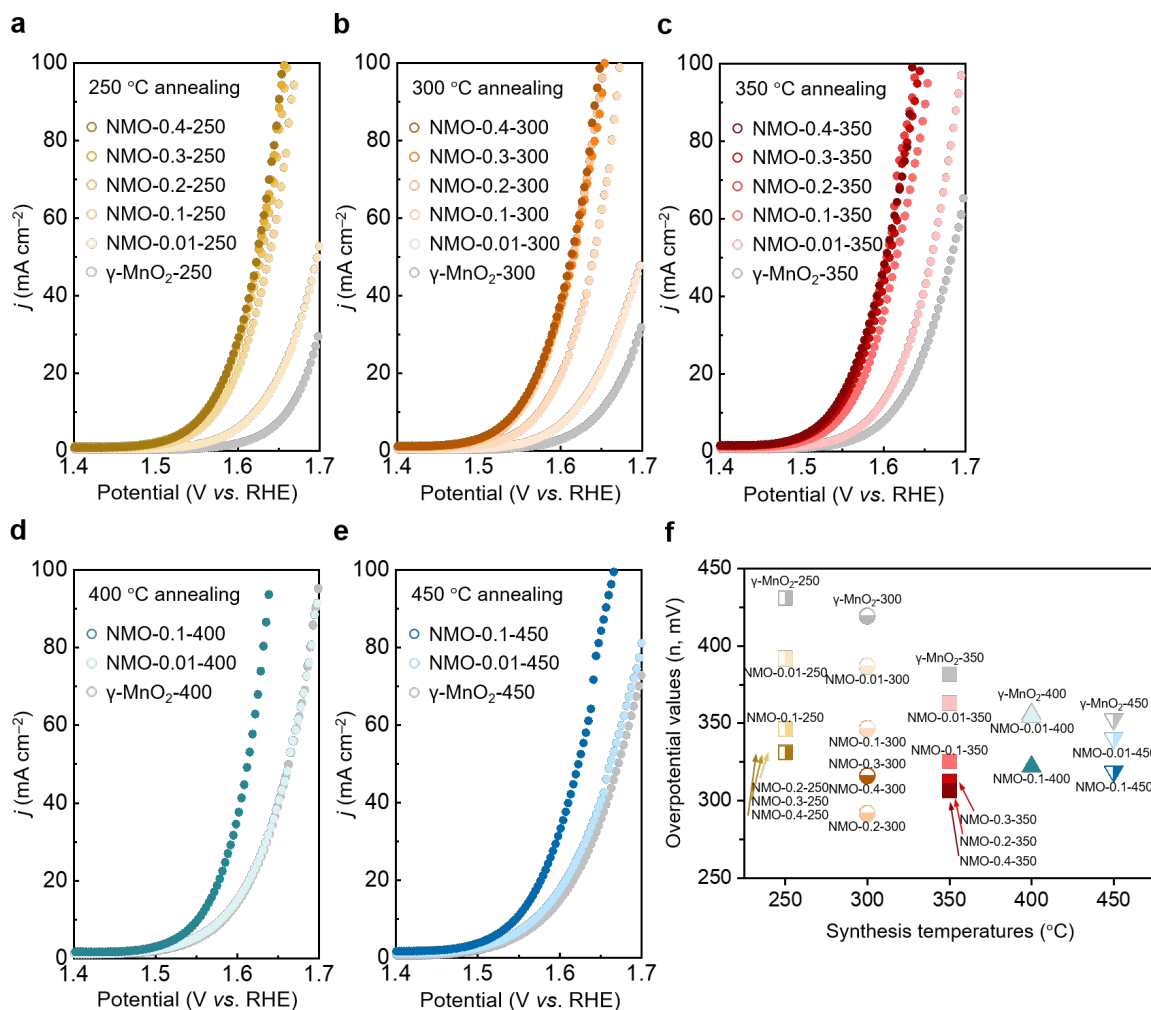
Supplementary Fig. 21 Mn K-edge EXAFS spectra and fitting results of (a) γ -MnO₂, and (b) NMO-0.2 samples. The fitting analysis was performed using Fourier-transformed k^3 -weighted Mn K-edge EXAFS spectra over the R range indicated by the blue boxes. The upper panels show the magnitude of the FT-EXAFS spectra, and the lower panels show their real parts. Experimental data are shown as open symbols and fitted curves as red lines. The optimized fitting parameters are provided in Supplementary Table 3, and detailed fitting procedures are described in Methods. R denotes the radial distance from the absorbing Mn atom.



Supplementary Fig. 22 Mn K-edge EXAFS spectra of $\gamma\text{-MnO}_2$ and a series of NMO samples. R denotes the radial distance from the absorbing Mn atom.

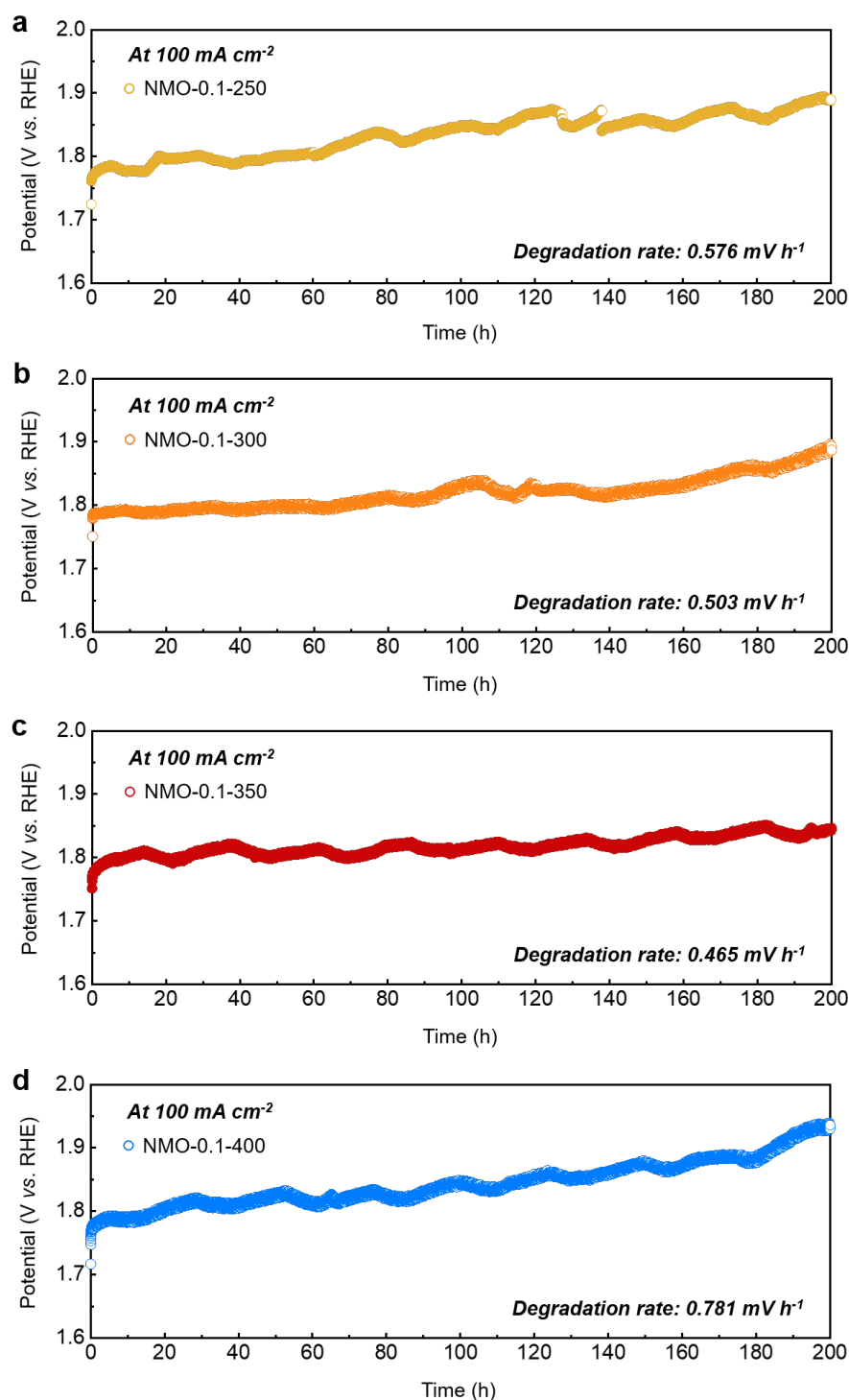


Supplementary Fig. 23 Polarization curves and overpotentials of γ -MnO₂ and NMO synthesized under various conditions. All electrode geometric areas were 1 cm². (a–e) Non-iR corrected LSV curves of γ -MnO₂ and a series of NMO catalysts. For γ -MnO₂-x, x represents the thermal decomposition temperature; for NMO-x-y, x denotes the Nd molar concentration in the precursor solution and y denotes the synthesis temperature.

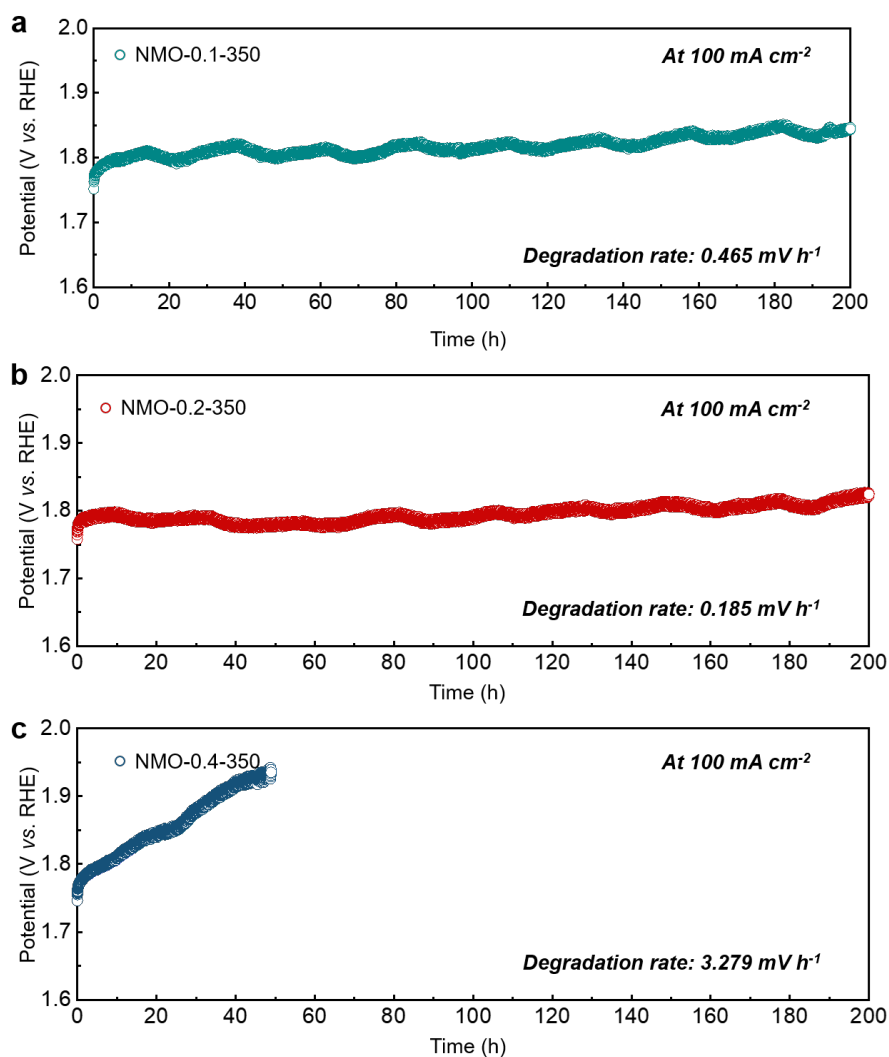


Supplementary Fig. 24 Polarization curves and overpotentials of γ -MnO₂ and NMO synthesized under various conditions. All electrode geometric areas were 1 cm². (a–e) LSV curves of γ -MnO₂ and a series of NMO catalysts. For γ -MnO₂-x, x represents the thermal decomposition temperature; for NMO-x-y, x denotes the Nd molar concentration in the precursor solution and y denotes the synthesis temperature. (f) Overpotentials at 10 mA cm⁻² for γ -MnO₂ and NMO catalysts synthesized under various conditions.

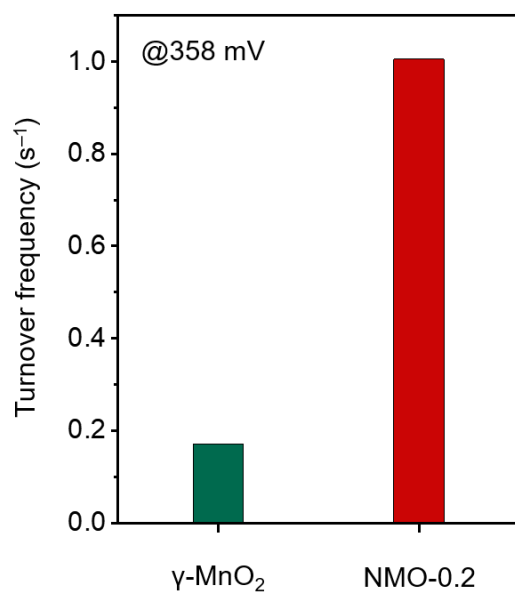
The measured R_s values were: (a) γ -MnO₂-250, 1.283±0.121 Ω ; NMO-0.01-250, 0.858±0.142 Ω ; NMO-0.1-250, 1.080±0.155 Ω ; NMO-0.2-250, 1.134±0.114 Ω ; NMO-0.3-250, 1.043±0.116 Ω ; and NMO-0.4-250, 1.097±0.084 Ω . (b) γ -MnO₂-300, 1.542±0.117 Ω ; NMO-0.01-300, 1.099±0.084 Ω ; NMO-0.1-300, 1.103±0.106 Ω ; NMO-0.2-300, 1.284±0.113 Ω ; NMO-0.3-300, 1.239±0.143 Ω ; and NMO-0.4-300, 1.042±0.101 Ω . (c) γ -MnO₂-350, 0.955±0.108 Ω ; NMO-0.01-350, 0.973±0.114 Ω ; NMO-0.1-350, 1.029±0.096 Ω ; NMO-0.2-350, 0.863±0.102 Ω ; NMO-0.3-350, 0.870±0.106 Ω ; and NMO-0.4-350, 1.033±0.163 Ω . (d) γ -MnO₂-400, 0.868±0.160 Ω , NMO-0.01-400, 0.861±0.109 Ω ; and NMO-0.1-400, 1.130±0.103 Ω . (e) γ -MnO₂-450, 1.431±0.314 Ω ; NMO-0.01-450, 0.940±0.124 Ω , and NMO-0.1-450, 1.069±0.107 Ω . Values are presented as mean ± SD.



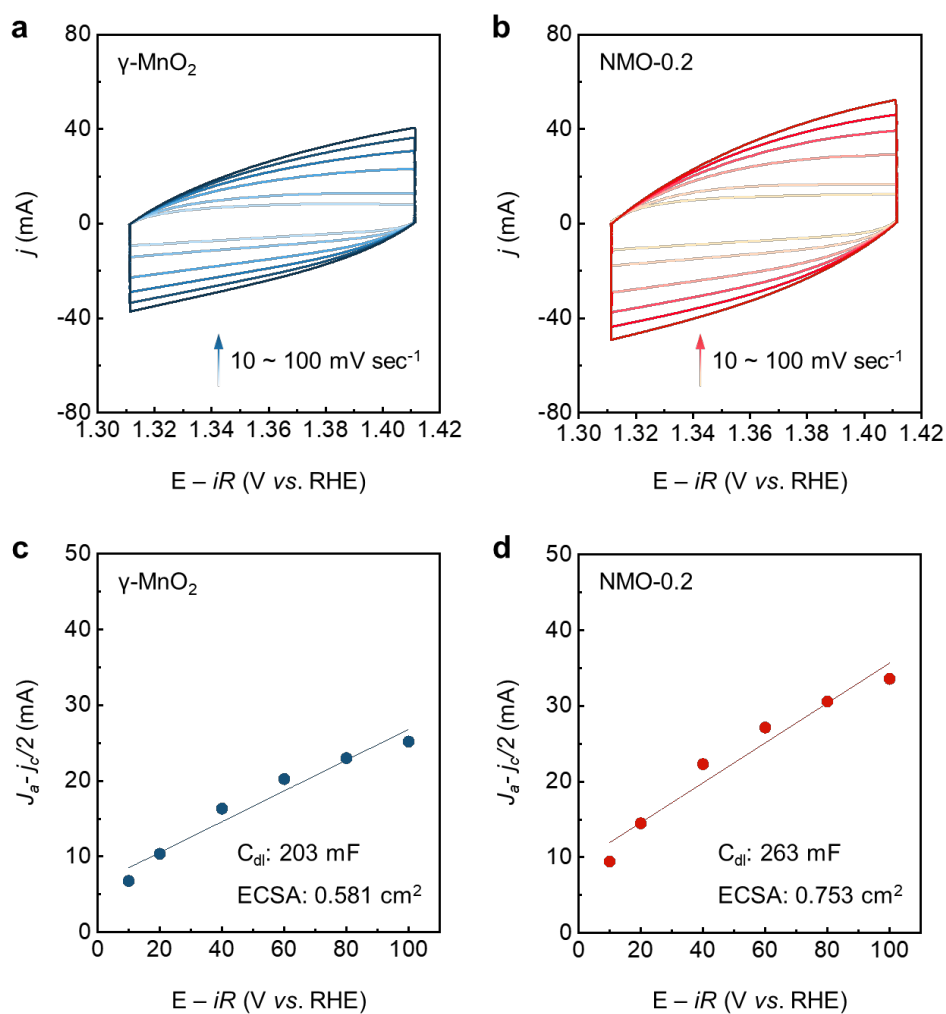
Supplementary Fig. 25 Chronopotentiometry tests conducted at 100 mA cm^{-2} under acidic conditions for a series of NMO-0.1 catalysts synthesized at different thermal decomposition temperatures: (a) NMO-0.1–250 (250 °C), (b) NMO-0.1-300 (300 °C), (c) NMO-0.1-350 (350 °C), and (d) NMO-0.1-400 (400 °C). Among these, the NMO-0.1-350 exhibited the lowest degradation rate, indicating that 350 °C is the optimal thermal decomposition temperature for NMO-0.1 synthesis. For NMO-x-y, x denotes the Nd molar concentration in the precursor solution and y denotes the synthesis temperature.



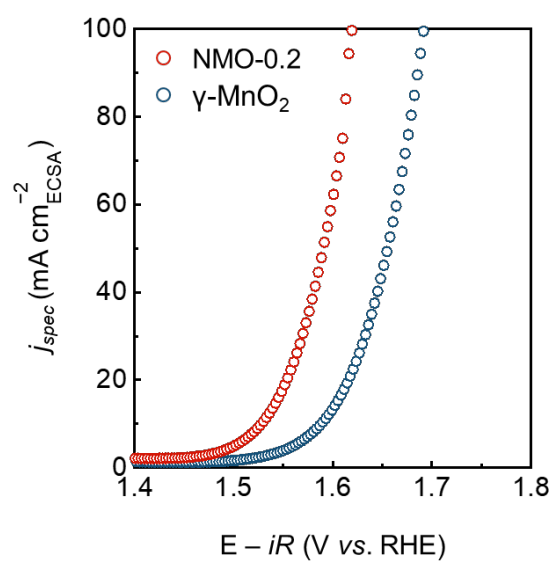
Supplementary Fig. 26 Chronopotentiometry tests conducted at 100 mA cm⁻² under acidic conditions for a series of NMO catalysts at a fixed calcination temperature of 350 °C with varying Nd doping levels: (a) NMO-0.1-350 (0.1 M Nd precursor), (b) NMO-0.2-350 (0.2 M Nd precursor), and (c) NMO-0.4-350 (0.4 M Nd precursor). Among them, the NMO-0.2-350 catalyst exhibited the lowest degradation rate, indicating that this Nd concentration is optimal. For NMO-x-y, x denotes the Nd molar concentration in the precursor solution and y denotes the synthesis temperature.



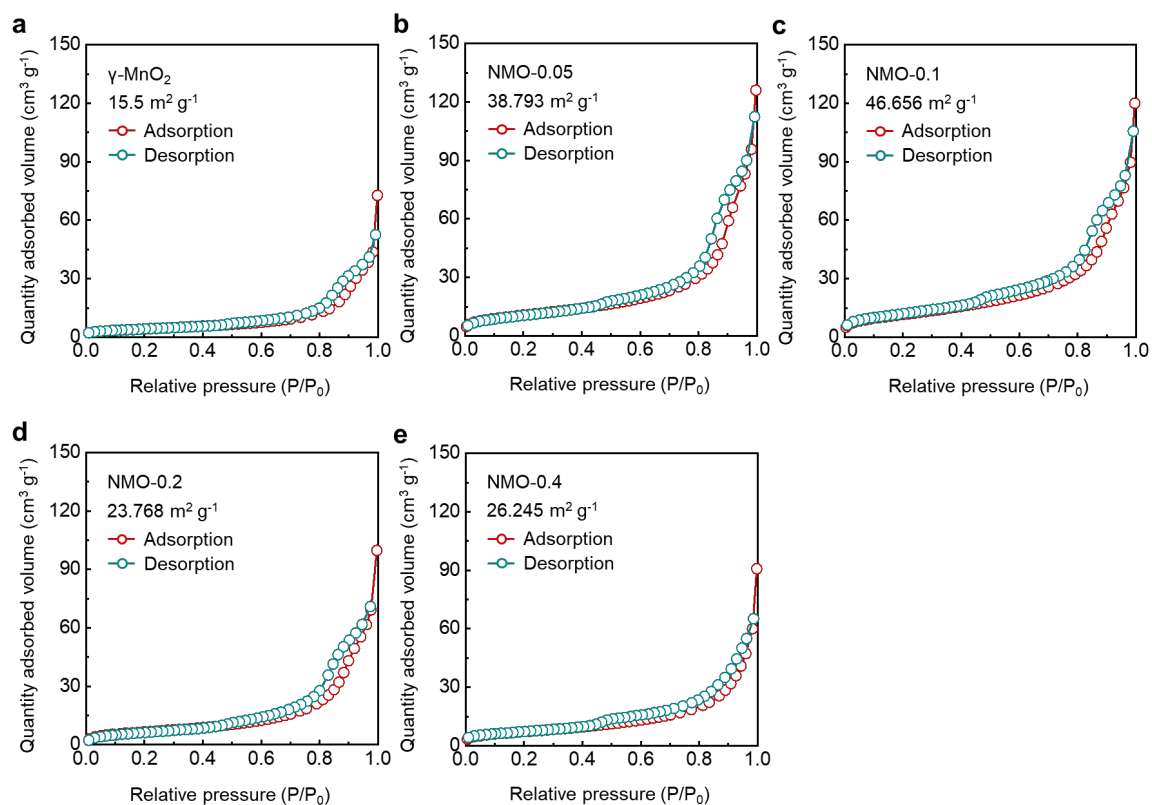
Supplementary Fig. 27 TOF values of γ -MnO₂ and NMO-0.2, calculated from current densities at 1.588 V_{RHE}.



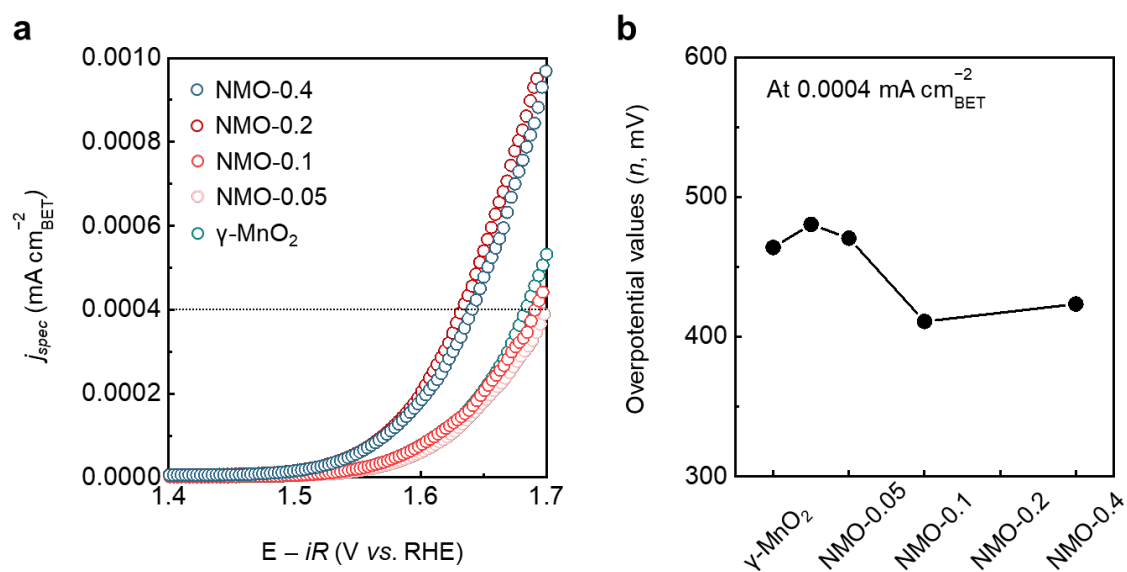
Supplementary Fig. 28 Estimation of C_{dl} using CV curves at various scan rates. (a, b) CV curves of $\gamma\text{-MnO}_2$ and NMO-0.2 catalysts shown in the upper panels. (c, d) Corresponding C_{dl} values estimated for $\gamma\text{-MnO}_2$ and NMO-0.2 in the lower panels. The ECSA was calculated using a specific capacitance (C_s) value of 0.35 mF cm^{-2} .



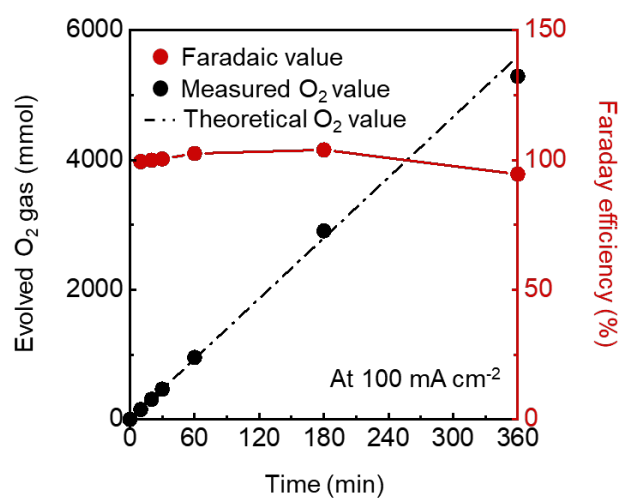
Supplementary Fig. 29 Specific OER activities normalized to ECSA.



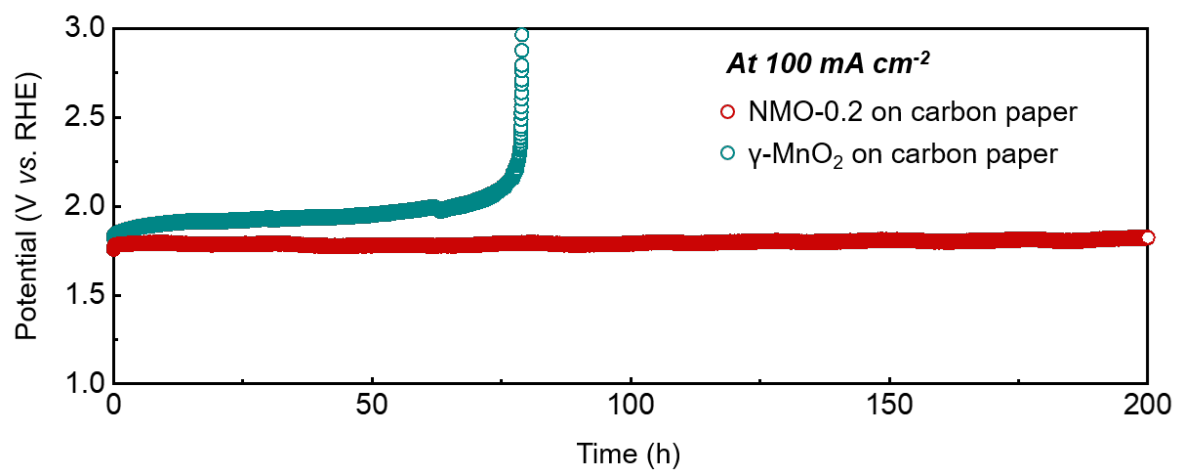
Supplementary Fig. 30 N_2 adsorption–desorption isotherms and corresponding BET surface areas. (a) $\gamma\text{-MnO}_2$. (b–e) NMO- x samples, where x denotes the Nd molar concentration varied from 0.05 to 0.4 M.



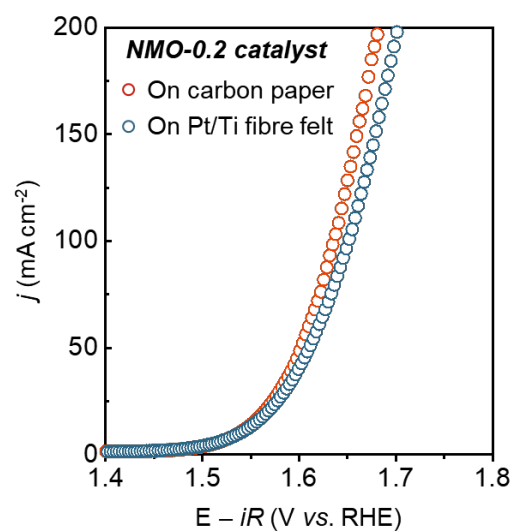
Supplementary Fig. 31 Specific OER activity normalized to the physical surface area. (a) OER activity normalized to the BET surface area and (b) the corresponding overpotentials at a current density of 0.0004 mA cm_{BET}⁻². These results suggest that the enhanced catalytic performance of NMO does not originate from the surface area effect.



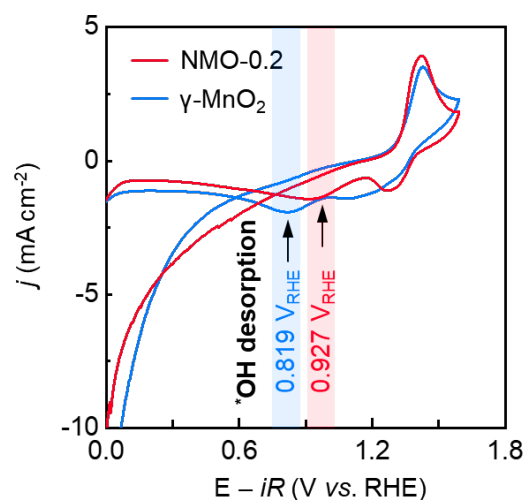
Supplementary Fig. 32 O₂ Faradaic efficiency of the NMO-0.2 measured as a function of electrolysis time at 1.65 V_{RHE} corresponding to a current density of 100 mA cm⁻².



Supplementary Fig. 33 Chronopotentiometry test conducted at 100 mA cm⁻² in 0.5 M H₂SO₄ electrolyte using catalysts loaded on carbon paper electrodes.

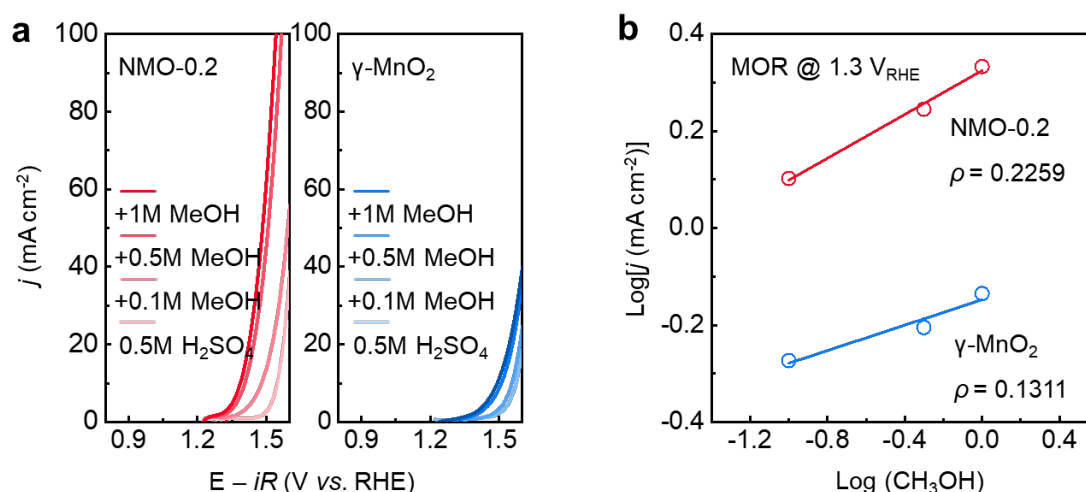


Supplementary Fig. 34 Polarization curves of the NMO-0.2 catalyst measured using different electrode substrates: carbon paper and Pt/Ti fiber felt.



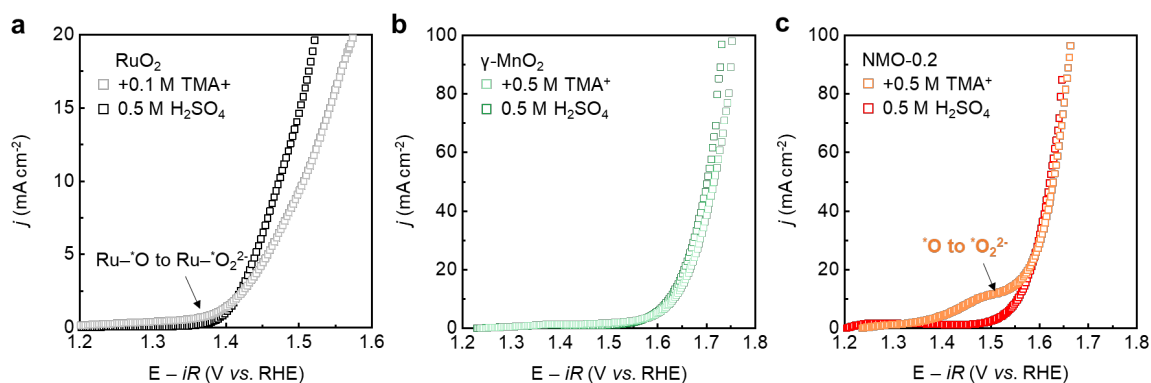
Supplementary Fig. 35 Cyclic voltammetry (CV) curves of $\gamma\text{-MnO}_2$ and NMO-0.2 in 0.5 M H_2SO_4 electrolyte.

Supplementary Note 8 To elucidate the adsorption strength of surface oxygenated intermediates, CV was conducted to monitor the redox feature of $^*\text{OH}$ species.¹⁵ During the negative potential sweep, distinct peaks between 0.6 and 0.95 V_{RHE} were observed for both $\gamma\text{-MnO}_2$ and NMO-0.2 samples, corresponding to the $^*\text{OH}$ desorption. In NMO-0.2, the onset potential for $^*\text{OH}$ desorption appeared at 0.927 V_{RHE} , slightly higher than that of $\gamma\text{-MnO}_2$ (0.819 V_{RHE}). Moreover, the irreversible $^*\text{OH}$ peak area was substantially smaller, indicating stronger $^*\text{OH}$ binding and more difficult desorption. These features can be attributed to the coexistence of O_V ,¹⁶ which can act as electrophilic adsorption sites, and stabilized Mn^{3+} centers, which facilitate flexible binding and release of oxygenated intermediates.¹⁷



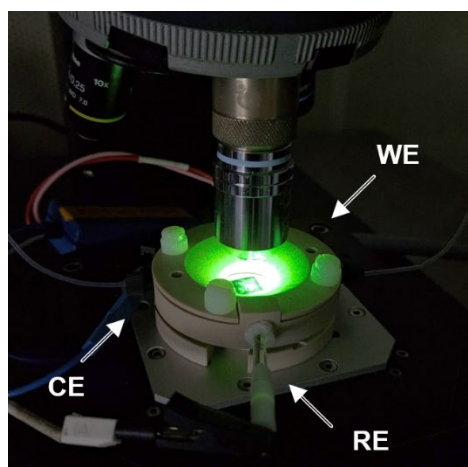
Supplementary Fig. 36 Methanol oxidation reaction (MOR) kinetics at varying CH_3OH concentrations. (a) Polarization curves of $\gamma\text{-MnO}_2$ and NMO-0.2 in CH_3OH -containing 0.5 M H_2SO_4 electrolyte. (b) Logarithmic plots between MOR current density versus CH_3OH concentration for different catalysts.

Supplementary Note 9 The surface $^*\text{OH}$ population was investigated by MOR analysis, a well-established electrochemical molecular probing method, in which methanol is oxidized via nucleophilic attack on electrophilic $^*\text{OH}$ species adsorbed on the catalyst surface.¹⁸ NMO-0.2 exhibited markedly higher MOR activity than $\gamma\text{-MnO}_2$, consistent with the presence of abundant electrophilic $^*\text{OH}$ species (Supplementary Fig. 36a).¹⁹ In the reaction-order analysis, NMO-0.2 exhibited a steeper slope in the logarithmic plot of current density versus CH_3OH concentration, indicating accelerated MOR kinetics (Supplementary Fig. 36b). This enhancement can be attributed to the synergistic effect of O_v , which generates electrophilic adsorption sites, and stabilized Mn^{3+} centers, which promote the accumulation and reactivity of $^*\text{OH}$ intermediates.



Supplementary Fig. 37 Polarization curves of (a) commercial RuO_2 , (b) $\gamma\text{-MnO}_2$, and (c) NMO-0.2 samples in tetramethylammonium cation (TMA^+)-containing 0.5 M H_2SO_4 electrolyte.

Supplementary Note 10 The lattice oxygen-mediated (LOM) pathway was further examined using TMA^+ as a molecular probe for surface-bound peroxo (O_2^{2-}) species.²⁰ In the LOM process, such peroxo intermediates remain on the catalyst surface for relatively long lifetimes and are covalently bound to active metal centers.^{4,21} The strong interaction TMA^+ with O_2^{2-} typically suppresses OER kinetics by hindering the turnover of O_2^{2-} into molecular oxygen. As a reference, RuO_2 exhibited a characteristic redox peak at $\sim 1.32 \text{ V}_{\text{RHE}}$, corresponding to the $\text{Ru}-^*\text{O}$ to $\text{Ru}-^*\text{O}_2^{2-}$ transition, along with reduced OER activity, consistent with its well-known LOM behavior (Supplementary Fig. 37a). In contrast, $\gamma\text{-MnO}_2$ showed no significant changes in its polarization curve, indicating operation via the conventional adsorbate evolution mechanism (AEM) (Supplementary Fig. 37b). Interestingly, NMO-0.2 exhibited a distinct redox peak at $1.48 \text{ V}_{\text{RHE}}$ attributed to the $^*\text{O}$ to $^*\text{O}_2^{2-}$ transition; however, the polarization behavior remained essentially unaffected (Supplementary Fig. 37c). These observations suggest that, despite the transient formation of $^*\text{O}_2^{2-}$ -like intermediates, NMO-0.2 does not follow either the conventional LOM or AEM pathways but instead proceeds through an alternative OER mechanism.²²

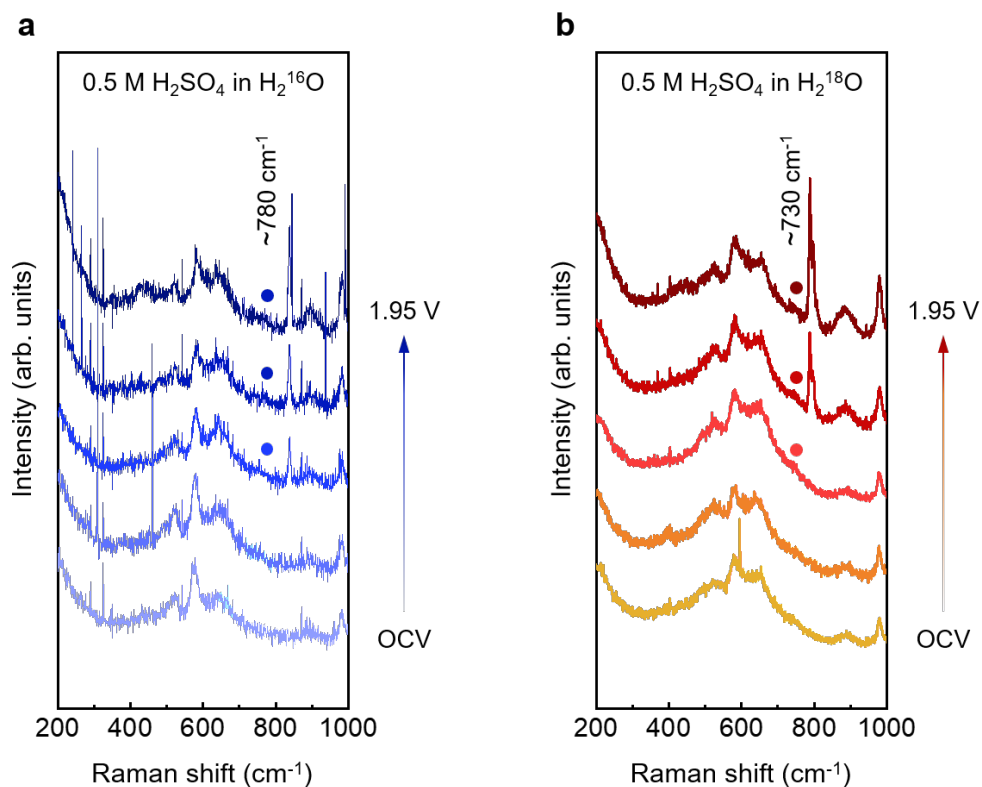


✓ *In situ* Raman spectroscopy

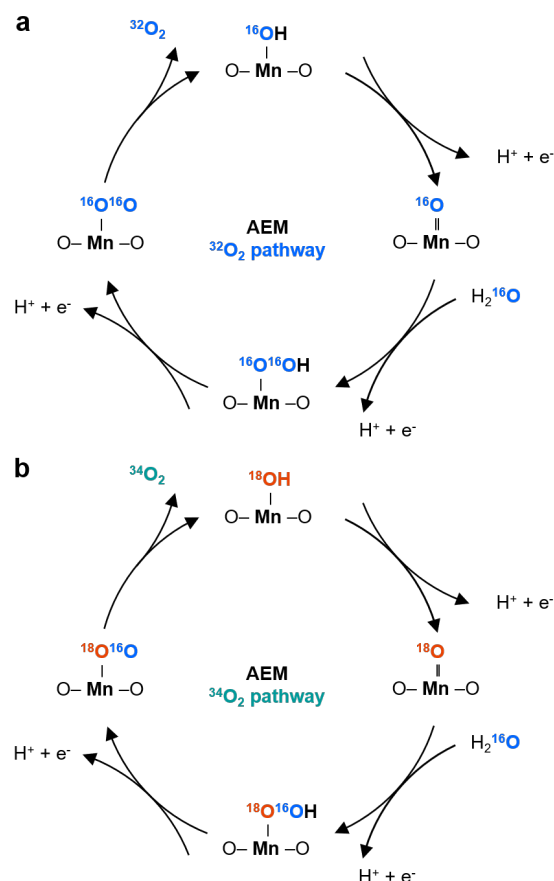
Laser wavelength: 532 nm

Laser power: 1 mW

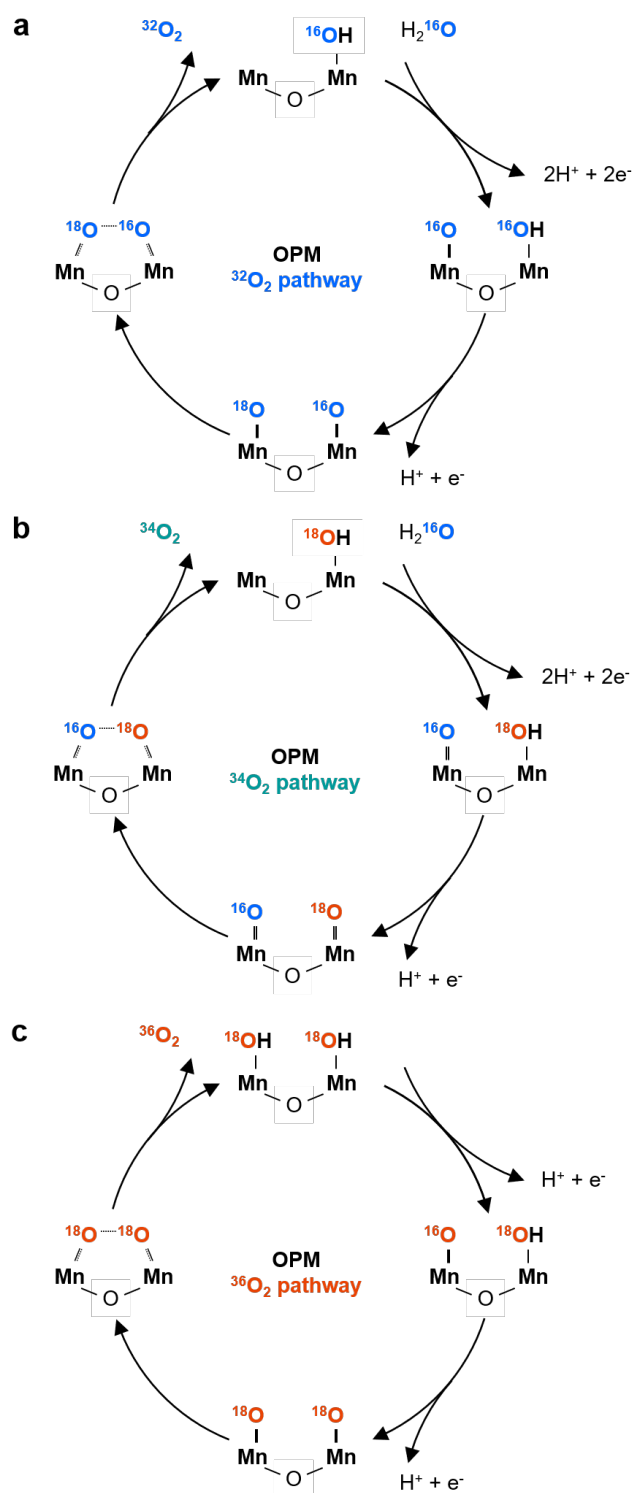
Supplementary Fig. 38 Photograph of custom-designed *in situ* Raman electrochemical cell showing the working (WE), counter (CE), and reference (RE) electrodes.



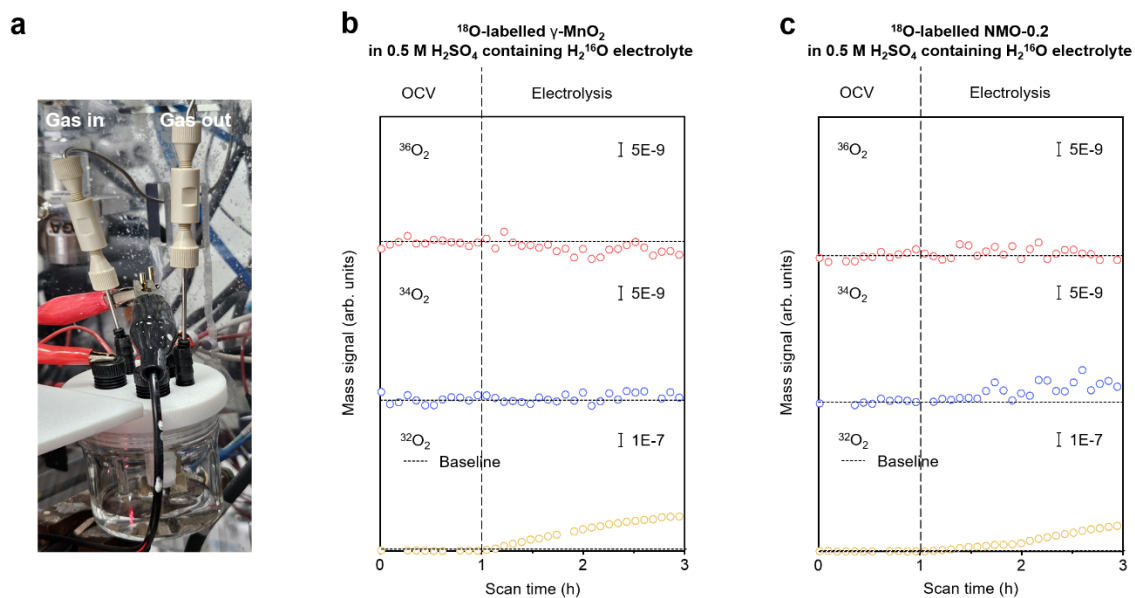
Supplementary Fig. 39 Isotope ¹⁸O-labelling *in situ* Raman spectra of NMO-0.2 during acidic OER. Potential-dependent Raman spectra of NMO-0.2 measured in 0.5 M H₂SO₄ prepared with (a) H₂¹⁶O and (b) H₂¹⁸O. The Mn=O* Raman feature shifts from ~780 cm⁻¹ in H₂¹⁶O to ~730 cm⁻¹ in H₂¹⁸O, supporting its assignment to a Mn-oxo intermediate, such as Mn=O*.



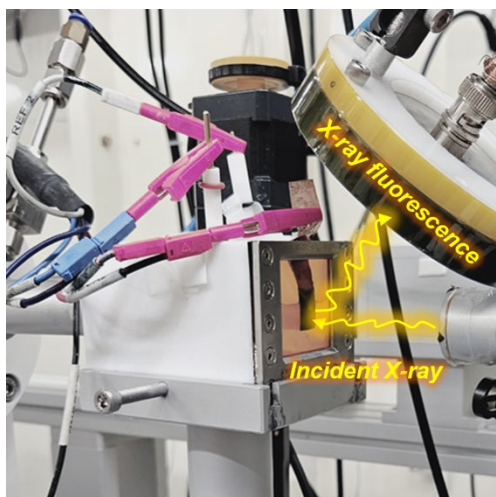
Supplementary Fig. 40 Schematic illustration of the proposed formation pathways of isotope-labelled oxygen products during OER in H_2^{16}O electrolyte via the conventional adsorbate evolution mechanism (AEM). Proposed formation pathways for the formation of (a) $^{32}\text{O}_2$ ($^{16}\text{O}^{16}\text{O}$) and (b) $^{34}\text{O}_2$ ($^{18}\text{O}^{16}\text{O}$). Under the AEM pathway, only one catalyst-derived oxygen atom can participate in O_2 formation, and therefore $^{36}\text{O}_2$ ($^{18}\text{O}^{18}\text{O}$) is not expected.



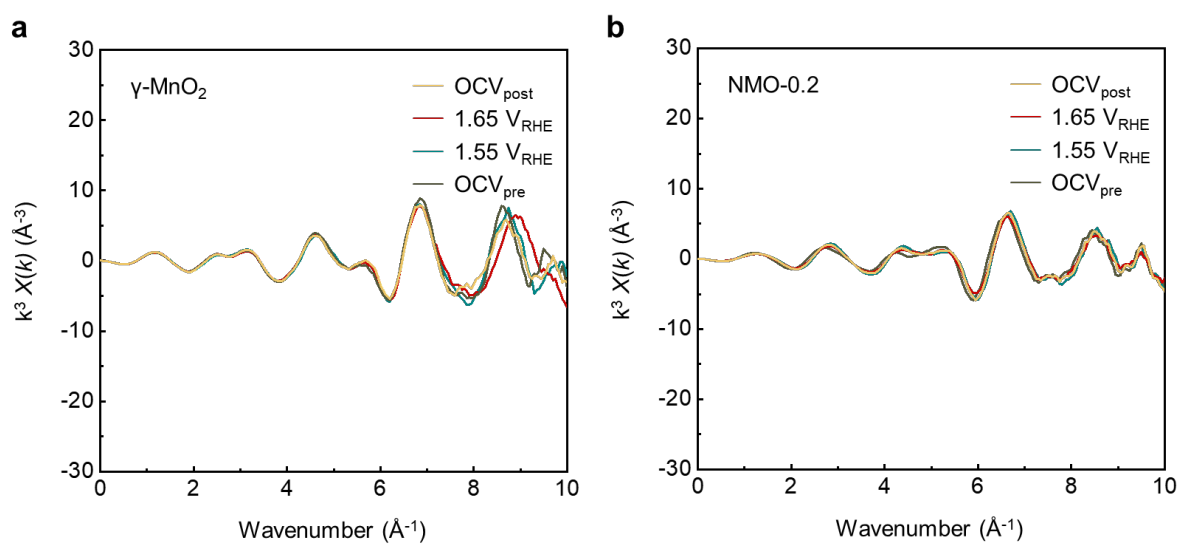
Supplementary Fig. 41 Schematic illustration of the proposed formation pathways of isotope-labelled oxygen products during OER in H_2^{16}O electrolyte via the oxide path mechanism (OPM). Proposed pathways for the formation of (a) $^{32}\text{O}_2$ ($^{16}\text{O}^{16}\text{O}$), (b) $^{34}\text{O}_2$ ($^{18}\text{O}^{16}\text{O}$), and (c) $^{36}\text{O}_2$ ($^{18}\text{O}^{18}\text{O}$). In contrast to the AEM pathway, coupling between two catalyst-associated oxygen species can produce $^{36}\text{O}_2$, providing a characteristic isotopic signature of oxygen participation from the catalyst.



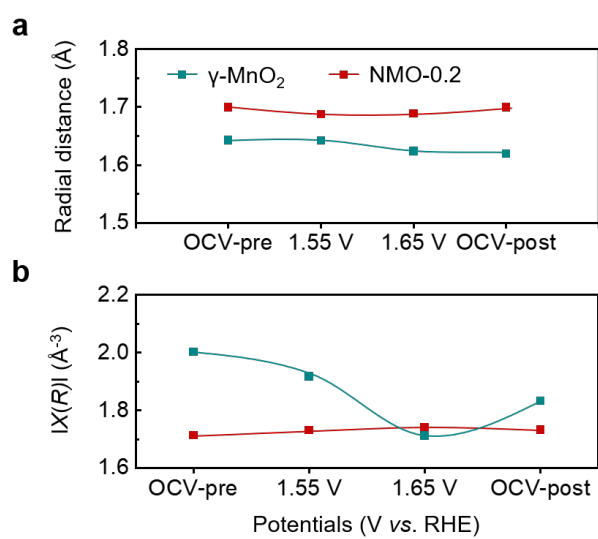
Supplementary Fig. 42 *In situ* DEMS analysis of ^{18}O -labelled $\gamma\text{-MnO}_2$ and NMO-0.2 during acidic OER. (a) Photograph of custom-designed *in situ* DEMS cell showing the working (WE), counter (CE), and reference (RE) electrodes. *In situ* DEMS profiles of ^{18}O -labelled (b) $\gamma\text{-MnO}_2$ and (c) NMO-0.2 measured in H_2^{16}O -containing 0.5 M H_2SO_4 under a constant current density of $\sim 50 \text{ mA cm}^{-2}$. The $m/z = 32, 34$, and 36 signals correspond to $^{32}\text{O}_2$ ($^{16}\text{O}^{16}\text{O}$), $^{34}\text{O}_2$ ($^{18}\text{O}^{16}\text{O}$), and $^{36}\text{O}_2$ ($^{18}\text{O}^{18}\text{O}$), respectively. Compared with $\gamma\text{-MnO}_2$, NMO-0.2 exhibits more pronounced isotope ^{18}O -labelled oxygen signals, particularly $^{34}\text{O}_2$ and $^{36}\text{O}_2$, supporting the participation of catalyst-associated ^{18}O species in O–O bond formation during OER.



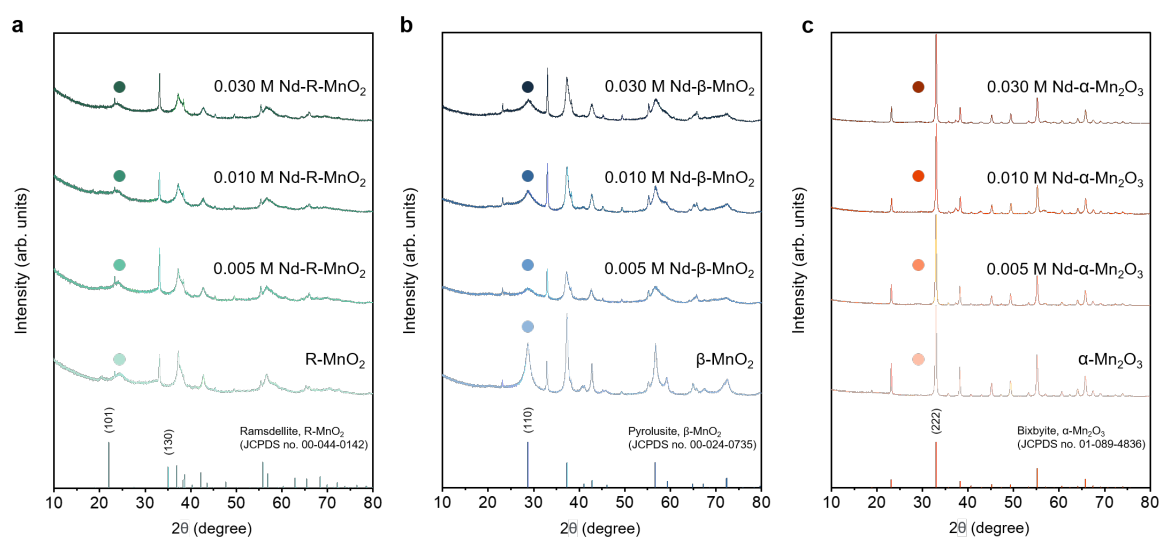
Supplementary Fig. 43 Photograph of the in situ XAS electrochemical cell used for fluorescence-mode measurements with a shortened electrolyte/X-ray path length.



Supplementary Fig. 44 k^3 -weighted EXAFS oscillations of Mn K-edge. The k^3 -weighted EXAFS oscillations of (a) $\gamma\text{-MnO}_2$, and (b) NMO-0.2, respectively.

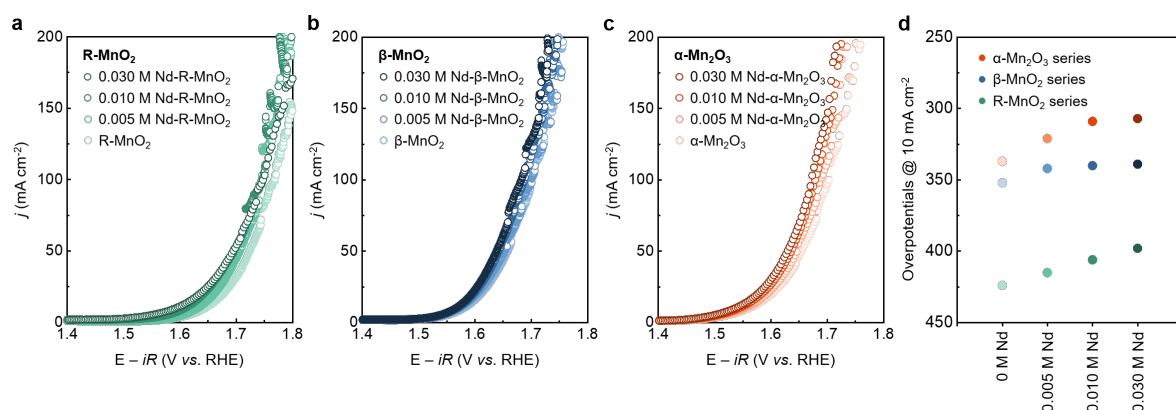


Supplementary Fig. 45 (a) Potential-dependent changes in the Mn–O radial distance and (b) Mn–O peak intensity extracted from the *in situ* EXAFS spectra.

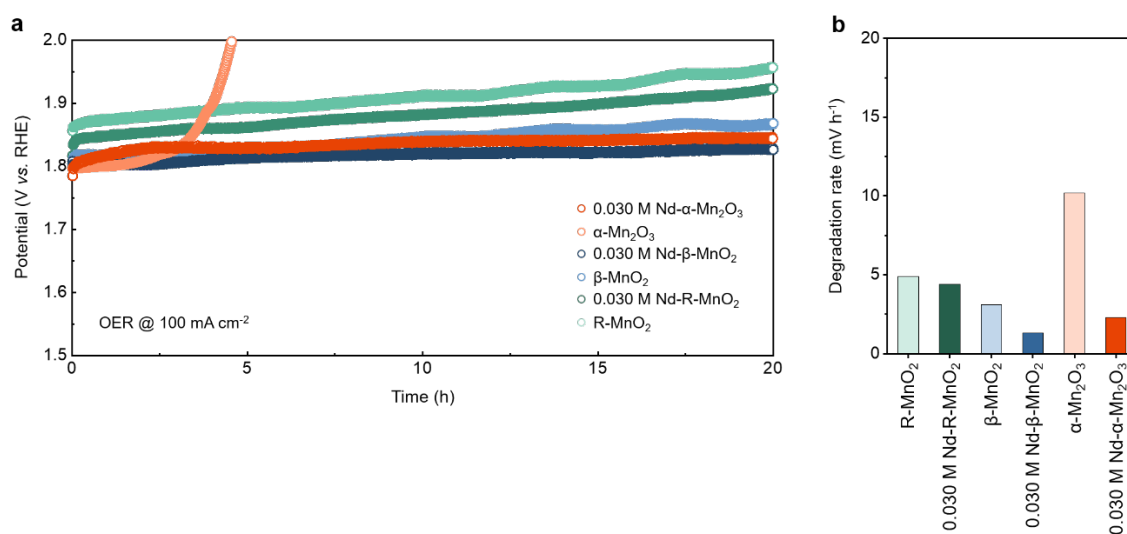


Supplementary Fig. 46 Phase-controlled synthesis of Mn oxide reference catalysts. XRD patterns of (a) R-MnO₂-rich, (b) β -MnO₂-rich, and (c) α -Mn₂O₃ reference catalysts prepared by thermal decomposition at different temperatures with varied Nd precursor concentrations. The characteristic reflections of R-MnO₂ (101), β -MnO₂ (110), and α -Mn₂O₃ (222) are marked by colored circles, confirming that the dominant Mn oxide phase can be partially controlled by adjusting the thermal-decomposition temperature while maintaining the same synthesis platform used for NMO.

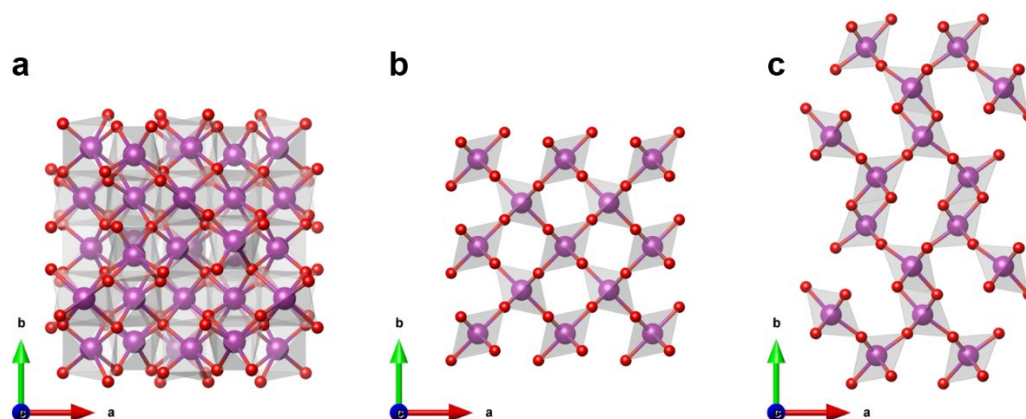
To prepare phase-rich Mn oxides, the precursor solutions were thermally decomposed at different temperatures to selectively obtain R-, β -, and α -phase-rich Mn oxides. Specifically, calcination was carried out at 220, 400, and 500 °C to obtain the R-, β -, and α -phase-rich Mn oxides, respectively. For pristine Mn oxides, 60 μ L of a 3 M Mn(NO₃)₂·4H₂O precursor solution was drop-cast onto carbon fiber paper and thermally decomposed at the designated temperature. For Nd-doped phase-rich Mn oxides, Nd(NO₃)₃·6H₂O precursor solutions (0.005, 0.010, or 0.030 M) were added to the 3 M Mn(NO₃)₂·4H₂O solution. Subsequently, 60 μ L of each mixed precursor solution was drop-cast onto carbon fiber paper and calcined at the corresponding temperature.



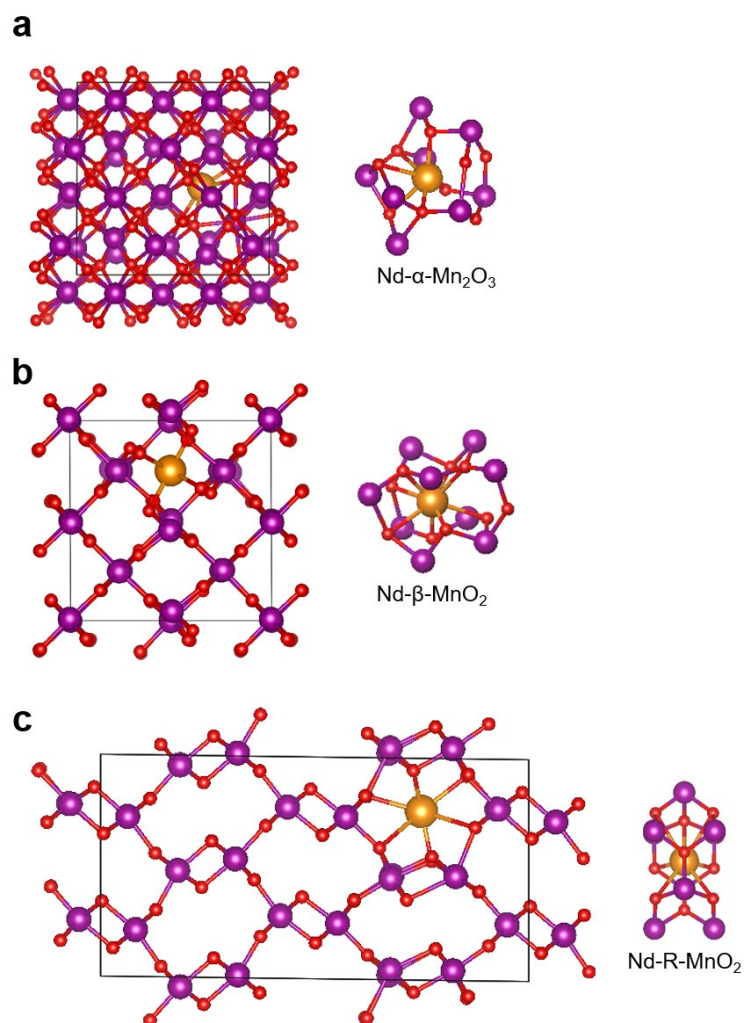
Supplementary Fig. 47 Phase-dependent OER activity of Nd-doped Mn oxide reference catalysts. Polarization curves of (a) R-MnO₂-rich, (b) β-MnO₂-rich, and (c) α-Mn₂O₃-rich catalysts with and without Nd doping. (d) Comparison of the overpotential at 10 mA cm⁻² for the corresponding phase-rich Mn oxides as a function of Nd concentrations.



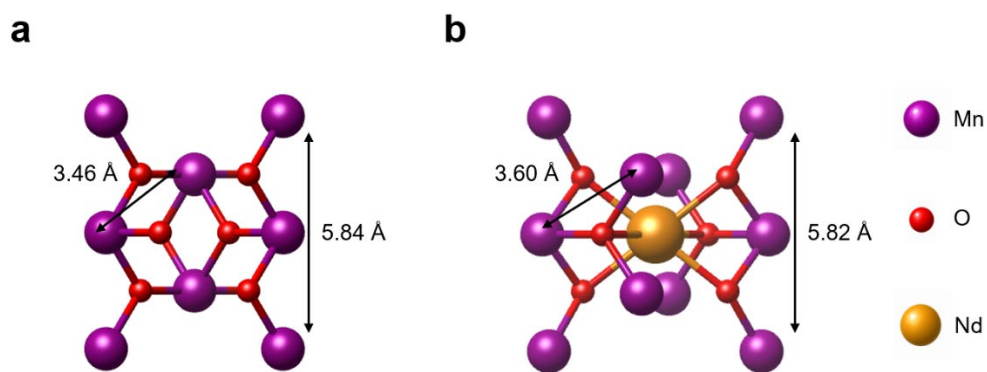
Supplementary Fig. 48 Phase-dependent OER stability of Nd-doped Mn oxide reference catalysts. (a) Chronopotentiometric stability curves of phase-controlled R- MnO_2 -rich, β - MnO_2 -rich, and α - Mn_2O_3 reference catalysts with and without Nd doping measured at 100 mA cm⁻² in 0.5 M H_2SO_4 . (b) Comparison of degradation rates derived from the chronopotentiometric stability tests.



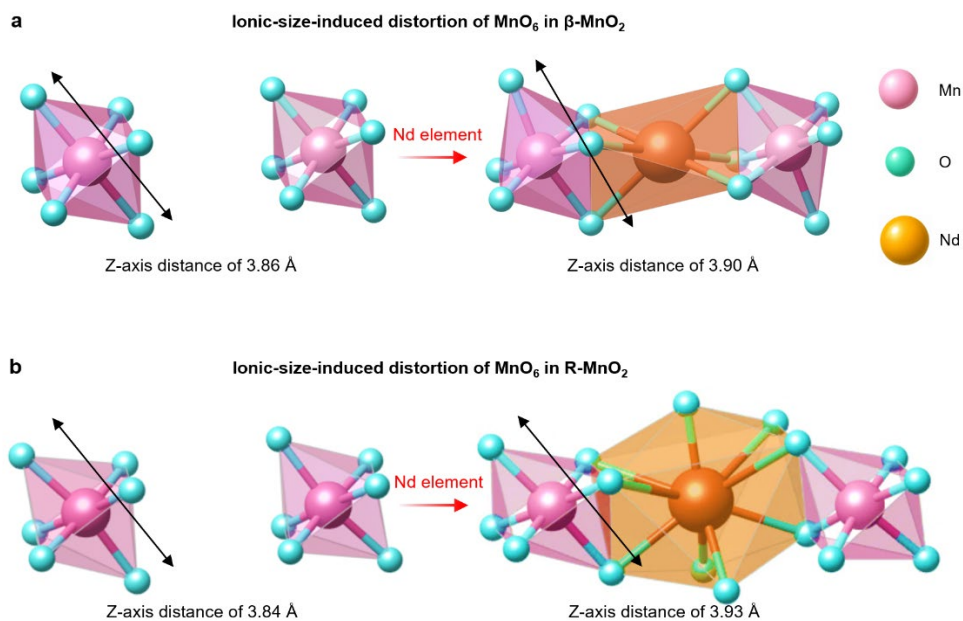
Supplementary Fig. 49 Structural models of Mn oxide polymorphs. Top-view atomic structures of (a) α - Mn_2O_3 , (b) β - MnO_2 , and (c) R-MnO_2 models used for DFT calculations. Purple and red spheres represent Mn and O atoms, respectively. The red, green, and blue arrows indicate the a , b , and c crystallographic axes, respectively. The semi-transparent shaded polyhedra represent the MnO_6 octahedral coordination environment around Mn centers.



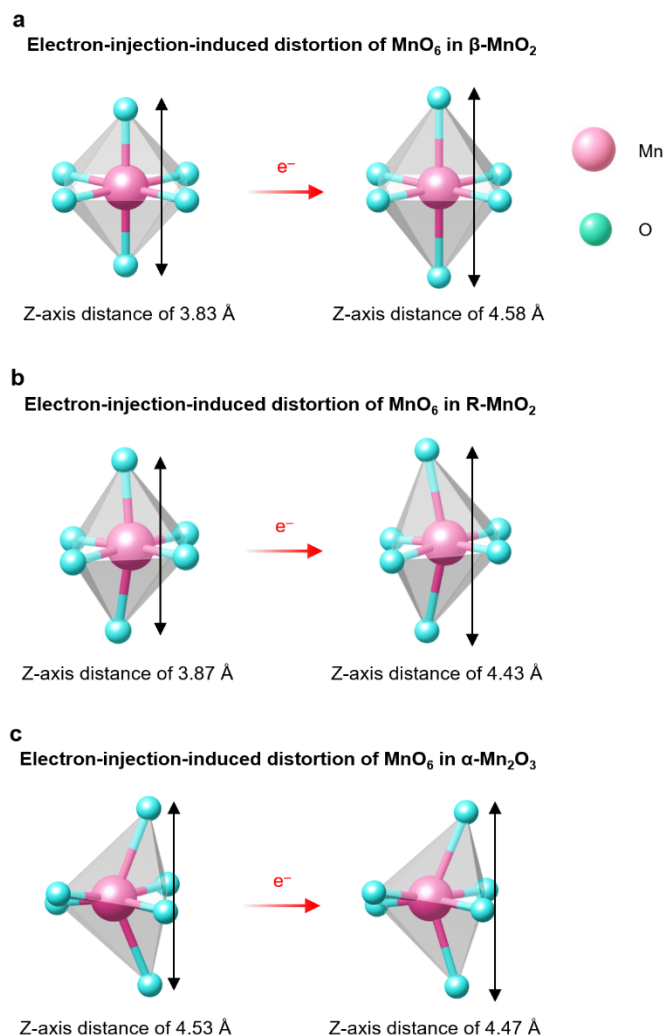
Supplementary Fig. 50 Structural models of Nd-doped Mn oxide polymorphs. Top-view atomic structures and corresponding local Nd coordination environments of (a) Nd- α -Mn₂O₃, (b) Nd- β -MnO₂, and (c) Nd-R-MnO₂ models used for DFT calculations. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively.



Supplementary Fig. 51 Local lattice distortion induced by interstitial Nd incorporation. (a) Atomic structure of the pristine Mn oxide model, showing the initial local Mn–Mn distance. (b) Atomic structure of the Nd-doped Mn oxide model with Nd located at an interstitial site, showing local expansion and asymmetric distortion of the neighboring Mn–O framework.

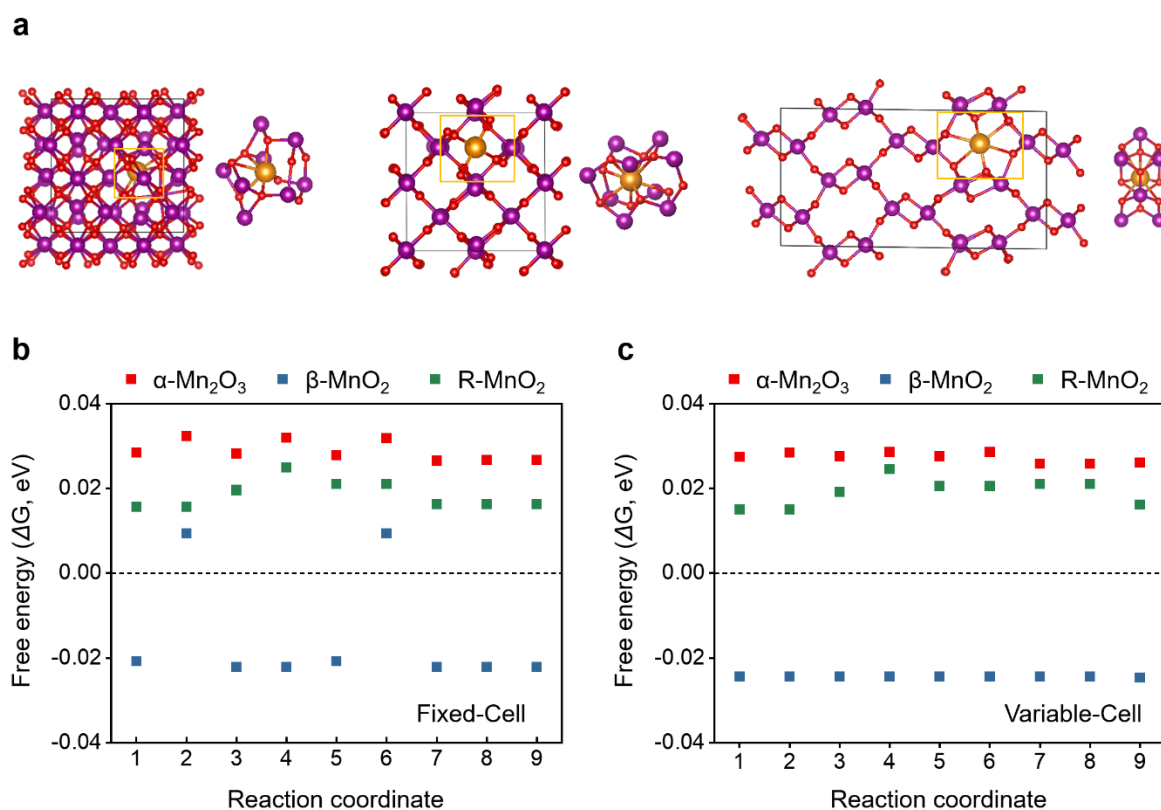


Supplementary Fig. 52 Nd-induced structural distortion of MnO_6 octahedra. (a) Structural distortion in $\beta\text{-MnO}_2$ octahedra, and (b) Structural distortion in R-MnO_2 octahedra.

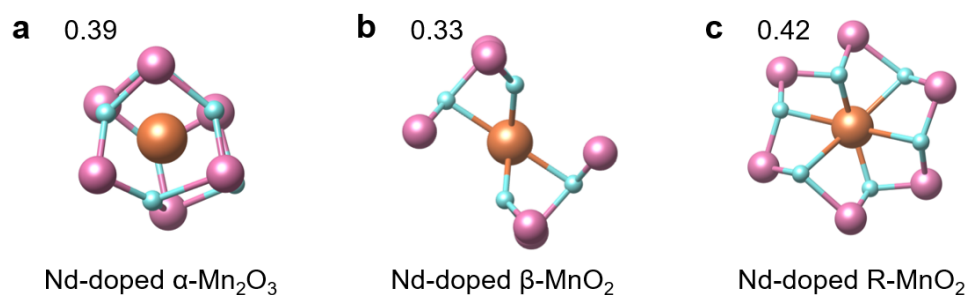


Supplementary Fig. 53 Electron-injection-induced distortion of MnO_6 octahedra. (a) Electronic distortion in $\beta\text{-MnO}_2$, and (b) Electronic distortion in R-MnO_2 . (c) Electronic distortion in $\alpha\text{-Mn}_2\text{O}_3$.

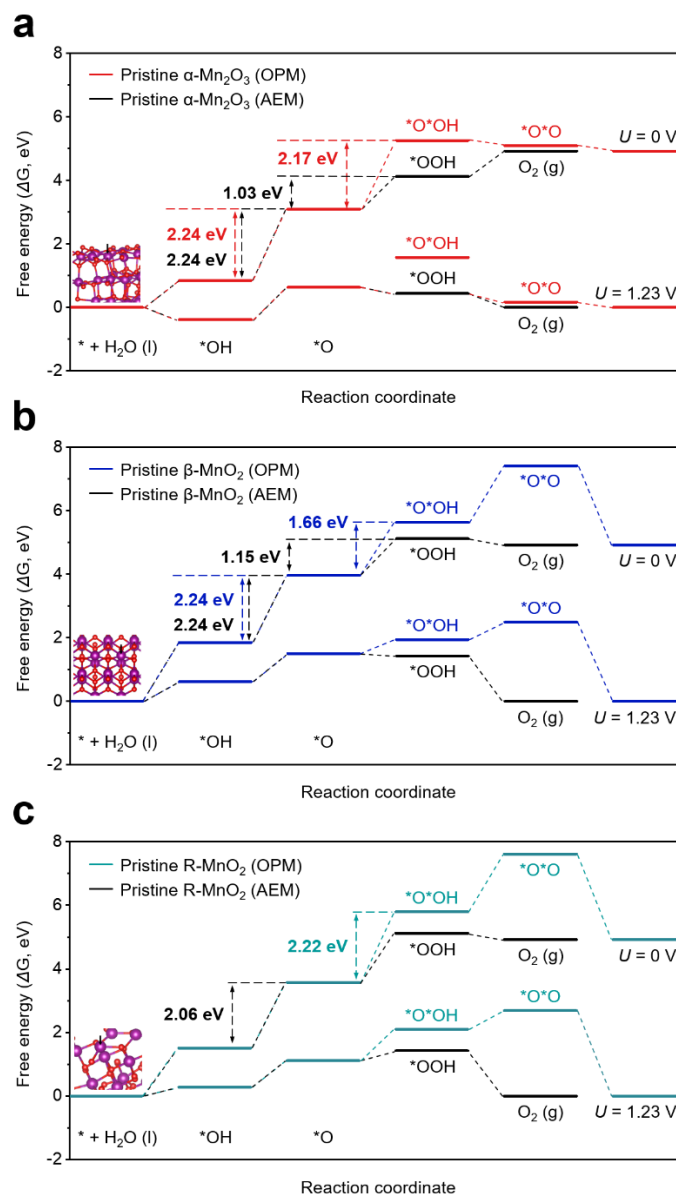
Supplementary Note 11 MnO_2 hosts Mn^{4+} in an O^{2-} -coordinated octahedral environment that imposes a weak ligand field, maintaining a high-spin d^3 (t_{2g}^3 , $S = 3/2$) configuration.²³ Upon reduction to Mn^{3+} (d^4), the electron preferentially fills the e_g level rather than pairing within t_{2g} , consistent with the low ligand-field splitting. This e_g occupation triggers a Jahn–Teller distortion and introduces local structural flexibility. In contrast, $\alpha\text{-Mn}_2\text{O}_3$ already contains Mn^{3+} (e_g^1) centers with intrinsic Jahn–Teller distortion, so further electron injection leads to only marginal additional lattice perturbation.



Supplementary Fig. 54 Oxygen-vacancy models and structural responses in Nd-doped Mn oxides. (a) Oxygen-vacancy candidate sites generated by removing first-nearest-neighbor oxygen atoms around interstitial Nd dopants in Nd- $\alpha\text{-Mn}_2\text{O}_3$, Nd- $\beta\text{-MnO}_2$, and Nd-R-MnO₂. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively, and the orange boxes highlight the local Nd coordination environments considered for oxygen-vacancy generation. (b, c) Oxygen-vacancy formation energies calculated under fixed-cell and variable-cell relaxation conditions, respectively.



Supplementary Fig. 55 Bader charge analysis of neighboring Mn atoms around Nd dopant in (a) Nd- α - Mn_2O_3 , (b) Nd- β - MnO_2 , (c) Nd-R- MnO_2 . The values indicate Bader charge difference of neighboring Mn atoms induced by Nd doping. Orange, pink, and cyan spheres represent Nd, Mn, and O atoms, respectively.



Supplementary Fig. 56 Gibbs free energy profiles comparing AEM and OPM pathways for pristine (a) α - Mn_2O_3 (111), (b) β - MnO_2 (110), and (c) R-MnO_2 (100) slabs. All pristine Mn oxide polymorphs preferentially follow the AEM pathway. Purple and red spheres represent Mn and O atoms, respectively.

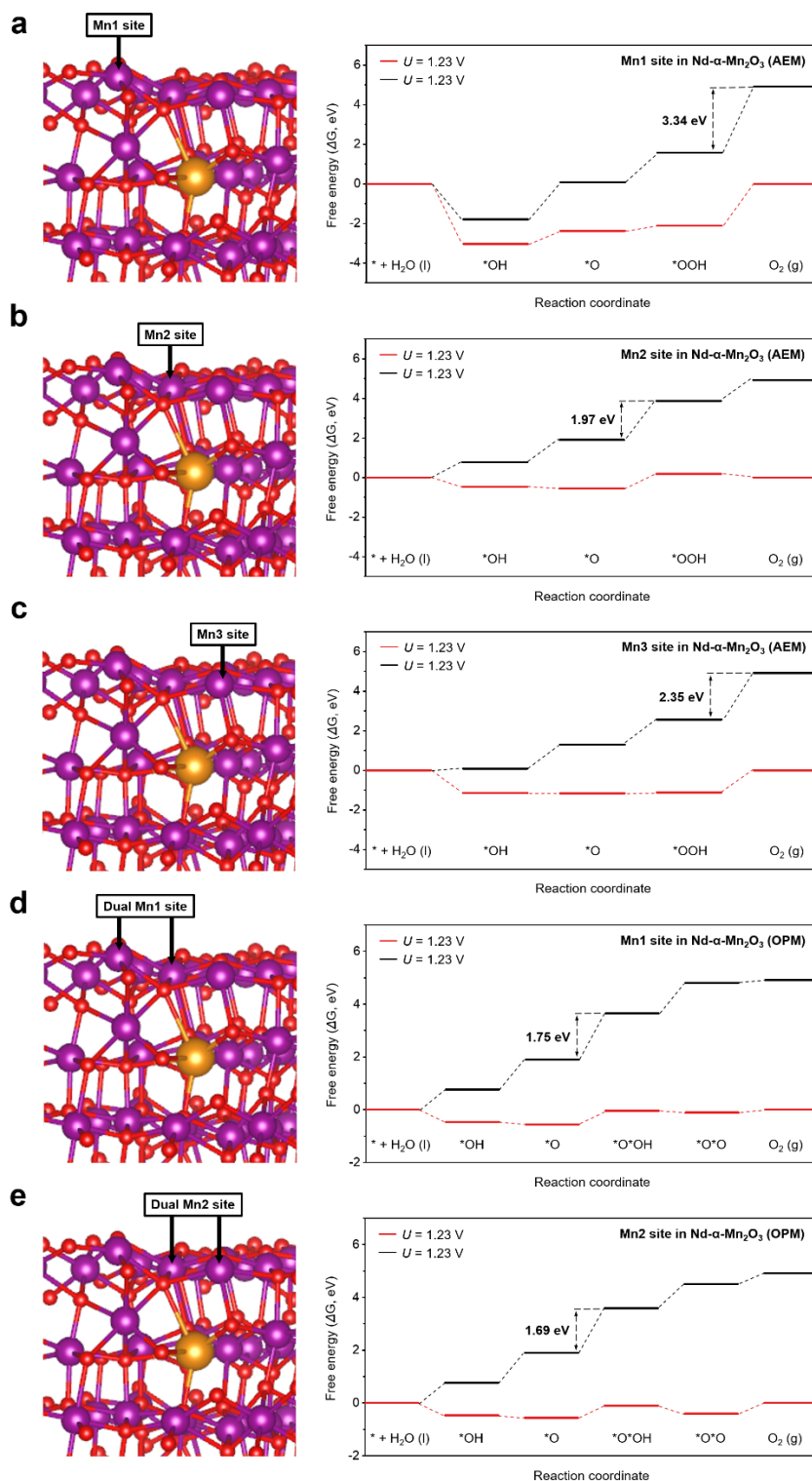
Supplementary Note 12 The Gibbs free energy profiles of AEM and OPM were calculated for pristine α - Mn_2O_3 (111), β - MnO_2 (110), and R-MnO_2 (100) slabs.

For pristine α - Mn_2O_3 , both AEM and OPM share the same rate-determining step (RDS), namely the $^*\text{OH}$ -to- $^*\text{O}$ conversion, with a ΔG value of 2.24 eV (Supplementary Fig. 56a). However, the subsequent $^*\text{O}$ -to- $^*\text{OOH}$ step in the AEM requires a lower energy barrier (1.03 eV) than the corresponding $^*\text{O}$ -to- $^*\text{O}^*\text{OH}$ step in the OPM (2.17 eV), indicating that α - Mn_2O_3 preferentially follows the AEM pathway.

A similar trend is observed for pristine β -MnO₂ (Supplementary Fig. 56b). The *OH-to-*O step is the RDS for both pathways with a ΔG value of 2.24 eV, whereas the subsequent AEM step requires a lower barrier of 1.15 eV than the corresponding OPM step (1.66 eV). Therefore, β -MnO₂ also favors the conventional AEM pathway.

For pristine R-MnO₂, the AEM pathway is likewise energetically preferred (Supplementary Fig. 56c). The RDS is the *OH-to-*O step with a ΔG value of 2.06 eV, whereas the OPM pathway is limited by the *O-to-*O*OH step with a higher ΔG value of 2.22 eV.

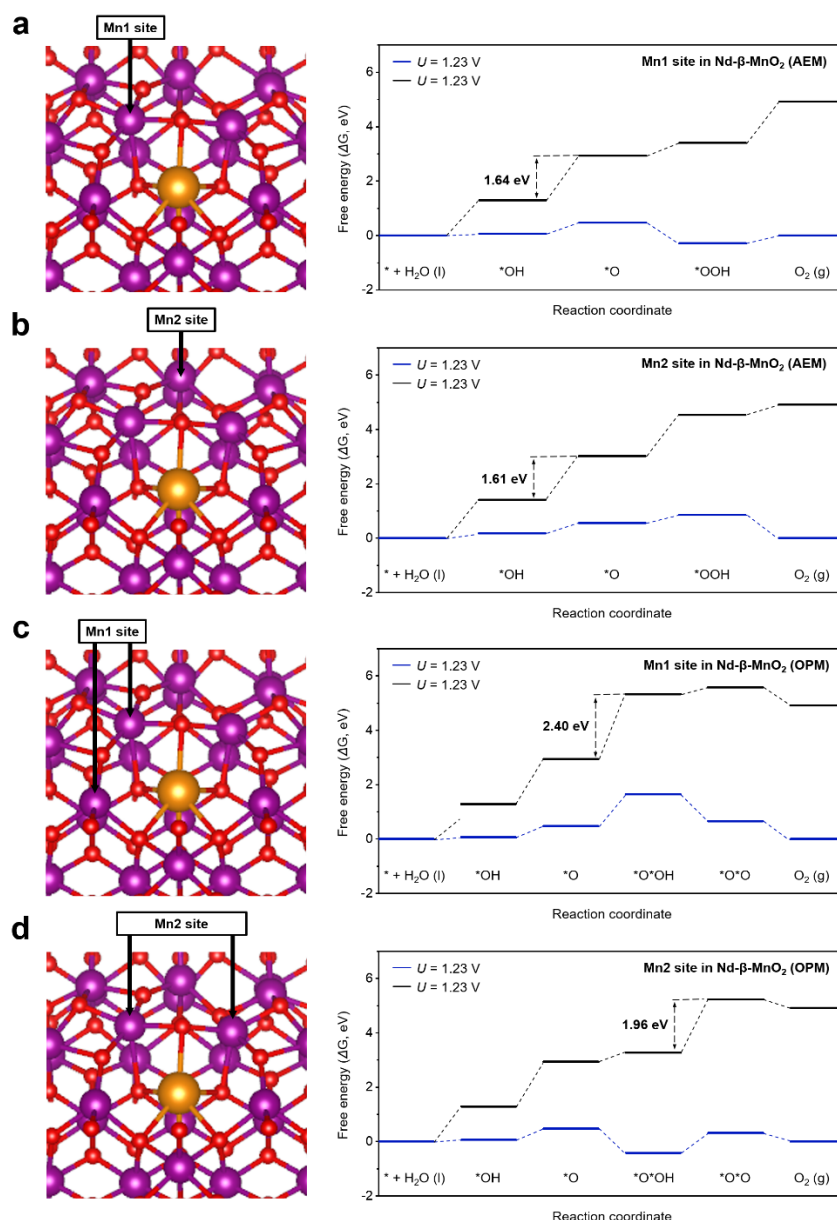
Overall, the calculated Gibbs free energy profiles demonstrate that all pristine Mn oxide phases preferentially follow the conventional AEM pathway rather than the OPM pathway.



Supplementary Fig. 57 Gibbs free energy profiles comparing AEM and OPM pathways at different surface Mn sites of Nd-doped α - Mn_2O_3 (111). AEM pathways were calculated at (a) Mn1, (b) Mn2, and (c) Mn3 sites, while OPM pathways were calculated at (d) Mn1 and (e) Mn2 sites. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively.

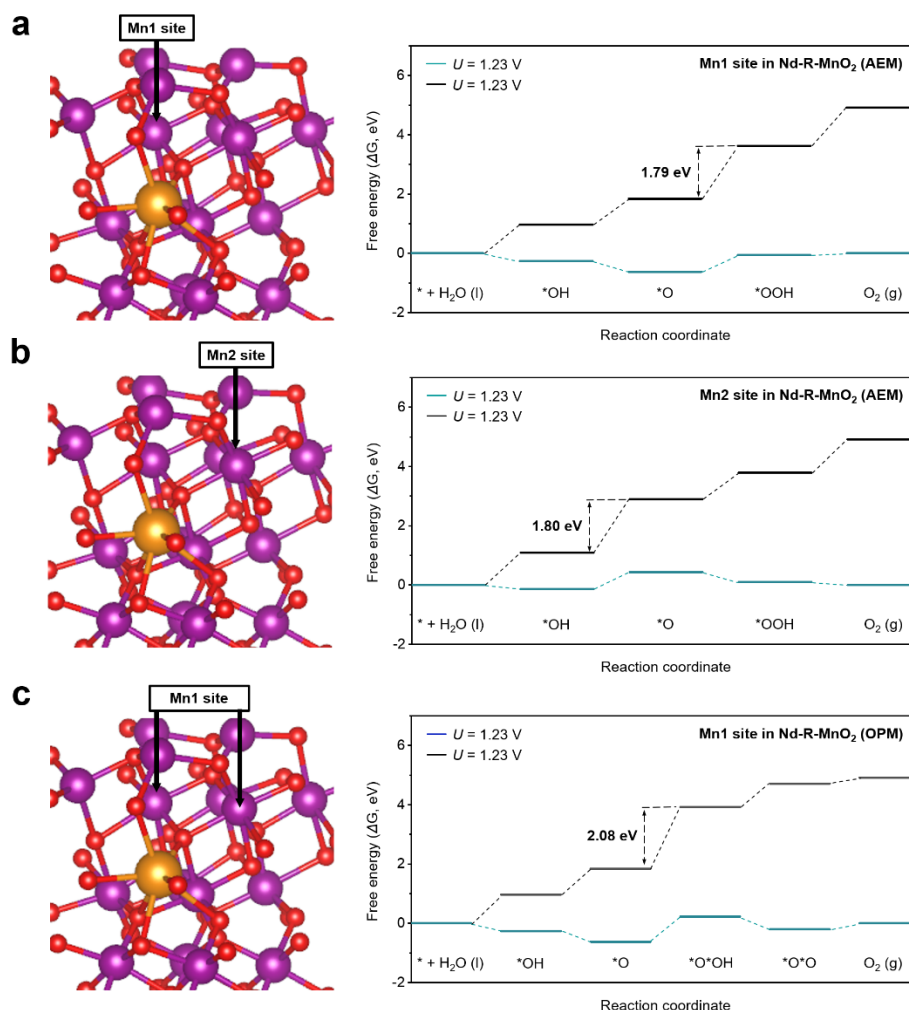
Supplementary Note 13 The Gibbs free energy profiles of the AEM and OPM pathways were calculated at different surface Mn sites in Nd- α - Mn_2O_3 . For the AEM pathway, Mn1, Mn2, and

Mn3 sites were evaluated (Supplementary Figs. 57a–c). The RDSs are the *OOH-to-O₂ step at the Mn1 site ($\Delta G = 3.34$ eV), the *O-to-*OOH step at the Mn2 site ($\Delta G = 1.97$ eV), and the *OOH-to-O₂ step at the Mn3 site ($\Delta G = 2.35$ eV). For the OPM pathway, Mn1 and Mn2 sites were considered (Supplementary Figs. 57d–e), where the *O-to-*O*OH step is the RDS with ΔG values of 1.75 and 1.69 eV, respectively. Among the examined reaction sites and pathways, the Mn2-site OPM pathway exhibits the lowest RDS energy barrier of 1.69 eV, suggesting that Nd-doped α -Mn₂O₃ preferentially favors the OPM route.



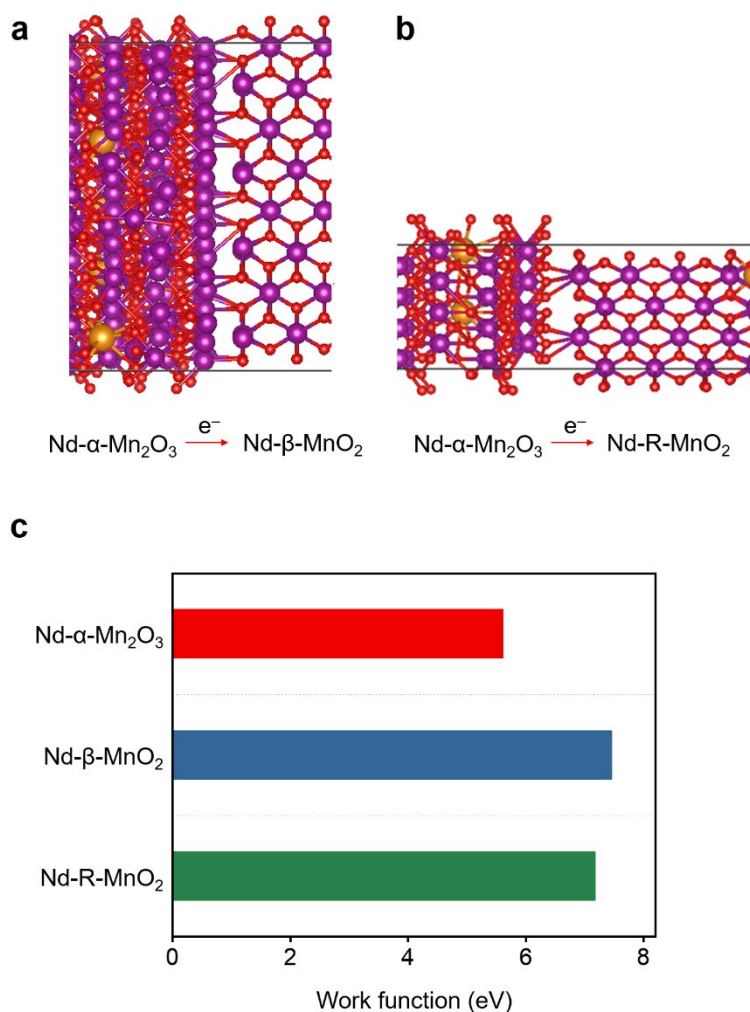
Supplementary Fig. 58. Gibbs free energy profiles comparing AEM and OPM pathways at different surface Mn sites of Nd-doped β - MnO_2 (110). AEM pathways were calculated at (a) Mn1 and (b) Mn2 sites, while OPM pathways were calculated at (c) Mn1 and (d) Mn2 sites. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively.

Supplementary Note 14 The Gibbs free energy profiles of the AEM and OPM pathways were calculated at different surface Mn sites in Nd- β - MnO_2 (110). For the AEM pathway, two Mn sites were evaluated (Supplementary Figs. 58a–b). The $\ast\text{OH}$ -to- $\ast\text{O}$ step is identified as the RDS at both Mn1 and Mn2 sites, with ΔG values of 1.64 and 1.61 eV, respectively. For the OPM pathway, two reaction sites were considered (Supplementary Figs. 58c–d). The RDSs are the $\ast\text{O}$ -to- $\ast\text{O}^\ast\text{OH}$ step at the Mn1 site ($\Delta G = 2.40 \text{ eV}$) and the $\ast\text{O}^\ast\text{OH}$ -to- O_2 step at the Mn2 site ($\Delta G = 1.96 \text{ eV}$). Among the examined sites and pathways, the AEM pathway at the Mn2 site exhibits the lowest RDS barrier of 1.61 eV, suggesting that Nd-doped β - MnO_2 preferentially follows the AEM route.

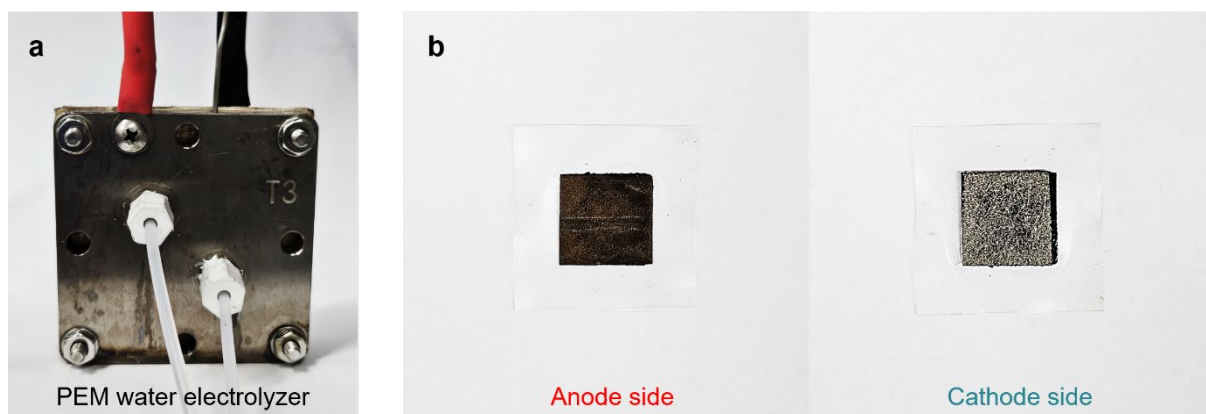


Supplementary Fig. 59. Gibbs free energy profiles comparing AEM and OPM pathways at different surface Mn sites of Nd-doped R-MnO₂ (100). AEM pathways were calculated at (a) Mn1 and (b) Mn2 sites, while the OPM pathway was calculated at (c) the Mn1 site. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively.

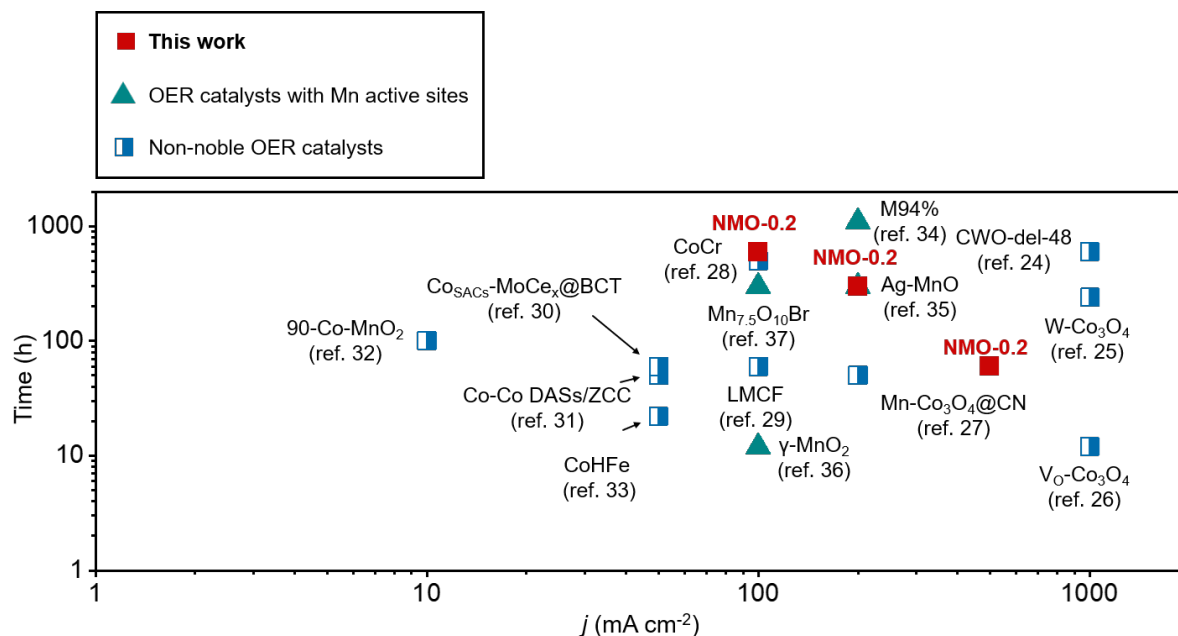
Supplementary Note 15 The Gibbs free energy profiles of the AEM and OPM pathways were calculated at different surface Mn sites in Nd-R-MnO₂. For the AEM pathway, two Mn sites were evaluated (Supplementary Figs. 59a–b). The RDSs are the *O-to-*OOH step at the Mn1 site ($\Delta G = 1.79$ eV) and the *OH-to-*O step at the Mn2 site ($\Delta G = 1.80$ eV). For the OPM pathway, the *O-to-*O*OH step is identified as the RDS with $\Delta G = 2.08$ eV (Supplementary Fig. 59c). Among the examined sites and pathways, the AEM pathway exhibits a lower RDS barrier than the OPM pathway, indicating that Nd-doped R-MnO₂ preferentially follows the AEM route.



Supplementary Fig. 60 Work-function comparison of Mn-oxide polymorphs. (a) Schematic illustration of interfacial electron transfer from Nd- α -Mn₂O₃ to Nd- β -MnO₂ and (b) from Nd- α -Mn₂O₃ to Nd-R-MnO₂, driven by the work-function difference. Purple, red, and orange spheres represent Mn, O, and Nd atoms, respectively. (c) Calculated work functions of Nd- α -Mn₂O₃ (111), Nd- β -MnO₂ (110), and Nd-R-MnO₂ (100) slab models. The lower work function of α -Mn₂O₃ relative to β -MnO₂ and R-MnO₂ suggests a thermodynamic driving force for electron redistribution from α -Mn₂O₃-rich domains toward MnO₂-rich domains upon interphase contact, providing a possible origin of interphase electronic interaction at mixed-phase domain boundaries. Such interphase charge redistribution may locally modulate the Mn–O electronic structure and help stabilize catalytically relevant Mn³⁺ species near mixed-phase domain boundaries.



Supplementary Fig. 61 Photographs of the (a) PEMWE setup and the corresponding (b) MEA.



Supplementary Fig. 62 Benchmarking of non-noble metal-based OER catalysts in PEMWE systems: current densities and testing times plotted on a logarithmic scale. The red box highlights this work. Blue semi-rectangular boxes denote previously reported non-noble OER catalysts,²⁴⁻³³ and green triangles indicate Mn-centered catalysts.³⁴⁻³⁷

Supplementary Table 1 Crystallographic parameters of NMO-0.2 and γ -MnO₂ determined from Rietveld refinement of synchrotron PXRD patterns and DFT calculation.

γ-MnO₂						
R _p (%) = 7.54%, R _{wp} = 11.31%						
x ² = 1.93						
Phase	Phase fraction (mol%)	Space group	a (Å)	b (Å)	c (Å)	Vol. (Å ³)
β -MnO ₂	94.1	P42/mnm	4.40776	4.40776	2.8784	55.922
R-MnO ₂	5.9	Pbnm	4.16705	6.50805	2.24704	60.938
NMO-0.2						
R _p (%) = 7.41%, R _{wp} = 11.12%						
x ² = 2.16						
Phase	Phase fraction (mol%)	Space group	a (Å)	b (Å)	c (Å)	Vol. (Å ³)
α -Mn ₂ O ₃	11.6	Ia-3	9.42971	9.42971	9.42971	838.485
β -MnO ₂	32.1	P42/mnm	4.39226	4.39226	2.90876	56.116
R-MnO ₂	56.3	Pbnm	4.60591	8.78903	2.85131	115.425
DFT results						
Phase	Δ (Cal. – Exp., %)		a (Å)	b (Å)	c (Å)	Vol. (Å ³)
α -Mn ₂ O ₃	6.6		9.63236	9.65096	9.66345	898.329
β -MnO ₂	13.57		4.68634	4.76633	2.90666	64.925
R-MnO ₂	10.32		4.79480	9.25642	2.90019	128.718

Supplementary Table 2 Elemental composition of γ -MnO₂ and a series of NMO samples determined by XPS, EDS, and ICP-OES. These complementary analyses yielded consistent results, confirming the successful doping of Nd across the series, with minor discrepancies attributed to differences in spatial resolution and probing depth.

γ -MnO ₂	Mn	Nd	O	—
XPS at%	17.63	—	82.37	—
EDS at%	30.19	—	69.81	—
ICP-OES at%	100	—	—	—
NMO-0.05	Mn	Nd	O	Nd/Mn (%)
XPS at%	18.58	0.79	80.63	4.25
EDS at%	95.91	4.08	—	4.25
ICP-OES at%	97.40	2.60	—	2.67
NMO-0.1	Mn	Nd	O	Nd/Mn (%)
XPS at%	13.64	1.28	85.08	9.38
EDS at%	91.44	8.56	—	9.36
ICP-OES at%	93.89	6.11	—	6.51
NMO-0.2	Mn	Nd	O	Nd/Mn (%)
XPS at%	20.04	1.6	78.36	7.98
EDS at%	92.61	7.39	—	7.98
ICP-OES at%	87.22	12.78	—	14.65
NMO-0.4	Mn	Nd	O	Nd/Mn (%)
XPS at%	—	—	—	—
EDS at%	—	—	—	—
ICP-OES at%	72.70	27.30	—	37.55

Supplementary Table 3 Fitting parameters of the Mn K-edge EXAFS spectra for γ -MnO₂ and NMO-0.2 samples and comparison of Mn–O bond length from experimental data and DFT calculations.

Samples	N	R (Å)	σ^2 (Å ²)	S_0^2	Reduced chi-square	R-factor
γ -MnO ₂	6.0	1.8263	0.0010	0.5735	23.1888	0.0323
NMO-0.2	5.8	1.8649	0.0103	0.5735	4.1226	0.0192

Mn–O bond	Experimental ΔR	DFT-calculated ΔR
ΔR (Å)	0.030	0.033

Supplementary Table 4 Performance metrics of previously reported non-noble-metal-based acidic OER catalysts,

Catalyst	Electrolyte	Overpotential in a half cell	Stability in a half cell	Ref.
NMO-0.2	0.5 H ₂ SO ₄	308 mV @ 10 mA cm ⁻²	1000 h @ 200 mA cm ⁻²	This work
^b M60%	1 M H ₂ SO ₄	~ 410 mV @ 10 mA cm ⁻²	~ 50 h @ 200 mA cm ⁻²	15
^b M67%	1 M H ₂ SO ₄	~ 410 mV @ 10 mA cm ⁻²	~ 400 h @ 200 mA cm ⁻²	15
^b M85%	1 M H ₂ SO ₄	~ 410 mV @ 10 mA cm ⁻²	~ 800 h @ 200 mA cm ⁻²	15
^b M94%	1 M H ₂ SO ₄	~ 410 mV @ 10 mA cm ⁻²	~ 2200 h @ 200 mA cm ⁻²	15
M94%_P (P: pumping)	1 M H ₂ SO ₄	N/A	~ 3200 h @ 200 mA cm ⁻² 2500 h @ 500 mA cm ⁻² 750 h @ 1000 mA cm ⁻²	15
Nd-γ-MnO ₂	1 M H ₂ SO ₄	391 mV @ 10 mA cm ⁻²	700 h @ 200 mA cm ⁻²	16
γ-MnO ₂	1.0 M H ₂ SO ₄	428 mV @ 10 mA cm ⁻²	8000 h @ 10 mA cm ⁻² , pH 2	17
Ag/MnO	0.5 M H ₂ SO ₄	196 mV @ 10 mA cm ⁻²	N/A	18
MnO ₂ -350	1 M H ₂ SO ₄	522 mV @ 100 mA cm ⁻²	1000 h @ 100 mA cm ⁻²	27
^a Mn-CO ₃ O ₄ @CN	0.5 M H ₂ SO ₄	395 mV @ 10 mA cm ⁻²	120 h @ 10 mA cm ⁻²	28
Ni _{0.5} Mn _{0.5} Sb _{1.7} O _y	1.0 M H ₂ SO ₄	672 mV @ 10 mA cm ⁻²	168 h @ 10 mA cm ⁻²	29
Ti-MnO ₂	0.05 M H ₂ SO ₄	670 mV @ 10 mA cm ⁻²	2 h @ 1.9 V _{RHE}	30
^c LMCF	0.1 M HClO ₄	353 mV @ 10 mA cm ⁻²	360 h @ 10 mA cm ⁻²	31
Mn _{7.5} O ₁₀ Br	0.5 M H ₂ SO ₄	295 mV @ 10 mA cm ⁻²	500 h @ 10 mA cm ⁻²	32
Ni _{0.5} Mn _{0.5} Sb _y O _x	0.5 M H ₂ SO ₄	598 mV @ 10 mA cm ⁻²	168 h @ 10 mA cm ⁻²	33
Co ₂ MnO ₄	pH 1 H ₃ PO ₄	600 mV @ 1000 mA cm ⁻²	1500 h @ 200 mA cm ⁻²	34
NiMn _{1.5} Co ₃ O _{4-d}	0.5 M H ₂ SO ₄	280 mV @ 10 mA cm ⁻²	40 h @ 10 mA cm ⁻²	35
^d CoSAC-	0.5 M H ₂ SO ₄	239 mV @ 10 mA cm ⁻²	12 h @ 10 mA cm ⁻²	36
MoCe _x @BCT				
Co ₃ O ₄	0.5 M H ₂ SO ₄	570 mV @ 10 mA cm ⁻²	12 h @ 10 mA cm ⁻²	37
CoFePbO _x	pH 1 H ₂ SO ₄	430 mV @ 10 mA cm ⁻²		38
Co _{0.05} Fe _{0.95} O _y	0.5 M H ₂ SO ₄	650 mV @ 10 mA cm ⁻²	50 h @ 10 mA cm ⁻²	39
Co ₃ O ₄ /CeO ₂	0.5 M H ₂ SO ₄	410 mV @ 10 mA cm ⁻²	50 h @ 10 mA cm ⁻²	40
CoCr	0.1 M HClO ₄	360 mV @ 10 mA cm ⁻²	100 h @ 10 mA cm ⁻²	41
^e Co-Co	0.5 M H ₂ SO ₄	155 mV @ 10 mA cm ⁻²	40 h @ 10 mA cm ⁻²	42
DASSs/ZCC				
Co ₃ O ₄ @C	0.5 M H ₂ SO ₄	370 mV @ 10 mA cm ⁻²	86.8 h @ 100 mA cm ⁻²	43
V-CoP ₂	0.5 M H ₂ SO ₄	91 mV @ 10 mA cm ⁻²	20 h @ 10 mA cm ⁻²	44
V _O -Co ₃ O ₄	0.5 M H ₂ SO ₄	265 mV @ 10 mA cm ⁻²	130 h @ 20 mA cm ⁻²	45
@HNC				
TaCo _{3-x} O ₄	0.05 M H ₂ SO ₄	378 mV @ 10 mA cm ⁻²	140 h @ 10 mA cm ⁻²	46

^f Co ₃ O ₄ @C/GPO	1 M H ₂ SO ₄	360 mV @ 10 mA cm ⁻²	40 h @ 10 mA cm ⁻²	47
W-Co ₃ O ₄	0.5 M H ₂ SO ₄	251 mV @ 10 mA cm ⁻²	250 h @ 10 mA cm ⁻²	48
^g CWO-del-48	0.5 M H ₂ SO ₄	288 mV @ 10 mA cm ⁻²	175 h @ 10 mA cm ⁻²	49
Co _{3-x} Ba _x O ₄	0.5 M H ₂ SO ₄	278 mV @ 10 mA cm ⁻²	110 h @ 10 mA cm ⁻²	50
90-Co-MnO ₂ with Co ²⁺	0.1 M HClO ₄	801 mV @ 10 mA cm ⁻²	260 h @ 10 mA cm ⁻²	51

a: Mn-Co₃O₄@CN; N-doped-carbon-layer clothed Mn-doped-Co₃O₄), b: M % series; γ -MnO₂ samples based on the concentration of planar oxygen; O_{pla}, c: LMCF; La- and Mn-codoped porous cobalt spinel fibers, d: CoSAC-MoCe_x@BCT; Amorphous Mo-Ce oxide supported single atom Co encapsulated in bamboo-like carbon nanotubes, e: Co-Co DAs/ZCC; Co-Co dinuclear active sites catalysts that atomically dispersed zirconium doped Co₉S₈/Co₃O₄ heterostructure, f: Co₃O₄@C/GPO; Cobalt oxide covered by nitrogen-doped-carbon coating with graphite and paraffin oil, g: CWO-del-48; Delaminated cobalt tungstate.

Supplementary Table 5. Performance metrics of previously reported non-noble-metal-based acidic OER catalysts in PEMWE systems, used for the benchmarking plot shown in Supplementary Fig. 62.

Catalyst	Temp. (°C)	Loading (mg cm ⁻²)	Membrane	Electrolyte	<i>iR</i> Correction	Activity	Durability	Ref.
NMO-0.2	80	~8.0	Nafion 117	0.5 M H ₂ SO ₄	Uncorrected	1.88 V @ 1.0 A cm ⁻²	60 h @ 0.5 A cm ⁻² 300 h @ 0.2 A cm ⁻² 600 h @ 0.1 A cm ⁻²	This work
CWO-del-48	80	3.0	Nafion 117	DI water	Uncorrected	2.00 V @ 1.8 A cm ⁻² 1.72 V @ 0.5 A cm ⁻²	600 h @ 1.0 A cm ⁻²	24
W-Co ₃ O ₄	80	2.5	Nafion 117	DI water	Uncorrected	1.83 V @ 1.0 A cm ⁻² 2.04 V @ 2.0 A cm ⁻²	240 h @ 1.0 A cm ⁻²	25
Vo-Co ₃ O ₄	80	2.0	Nafion 212	DI water	Uncorrected	1.82 V @ 1.0 A cm ⁻²	100 h @ 1.0 A cm ⁻²	26
Mn-Co ₃ O ₄ @CN	80	2.0	Nafion 117	DI water	Uncorrected	1.65 V @ 0.2 A cm ⁻²	50 h @ 0.2 A cm ⁻² 500 h @ 0.1 A cm ⁻²	27
CoCr	80	2.0	Nafion 115	0.1 M HClO ₄	Uncorrected	2.17 V @ 1.5 A cm ⁻²	100 h @ 0.5 A cm ⁻²	28
LMCF	80	2.0	Nafion 117	DI water	Uncorrected	2.20 V @ 2.0 A cm ⁻²	600 h @ 0.1 A cm ⁻²	29
CoSAC-MoCex@BCT	RT (~25)	0.5	N/A	0.5 M H ₂ SO ₄	95% <i>iR</i> -corrected	12 h @ 10 mA cm ⁻²	N/A	30
Co-Co DASSs/ZCC	80	2.0	Nafion 117	DI water	Uncorrected	2.14 V @ 120 A g ⁻¹	50 h @ 0.05 A cm ⁻²	31
90-Co-MnO ₂	80	2.0	Nafion 117	DI water	Uncorrected	~2.10 V @ 10 mA cm ⁻²	100 h @ 10 mA cm ⁻²	32
CoHFe	80	1.5	Nafion 115	0.1 M H ₂ SO ₄	Uncorrected	2.15 V @ 0.1 A cm ⁻²	22 h @ 0.05 A cm ⁻²	33
M60%	80	2.5	Nafion 117	DI water	Uncorrected	> 2.00 V @ 1.0 A cm ⁻²	100 h @ 0.2 A cm ⁻²	34
M67%	80	2.5	Nafion 117	DI water	Uncorrected	~1.95 V @ 1.0 A cm ⁻²	300 h @ 0.2 A cm ⁻²	34
M85%	80	2.5	Nafion 117	DI water	Uncorrected	~1.95 V @ 1.0 A cm ⁻²	1000 h @ 0.2 A cm ⁻²	34
M94%	80	2.5	Nafion 117	DI water	Uncorrected	1.88 V @ 1.0 A cm ⁻²	1100 h @ 0.2 A cm ⁻²	34
Ag/MnO	80	2.0	Nafion 117	DI water	Uncorrected	2.00 V @ 0.4 A cm ⁻²	300 h @ 0.2 A cm ⁻²	35
γ-MnO ₂	RT (~25)	1.0	N/A	0.5 M H ₂ SO ₄	100% <i>iR</i> -corrected	1.71 V @ 10 mA cm ⁻²	12 h @ 0.1 A cm ⁻²	36
Mn _{7.5} O ₁₀ Br	80	2.0	Nafion 117	DI water	Uncorrected	~1.85 V @ 0.1 A cm ⁻²	300 h @ 0.1 A cm ⁻²	37

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