

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

Corresponding Author: Professor Jungki Ryu

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Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript presents a highly significant advancement in the field of non-noble metal catalysts for OER under acidic conditions. Nd-doped Mn oxide achieves high stability, providing an effective strategy to the challenge of Mn³⁺ instability in acid for Mn-based OER catalyst. This work will be of great interest to the communities working on electrocatalysis, water splitting, and energy materials. However, there are several issues needed to be addressed:

1. Nd doping was found to alter the structural parameters of Mn oxides. Did the changes of Mn-Mn and Mn-O bond lengths in the DFT models agree with the experimental observations? This will largely affect the electronic structures. Besides, did the author consider the oxygen vacancies in building the DFT model? The structural models used for calculations are idealized and considering the effect of oxygen vacancies and Nd doping concentration on the lattice structure would make the simulations more consistent with experimental results.
2. The NMO catalyst is identified as a mixed phase of α -Mn₂O₃, β -MnO₂, and R-MnO₂. While the synergistic effect is highlighted, the individual contribution of each phase to the overall activity and stability is not fully decoupled. However, the DFT calculations appropriately model the three phases separately. But it remains unclear from the experimental data whether one phase is primarily responsible for activity while another enhances stability. Please state the experimental basis of the DFT models. The authors should also discuss the potential role of heterointerfaces in facilitating charge transfer or stabilizing active sites.
3. In Figure 4a, comparison of α -Mn₂O₃ and Nd-doped α -Mn₂O₃ is not proper as there is no α -Mn₂O₃ in the non-Nd-doped γ -MnO₂.
4. The authors propose the OPM mechanism through O-O coupling facilitated by labile *O species. But there is lack of both direct experimental and DFT evidences. The authors could consider using ¹⁸O isotope labeling coupled with in-situ mass spectrometry to directly verify the source of oxygen in the produced O₂ and confirm the O-O bond formation pathway
5. It is recommended to compare the calculated adsorption energies of OER intermediates, which helps validate the theoretical model. Besides, the DFT energy profile for the whole OER pathway will also claim the of feasibility the OPM mechanism.

Reviewer #2

(Remarks to the Author)

This manuscript presents a promising strategy for enhancing the acidic oxygen evolution reaction (OER) performance of Mn-based catalysts through Nd doping. The topic is of high interest for proton-exchange membrane water electrolysis, and the reported improvements in activity and stability are noteworthy. However, several key issues require clarification and additional experimental support before the work can be considered suitable for publication. The following points should be addressed to strengthen the conclusions and ensure the robustness of the study.

1. The study investigates α -Mn₂O₃, β -MnO₂, and R-MnO₂ but does not thoroughly explore potential synergistic effects between these phases in the catalytic system. It is important to clarify whether the observed performance arises from a specific phase or from interactions between multiple phases.

2. The choice of Nd as a dopant needs clearer justification. Why was Nd selected over other rare-earth or transition metals? A comparative study involving other dopants (e.g., La, Ce, Pr, or non-rare-earth metals) would help establish whether the enhancement is unique to Nd or a more general phenomenon. Discussing the specific electronic or structural effects induced by Nd doping (e.g., charge redistribution, oxygen vacancy formation, or structural stabilization) is essential to support its selection.
3. In Figure 2e, MnO₂ is tested on a carbon substrate, while Nd-doped catalysts are tested on a porous transport layer (PTL). Carbon corrosion and catalyst detachment under OER conditions may unfairly penalize the MnO₂ performance. To ensure a fair comparison, MnO₂ should also be tested on the same PTL substrate under identical conditions. This will isolate intrinsic catalytic differences from substrate-related artifacts.
4. The Raman signals presented are exceptionally weak, raising concerns about signal-to-noise ratio and the reliability of the phase identification. It is recommended to repeat the measurements with optimized experimental conditions (e.g., longer acquisition time, higher laser power, or alternative excitation wavelengths) or to supplement with additional techniques (e.g., FTIR or high-resolution TEM) to confirm the proposed phase composition.
5. The authors propose an oxide path mechanism (OPM) for OER. To substantiate this claim, differential electrochemical mass spectrometry (DEMS) experiments should be conducted to directly monitor oxygen evolution and possible intermediate species. This would provide critical evidence to distinguish between OPM and alternative mechanisms such as the adsorbate evolution mechanism (AEM).
6. Figure 5A,B lacks a direct comparison with undoped MnO₂ in the same electrolyzer configuration. Including MnO₂ tested under identical conditions is necessary to objectively evaluate the improvement offered by Nd doping.
7. Figure 5c indicates noticeable performance degradation over time. The origin of this deactivation should be discussed in detail.

Reviewer #3

(Remarks to the Author)

This manuscript reported a Nd-doped Mn oxide (NMO) to stabilize J–T active Mn³⁺ centers, which showed a stable operation over 300 h at 200 mA cm⁻². A PEMWE with NMO as the anode also showed a stable operation for 160 h at 200 mA cm⁻². In situ Raman, in situ XAS, and DFT calculations have been used to reveal the working mechanism. The performance with 300 h operation at 200 mA cm⁻² is good for noble-metal-free catalysts used in PEMWE. However, Mn based catalysts already showed much better catalytic performance for PEMWE, as reported in the literature (some of them in Fig. 2f). Especially, the Nd doped Mn oxide has been reported in a very similar paper in 2025 (DOI:10.1002/adfm.202423709), which labeled as Nd-γ-MnO₂ catalyst while in this work it is Nd-doped Mn oxide (NMO). The structures in these two papers revealed by XAS are also similar, which are mainly MnO₂ (Mn⁴⁺) with a slight reduction of Mn to Mn³⁺. The literature also showed that Nd-doping would result in optimized binding energy between the catalyst and the oxygen intermediates. Most importantly, the Nd-γ-MnO₂ catalyst showed a much better performance for over 700 h stability at 200 mA cm⁻² and over 1000 h at 100 mA cm⁻² (300 h at 200 mA cm⁻² in this work). Considering the similar composition and structure but the much lower performance, I am not sure about the advancement of this work. There are also some other critical issues should be addressed:

1. In this work the authors emphasize the significant contribution of Mn³⁺ in Mn₂O₃ (from XRD), which is different from typical MnO₂. However, from the XAS data in Fig. 1d, it is mainly MnO₂ (Mn⁴⁺) with only a slight reduction, which is obviously different from the spectrum of Mn₂O₃. So the main content in NMO-0.2 should be MnO₂. The EXAFS spectra in Fig. 1e also confirm this conclusion.
2. The authors claim that “their catalytic activity and stability are limited by the instability of Jahn–Teller (J–T) active Mn³⁺ centers that readily disproportionate in acid and by their narrow potential window” and discuss this point in the introduction part. However, the related references for the importance of Jahn–Teller (J–T) active Mn³⁺ centers (Refs 16–19) are ten years ago, while in recent years significant progress has been made in this research field, in which γ-MnO₂ with Mn⁴⁺ can even work for 1000 h at 200 mA cm⁻² (DOI:10.1038/s41929-023-01091-3). I am not sure about the importance of Mn³⁺ in Mn₂O₃ for the PEMWE. Actually, the Nd-γ-MnO₂ catalyst with similar Mn reduction but without the presence of Mn₂O₃ showed a much better performance.
3. The authors have used in situ XAS to reveal the stability of NMO-0.2 in Fig. 3. Although the white line peak position for NMO-0.2 in Fig. 3e shows only slight changes, the EXAFS curves in Fig. 3h indicate that the Mn–O has become obviously shorter at 1.8 V, which normally means the increased chemical state of Mn. Another abnormal phenomenon is the in situ XAS spectra of γ-MnO₂ in Fig. 3g. The Mn–O bond of γ-MnO₂ should be shorten if the valence state of Mn increases. However, the Mn–O bond has become longer indicating a possible lower chemical state at high voltages. The authors should carefully check and explain the experimental data.
4. Differential electrochemical mass spectrometry (DEMS) data should be provided to confirm the OPM process.
5. Why the stability test and LVS curves were measured in 0.5 M H₂SO₄ but the in situ Raman and XAS were measured in 0.5 M HClO₄ solution?
6. In Table 3 the fitted bond length for NMO-0.2 shows too many decimal places.
7. The XAS spectra (both XANES and EXAFS) after reaction should be provided to check if the electronic structure can recover.

Reviewer #4

(Remarks to the Author)

The manuscript reported the construction of Nd doped γ-MnO₂ (NMO) to achieve durable acidic water oxidation. Combined DFT studies and spectroscopic analysis, the authors attributed the facilitated OER kinetics of NMO to enhanced Mn–O covalency through 4f–2p–3d orbital coupling and the stabilization of J–T–active Mn³⁺ site. However, from my point of view,

this work falls short as the performance characterization in some case exhibit an opposite conclusion compared to recent key study on γ -MnO₂ (Nat Catal 7, 252–261 (2024)). Moreover, the experimental evidence provided does not sufficiently support the proposed mechanism. Critical aspects, including surface electronic structure evolution and catalyst reconstruction under operating conditions, are inadequately addressed. The manuscript could be strengthened by providing more compelling discussion, particularly the individual contributions of different crystal phases. Therefore, in its current form, the novelty and systematic rigor are insufficient for publication in Nature Communications.

1. The confusing aspect is about the OER performance of pristine γ -MnO₂. Recent key study has already demonstrated that γ -MnO₂ exhibited robust OER activity under acidic conditions Nat Catal 7, 252–261 (2024). In contrast, the current manuscript claims that pristine γ -MnO₂ undergoes rapid activity decay within less than 30 h. This discrepancy is not adequately explained and raises concerns regarding the novelty of experimental design.

2. “Operando” XAS characterization section is questionable. The authors provided only Mn K-edge XANES and FT-EXAFS spectra, without showing the corresponding K-space spectra. In general, the observed backscattering signals in FT-EXAFS spectra are strongly affected by noise. Without showing the K-space data, the FT-EXAFS spectra presented in the manuscript are not convincing. In addition, the experimental details of the electrochemical XAS measurements are insufficiently described, including the electrochemical cell configuration, electrode preparation, catalyst loading, and the time resolution of the XAS measurements. Critical questions remain to be addressed, such as: How many spectra were collected at each applied potential? Was beam damage assessed? How were gas bubble formation issues mitigated? What changes in the spectra were observed when gas bubbles formed? The lack of such essential information renders the operando XAS results unconvincing and unacceptable.

3. From the electrochemical data (Figure 2), both γ -MnO₂ and NMO are expected to deliver current densities higher than 200 mA cm⁻² at 1.8 V vs. RHE. This means that under such a condition, substantial gas evolution is inevitable. Gas bubble formation can drastically distort spectroscopic signals. However, no such effects are apparent in the operando Raman and XAS data shown in Fig. 3, raising concerns about the validity of the measurements.

4. In Figure 3a,b, isotropic O18 labelling experiments should be conducted to confirm the assignment of Raman signatures at 750 cm⁻¹ to Mn4+=O.

5. The DFT calculations suggest that Nd doping may induce the formation of multiple crystal phases, including α -Mn₂O₃, β -MnO₂, and R-MnO₂. However, it remains unclear which phase contributes most significantly to the observed OER activity. Additional experimental studies (electrochemical characterizations) involving Nd doping in these individual MnO₂ phases are necessary to provide deeper mechanistic insights.

6. In Supplementary Table S3, the author should also provide the key fitting parameter of S0². Moreover, the σ^2 for NMO-0.2 appears unrealistically small. Typically, a smaller σ^2 corresponds to lower structural disorder and smaller coordination numbers, implying a highly ordered structure. This observation contradicts the central claims of structural distortion in the current study and therefore requires careful reassessment.

7. It is expected that rare earth element underwent oxidation and leached into the electrolyte, resulting structural amorphization (<https://doi.org/10.1038/s41929-025-01476-6>). In such a case, how to precisely model the investigated catalysts based on DFT calculations?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed all the comments raised in my previous review. All revisions, including supplementary experimental theoretical analyses, characterization discussion and mechanism interpretation, have been reasonably supplemented and well explained. I now recommend the acceptance of this paper for publication.

Reviewer #2

(Remarks to the Author)

The revised version is excellent and i would like to suggest the acceptance.

Reviewer #3

(Remarks to the Author)

The authors have provided more experimental data and carefully revised the manuscript. All my questions have been addressed. It can be published now.

Reviewer #4

(Remarks to the Author)

The authors performed additional experiments to address my concerns. In principle, the manuscript can be accepted for publication.

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Point-by-Point Response to the Reviewers

We sincerely thank the Editor and the Reviewers for their careful evaluation of our manuscript, “Nd Doping Enables Efficient and Durable Manganese-Based Water Oxidation Catalysts under Acidic Conditions.” We greatly appreciate the constructive comments and suggestions, which have been invaluable in improving the quality and clarity of our manuscript.

We have carefully considered all comments, performed additional experiments and analyses, and revised the manuscript accordingly. We believe these revisions have substantially strengthened the manuscript and hope that the revised version is now suitable for publication in *Nature Communications*.

For clarity, the reviewers' comments are reproduced in **black**, and our responses are provided in **blue**. All changes made in the revised manuscript are highlighted in **red**.

Reviewers' Comments:

Reviewer #1

The manuscript presents a highly significant advancement in the field of non-noble metal catalysts for OER under acidic conditions. Nd-doped Mn oxide achieves high stability, providing an effective strategy to the challenge of Mn^{3+} instability in acid for Mn-based OER catalyst. This work will be of great interest to the communities working on electrocatalysis, water splitting, and energy materials. However, there are several issues needed to be addressed.

Response: We sincerely thank the reviewer for the positive evaluation of our work and for recognizing its potential significance in developing non-noble-metal OER catalysts for acidic media. We also appreciate the reviewer's constructive comments, which helped us clarify the structural origin, phase-specific contribution, and mechanistic interpretation of Nd-doped Mn oxides.

In response to the reviewer's comments, we have revised the manuscript and Supplementary Information by adding new experimental comparison, additional DFT calculations, and expanded mechanistic discussion. These revisions clarify the roles of Nd doping, mixed-phase Mn oxide domains, and Mn^{3+} stabilization in improving acidic OER activity and durability. We believe the revised manuscript now presents a clearer and more robust structure–property–mechanism relationship.

R1–1. Nd doping was found to alter the structural parameters of Mn oxides. Did the changes of Mn-Mn and Mn-O bond lengths in the DFT models agree with the experimental observations? This will largely affect the electronic structures. Besides, did the author consider the oxygen vacancies in building the DFT model? The structural models used for calculations are idealized and considering the effect of oxygen vacancies and Nd doping concentration on the lattice structure would make the simulations more consistent with experimental results

Response: We thank the reviewer for this important and insightful comment. We agree that Nd-induced changes in Mn–Mn and Mn–O bond lengths can affect the electronic structure and therefore need to be validated against experimental structural information. We also agree that oxygen vacancies (O_V) should be considered because they may affect the local coordination environment of Nd-doped Mn oxides.

To address this point, we compared the Mn–O bond lengths obtained from the optimized DFT structures with those derived from EXAFS/XRD analyses (**Supplementary Table S3**). The calculated Mn–O bond lengths are in good agreement with the experimental values and reproduce the Nd-induced bond-length variation, supporting that the DFT models reasonably capture the local Mn–O coordination environment of the Nd-doped catalyst. Although the Nd concentration in the DFT models (3.125%) is lower than the experimentally estimated doping level (8–14%) for computational feasibility, the agreement in local structural parameters supports the validity of our DFT models for discussing the Nd-induced electronic structure modulation.

We further performed additional O_V calculations for Nd-doped α - Mn_2O_3 , β - MnO_2 , and R- MnO_2 (**Supplementary Fig. 52**). These calculations show that O_V formation is thermodynamically unfavorable in Nd- α - Mn_2O_3 and Nd-R- MnO_2 , whereas the O_V formation energy in Nd- β - MnO_2 is relatively low under the chosen reference condition, suggesting that O_V may be more accessible in this phase but do not dominate the overall structural evolution. Together with the electron-addition control calculations, these results support our conclusion that Nd-derived electron donation is the primary origin of the Mn-centered Jahn-Teller distortion, while O_V may contribute to local structural heterogeneity.

We have added the corresponding structural comparison and O_V calculations to the revised manuscript and Supplementary Information, as shown below.

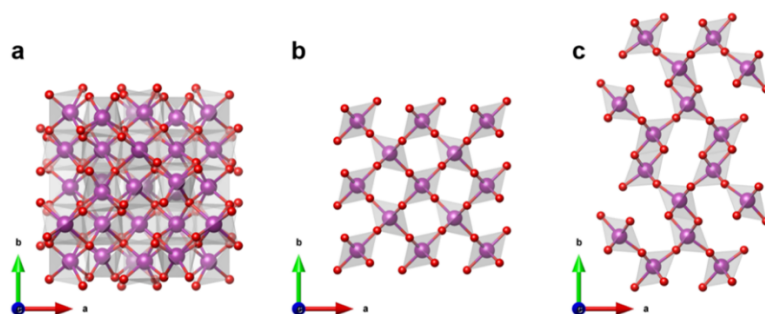
[Lines 370 to 400 in the revised manuscript]

Guided by the experimentally identified phase-dependent contributions, we next performed

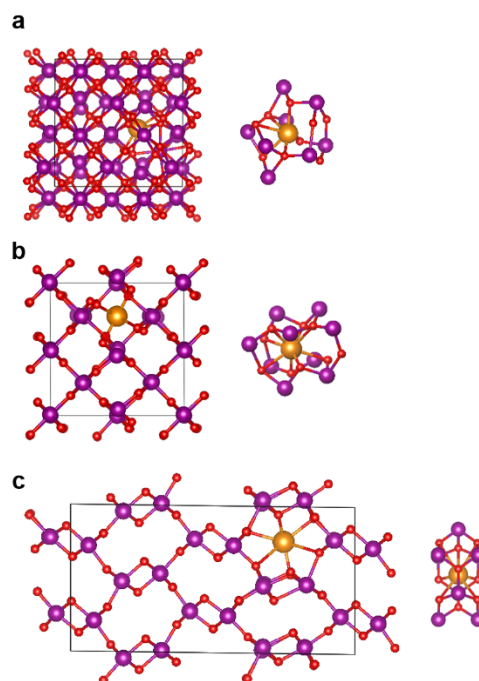
DFT calculations to examine how Nd incorporation modifies the local coordination structure and electronic properties of each Mn oxide polymorph. Based on the PXRD and HRTEM results, structural models were constructed for three representative Mn oxide polymorphs in the Nd-doped NMO catalyst: α -Mn₂O₃, β -MnO₂, and R-MnO₂ (**Supplementary Fig. 47 and Supplementary Table 1**). Although α -Mn₂O₃ is not present in the pristine γ -MnO₂ sample, the pristine α -Mn₂O₃ model was included as a phase-specific reference to evaluate how Nd incorporation modifies the α -Mn₂O₃ component observed in NMO. Nd-doped models were generated by placing Nd atoms at interstitial sites within the open-channel frameworks of each polymorph, considering the large ionic-radius mismatch between Mn and Nd (**Supplementary Fig. 48**).

The optimized DFT structures reproduce the experimentally observed local structural evolution. The calculated Mn-O bond lengths agree with the EXAFS/XRD-derived values and reproduce the Nd-induced bond-length variation (**Supplementary Fig. 49 and Supplementary Table S3**), supporting the validity of the models for describing the local coordination environment of Nd-doped Mn oxides. The optimized Nd-doped structures further reveal local distortion of the surrounding Mn-O polyhedra, indicating that Nd doping modifies the Mn-O coordination environment. In Mn⁴⁺-dominant β -MnO₂ and R-MnO₂, electron donation from Nd can partially convert Mn⁴⁺ toward a Mn³⁺-like electronic state, producing electronically driven Jahn–Teller distortion of the MnO₆ octahedra. In contrast, α -Mn₂O₃, which is already Mn³⁺-dominant and structurally distorted, shows a less pronounced additional distortion upon Nd incorporation.

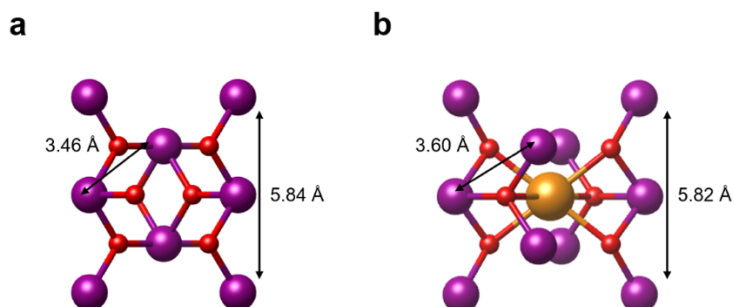
Although the observed distortion may also be affected by local strain arising from the large ionic size of Nd, control calculations in which extra electrons were artificially introduced into pristine β -MnO₂ and R-MnO₂ produced even stronger octahedral distortions than those in the Nd-doped Mn oxide systems (**Supplementary Figs. 50, 51**). This result suggests that the Jahn–Teller distortion is governed predominantly by Nd-derived electron donation rather than by ionic-size-induced lattice strain alone. Additional oxygen-vacancy (O_v) calculations further indicate that O_v formation does not dominate the observed structural evolution. Together, these control calculations support that Nd-derived electron donation is the primary origin of the Mn-centered Jahn–Teller distortion (**Supplementary Fig. 52**).



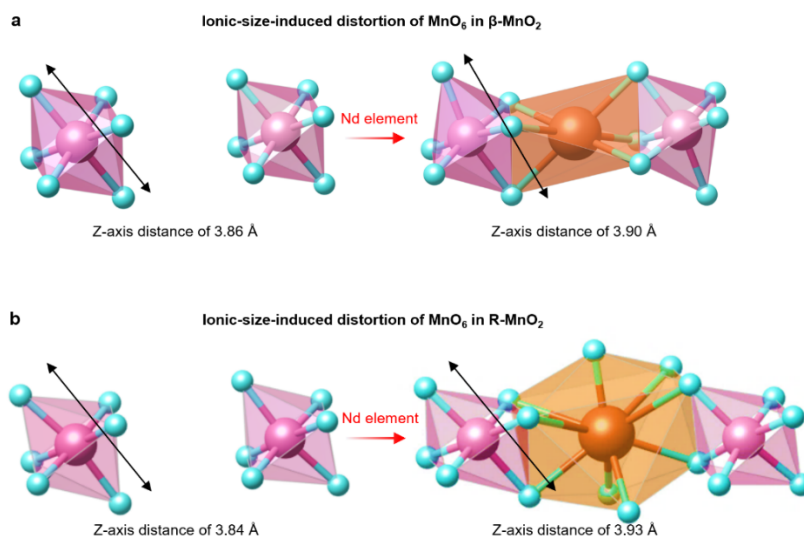
Supplementary Fig. 47 Structural models of Mn oxides polymorphs. Top-view atomic structures of (a) α - Mn_2O_3 , (b) β - MnO_2 , and (c) R-MnO_2 models used for DFT calculations.



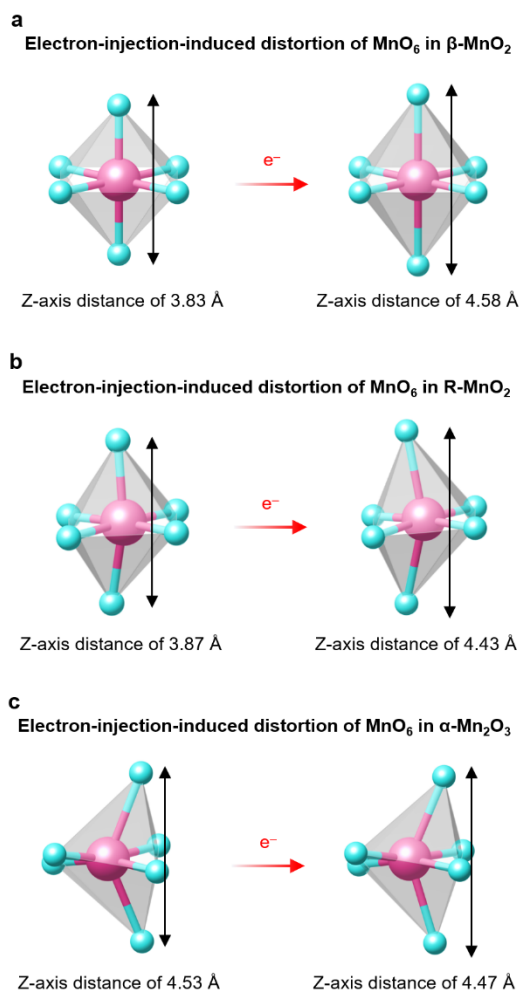
Supplementary Fig. 48 Structural models of Nd-doped Mn oxides polymorphs. Top-view atomic structures and corresponding local Nd coordination environments of (a) $\text{Nd-}\alpha\text{-Mn}_2\text{O}_3$, (b) $\text{Nd-}\beta\text{-MnO}_2$, and (c) Nd-R-MnO_2 models used for DFT calculations.



Supplementary Fig. 49 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.

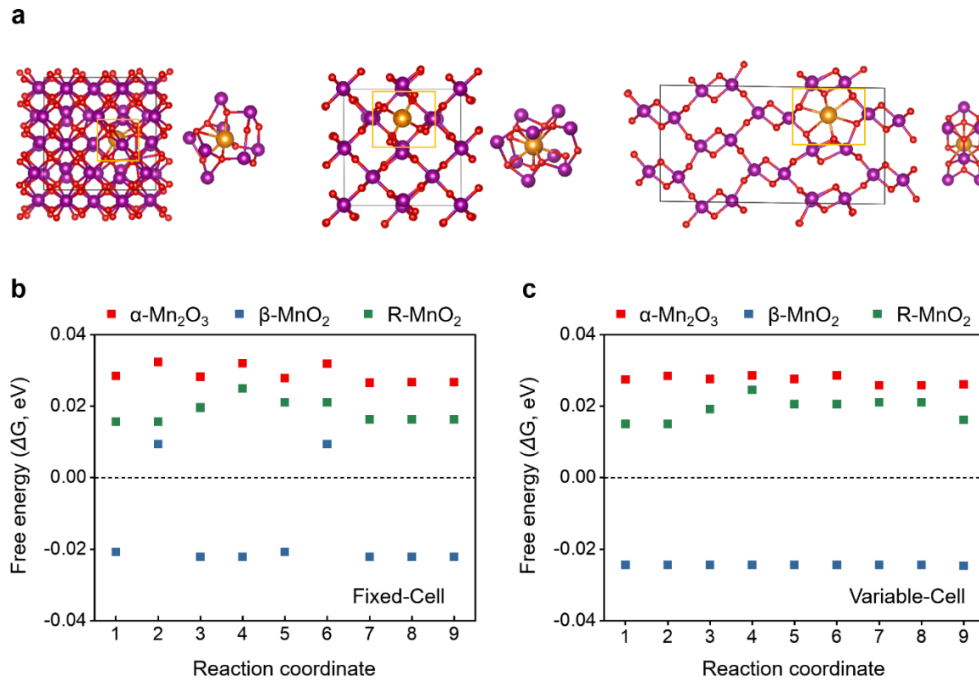


Supplementary Fig. 50 Nd-induced structural distortion of MnO_6 octahedra. (a) Structural distortion in $\beta\text{-MnO}_2$ octahedra, and (b) Structural distortion in R-MnO_2 octahedra.



Supplementary Fig. 51 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.²⁰ 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. 52 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 $\text{Nd-}\alpha\text{-Mn}_2\text{O}_3$, $\text{Nd-}\beta\text{-MnO}_2$, and Nd-R-MnO_2 . (b, c) Oxygen vacancy formation energies calculated under fixed-cell and variable-cell relaxation conditions, respectively.

Supplementary Table 3 Fitting parameters of the Mn K-edge EXAFS spectra for $\gamma\text{-MnO}_2$ 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
$\gamma\text{-MnO}_2$	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		

R1–2. The NMO catalyst is identified as a mixed phase of α -Mn₂O₃, β -MnO₂, and R-MnO₂. While the synergistic effect is highlighted, the individual contribution of each phase to the overall activity and stability is not fully decoupled. However, the DFT calculations appropriately model the three phases separately. But it remains unclear from the experimental data whether one phase is primarily responsible for activity while another enhances stability. Please state the experimental basis of the DFT models. The authors should also discuss the potential role of hetero interfaces in facilitating charge transfer or stabilizing active sites.

Response: We thank the reviewer for this important comment. We agree that the original manuscript did not sufficiently clarify the experimental basis for modeling α -Mn₂O₃, β -MnO₂, and R-MnO₂, separately, nor the phase-specific contributions of these polymorphs to the overall activity and stability of the mixed-phase NMO catalyst.

(1) Experimental basis for the DFT Models

The experimental basis for the DFT models is the structural characterization of NMO-0.2. PXRD/Rietveld refinement, HRTEM, and XAS analyses identify that NMO-0.2 is a Nd-doped MnO₂-rich mixed-phase oxide containing α -Mn₂O₃, β -MnO₂, and R-MnO₂. We therefore modeled these three experimentally observed polymorphs separately to decouple how Nd incorporation modifies their local structural and electronic properties.

To further clarify the phase-specific contribution experimentally, we prepared phase-enriched Mn oxide reference catalysts using the same thermal-decomposition platform and compared their OER activity and stability in 0.5 M H₂SO₄. Although complete phase purity could not be achieved because of the inherent coexistence of Mn oxide polymorphs during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. Electrochemical measurements showed that the α -Mn₂O₃-rich reference exhibited the highest OER activity, whereas the β /R-MnO₂-rich references displayed better stability under acidic OER conditions. Nd incorporation further improved the activity and/or stability of these phase-enriched references. These results suggest complementary phase contributions in NMO-0.2: α -Mn₂O₃ provides activity-promoting Mn³⁺-rich motifs, while the β /R-MnO₂-rich framework contributes structural robustness and additional electronically modulated Mn sites.

We note that the DFT calculations are intended to elucidate the electronic and structural consequences of Nd incorporation within each experimentally identified polymorph, rather than to directly predict the overall activity trend of the mixed-phase catalyst. The

experimentally observed activity and stability are additionally influenced by phase coexistence, the population of structural Mn^{3+} motifs, catalyst morphology, and stability under acidic OER conditions.

(2) Potential role of heterointerfaces (or mixed-phase domain boundaries)

We also agree that interphase electronic interaction may contribute to charge transfer and active-site stabilization in the mixed-phase NMO catalyst. To avoid over-assigning a specific idealized interface mechanism, we revised the wording from “heterointerface” to “mixed-phase domain boundary” throughout the manuscript. This terminology better reflects the thermally derived mixed-phase catalyst, which likely contains non-ideal domain boundaries with local disorder, defect distributions, and compositional fluctuations.

To assess the possible direction of interphase charge transfer, we compared the work functions of representative $\alpha\text{-Mn}_2\text{O}_3$ (111), $\beta\text{-MnO}_2$ (110), and R- MnO_2 (100) slab models. The lower work function of $\alpha\text{-Mn}_2\text{O}_3$ compared with $\beta\text{-MnO}_2$ and R- MnO_2 suggest a thermodynamic driving force for electron transfer from $\alpha\text{-Mn}_2\text{O}_3$ toward MnO_2 -rich domains upon interfacial contact. Such interphase charge redistribution could help stabilize catalytically relevant Mn^{3+} species and locally modulate the Mn–O electronic structure near mixed-phase domain boundaries. While direct verification of this process would require explicit interface models beyond the scope of the present study, we now discuss this possible contribution in the revised manuscript.

We have added the corresponding phase-enriched reference experiments, work-function analysis, and related discussion to the manuscript and Supplementary Information, as shown below.

[Lines 43 to 45 in the revised manuscript]

Phase-enriched reference experiments and density functional theory calculations show that Nd-doped $\alpha\text{-Mn}_2\text{O}_3$ promotes OPM through structural Mn^{3+} motifs, whereas $\beta/\text{R-MnO}_2$ -rich domains provide structural robustness.

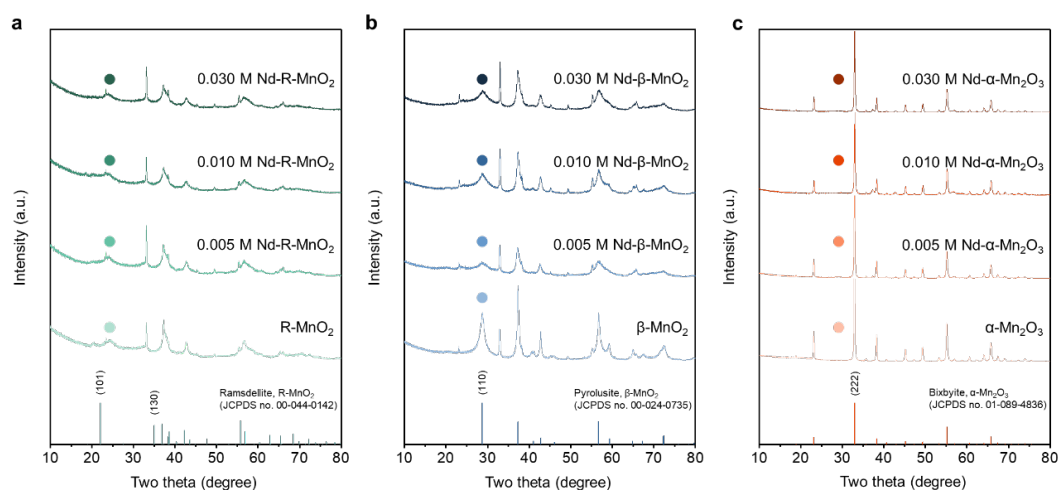
[Lines 89 to 94 in the revised manuscript]

Phase-enriched reference experiments reveal that $\alpha\text{-Mn}_2\text{O}_3$ -rich domains provide activity-promoting structural Mn^{3+} motifs, whereas $\beta/\text{R-MnO}_2$ -rich domains contribute structural robustness under acidic OER conditions. Density functional theory (DFT) calculations

further reveal phase-dependent OER pathways, with Nd-doped α -Mn₂O₃ favoring an OPM pathway and Nd-doped β /R-MnO₂ remaining absorbate evolution mechanism (AEM)-dominant with reduced OER barriers.

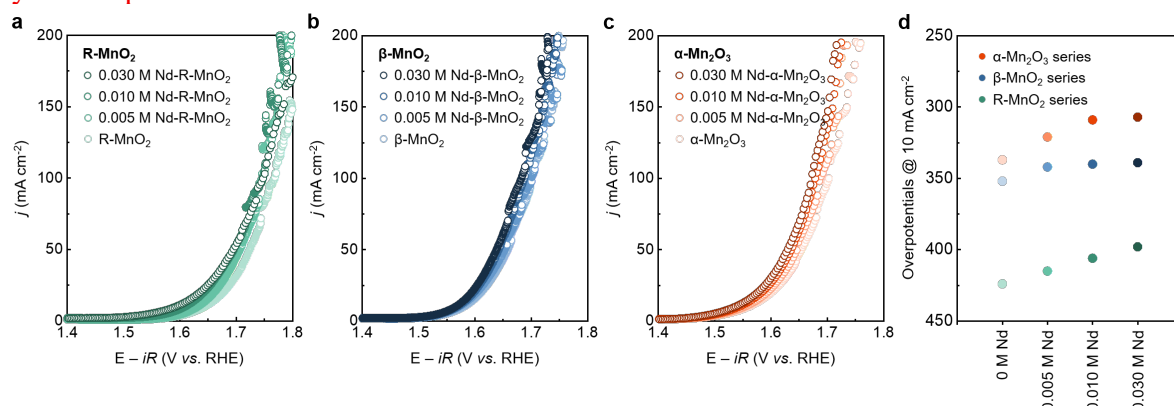
[Lines 344 to 358 in the revised manuscript]

To experimentally examine the role of each Mn oxide polymorph in the mixed-phase NMO catalyst, phase-enriched Mn oxide reference catalysts were prepared using the same thermal-decomposition platform (**Supplementary Fig. 44**). Although complete phase purity could not be achieved because of the inherent coexistence of Mn oxide polymorphs during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. Electrochemical measurements showed that the α -Mn₂O₃-rich reference exhibited the highest OER activity (**Supplementary Fig. S45**), whereas the β /R-MnO₂-rich references displayed superior stability under acidic conditions (**Supplementary Fig. 46**). Nd incorporation further improved the activity and/or stability of all phase-enriched references. Therefore, the enhanced OER performance of NMO-0.2 is attributed to the combined contribution of minority α -Mn₂O₃-derived structural Mn³⁺ motifs and electronically induced Mn³⁺ within the dominant MnO₂-rich framework, rather than to an α -Mn₂O₃-dominant phase. These results provide the experimental basis for the phase-specific DFT analysis presented below, where each polymorph is modeled separately to clarify how Nd incorporation modifies its local structural and electronic properties.

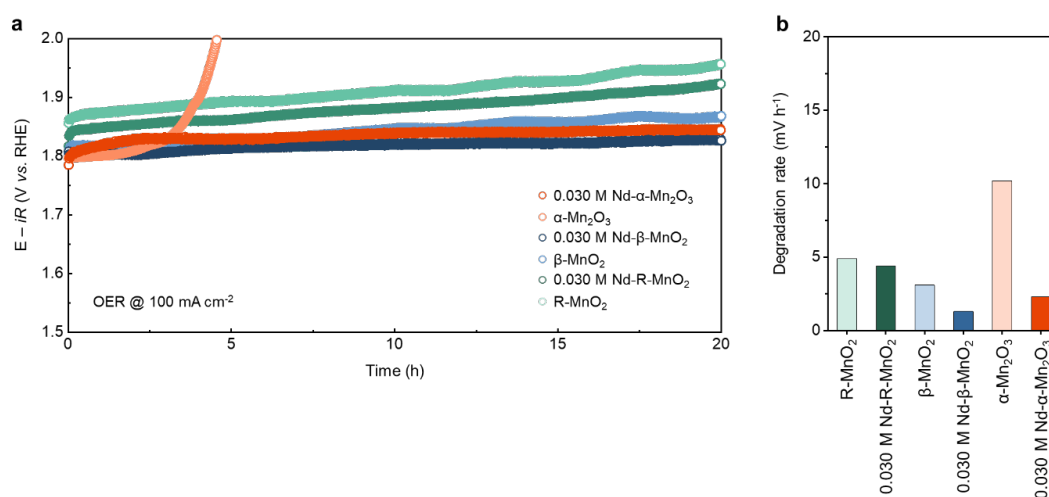


Supplementary Fig. 44 Phase-controlled synthesis of Mn oxide reference catalysts. XRD patterns of (a) R-MnO₂-rich, (b) β -MnO₂-rich, and (c) α -Mn₂O₃ reference catalysts prepared by thermal decomposition at different temperatures with varied Nd precursor concentrations. The characteristic reflections 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.



Supplementary Fig. 45 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.



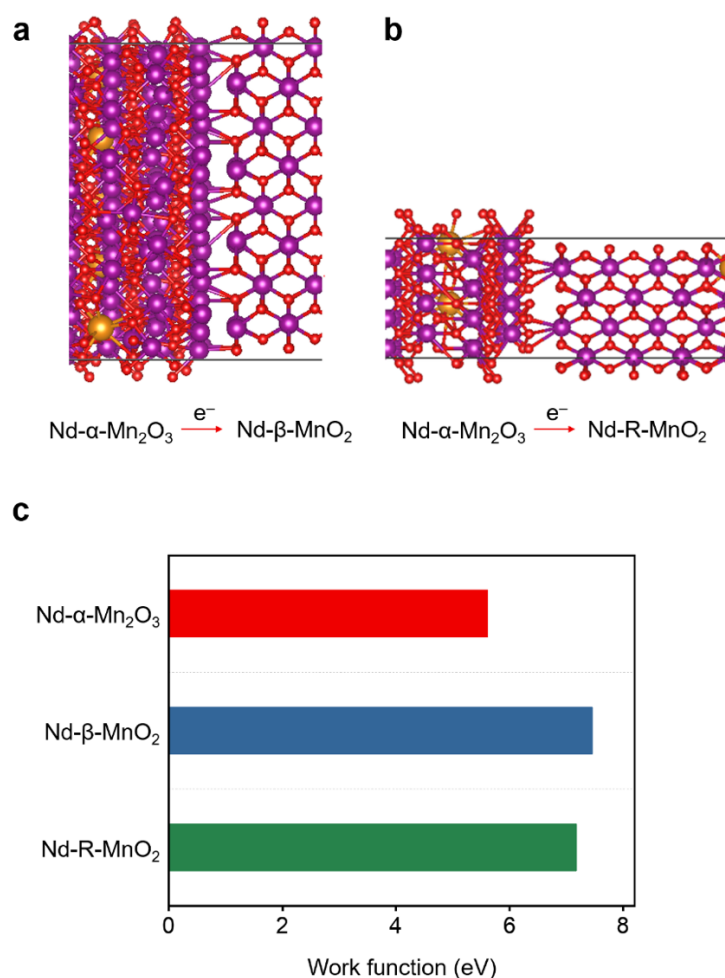
Supplementary Fig. 46 Phase-dependent OER stability of Nd-modified Mn oxide reference catalysts. (a) Chronopotentiometric stability curves of phase-controlled R-MnO₂-rich, β -MnO₂-rich, and α -Mn₂O₃ reference catalysts with and without Nd doping measured at 100 mA cm⁻² in 0.5 M H₂SO₄. (b) Comparison of degradation rates derived from the chronopotentiometric stability tests.

[Lines 139 to 143 in the revised manuscript]

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) further revealed that NMO-0.2 formed a mixed-phase domain boundary composed of distinct α -Mn₂O₃ (Fig. 1b, R1) and R-MnO₂ (Fig. 1b, R2) phases, together with clear evidence of Nd incorporation into the Mn oxide lattice (Fig. 1c; Supplementary Figs. 9–13).

[Lines 435 to 437 in the revised manuscript]

Work-function calculations further suggest possible interphase charge redistribution between α - Mn_2O_3 and MnO_2 -rich domains, which may additionally modulate the local Mn–O electronic structure (Supplementary Fig. 58).



Supplementary Fig. 58 Work-function comparison of Mn-oxide polymorphs. (a) Schematic illustration of interfacial electron transfer from $\text{Nd-}\alpha\text{-Mn}_2\text{O}_3$ to $\text{Nd-}\beta\text{-MnO}_2$ and (b) from $\text{Nd-}\alpha\text{-Mn}_2\text{O}_3$ to Nd-R-MnO_2 , driven by the work-function difference. (c) Calculated work functions of $\text{Nd-}\alpha\text{-Mn}_2\text{O}_3$ (111), $\text{Nd-}\beta\text{-MnO}_2$ (110), and Nd-R-MnO_2 (100) slab models. The lower work function of $\alpha\text{-Mn}_2\text{O}_3$ relative to $\beta\text{-MnO}_2$ and R-MnO_2 suggests a thermodynamic driving force for electron redistribution from $\alpha\text{-Mn}_2\text{O}_3$ -rich domains toward MnO_2 -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 Mn^{3+} species near mixed-phase domain boundaries.

[Lines 587 to 595 in the revised Supplementary Information]

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 $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ precursor solution was drop-cast onto carbon fiber paper and thermally decomposed at the designated temperature. For Nd-doped phase-rich Mn oxides, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor solutions (0.005, 0.010, or 0.030 M) were added to the 3 M $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution. Subsequently, 60 μ L of each mixed precursor solution was drop-cast onto carbon fiber paper and calcined at the corresponding temperature.

R1–3. In Figure 4a, comparison of α - Mn_2O_3 and Nd-doped α - Mn_2O_3 is not proper as there is no α - Mn_2O_3 in the non-Nd-doped γ - MnO_2 .

Response: We thank the reviewer for this insightful comment. We agree that pristine γ - MnO_2 does not contain an α - Mn_2O_3 phase; therefore, the comparison shown in Fig. 4a could be misleading if interpreted as a direct comparison between the experimentally prepared γ - MnO_2 and NMO samples

Our intention, however, was not to compare the pristine γ - MnO_2 catalyst with the Nd-doped NMO catalyst on a phase-to-phase basis. Instead, the pristine α - Mn_2O_3 model was included as a phase-specific reference to isolate the effect of Nd incorporation within the α - Mn_2O_3 framework, because α - Mn_2O_3 is experimentally identified as a minority phase in NMO. This reference allow us to evaluate how Nd modifies the electronic structure and local coordination environment of the α - Mn_2O_3 component observed in NMO.

To avoid this ambiguity, we have revised the manuscript to explicitly clarify the purpose of the pristine α - Mn_2O_3 reference model, as shown below.

[Lines 375 to 377 in the revised manuscript]

Although α - Mn_2O_3 is not present in the pristine γ - MnO_2 sample, the pristine α - Mn_2O_3 model was included as a phase-specific reference to evaluate how Nd incorporation modifies the α - Mn_2O_3 component observed in NMO.

R1–4. The authors propose the OPM mechanism through O–O coupling facilitated by labile $^*\text{O}$ species. But there is lack of both direct experimental and DFT evidences. The authors could consider using ^{18}O isotope labeling coupled with in-situ mass spectrometry to directly verify the source of oxygen in the produced O_2 and confirm the O–O bond formation pathway.

Response: We sincerely thank the reviewer for this valuable suggestion. We agree that isotope-labelling experiments coupled with *in situ* mass spectrometry provide important experimental

evidence for probing the suggested OPM mechanism in our NMO catalysts.

(1) Isotope Labelling Experiments

In response, we performed additional *in situ* differential electrochemical mass spectrometry (DEMS) measurements using ^{18}O -labelled $\gamma\text{-MnO}_2$ and NMO-0.2 catalysts in ^{16}O -containing 0.5 M H_2SO_4 electrolyte. The ^{18}O -labelled catalysts were prepared by electrochemical treatment in H_2^{18}O -based 0.5 M H_2SO_4 , followed by thorough rinsing with H_2^{16}O to remove physically adsorbed H_2^{18}O before DEMS measurements. Our isotope-labelling DEMS measurements show that NMO-0.2 exhibits substantially stronger ^{18}O -labelled oxygen signals than $\gamma\text{-MnO}_2$. In an OPM-type pathway, oxygen species associated with the catalyst surface or near-surface lattice sites can participate in O–O bond formation together with oxygen species supplied from the electrolyte. Therefore, the detection of isotope-labelled oxygen products at $m/z = 34$ ($^{18}\text{O}^{16}\text{O}$) and $m/z = 36$ ($^{18}\text{O}^{18}\text{O}$) provides evidence for the involvement of catalyst-associated oxygen species during OER (*Nat. Catal.* **2021**, 4, 1012). These observations are consistent with our *in situ* Raman results, which reveal earlier formation of labile $^*\text{O}$ species on NMO-0.2. Together, these complementary results provide additional experimental support for the proposed OPM-like pathway.

(2) DFT Calculations

In response, we calculated the full Gibbs free energy profiles of both AEM and OPM pathways for pristine and Nd-doped Mn oxide slabs, including the adsorption energetics of key OER intermediates, as described in our response to Comment 5. The calculations show that Nd doping lowers the OER barriers in all examined Mn oxide phases and that only Nd-doped $\alpha\text{-Mn}_2\text{O}_3$ preferentially follows the OPM pathway, whereas Nd-doped $\beta\text{-MnO}_2$ and R- MnO_2 remain AEM-dominant with reduced OER barriers.

Accordingly, we have added the *in situ* isotope-labelling DEMS results to the revised manuscript and Supplementary Information and updated the Methods section to describe the DEMS measurement protocol, as shown below.

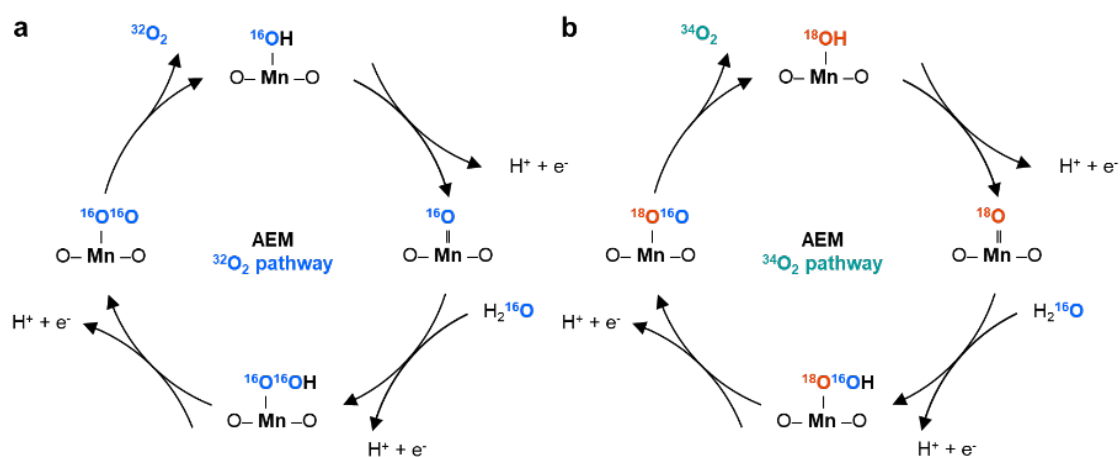
[Lines 41 to 43 in the revised manuscript]

In situ Raman/ X-ray spectroscopy and isotope-labelling experiments support an oxide path mechanism (OPM) and suppressed Mn overoxidation and dissolution.

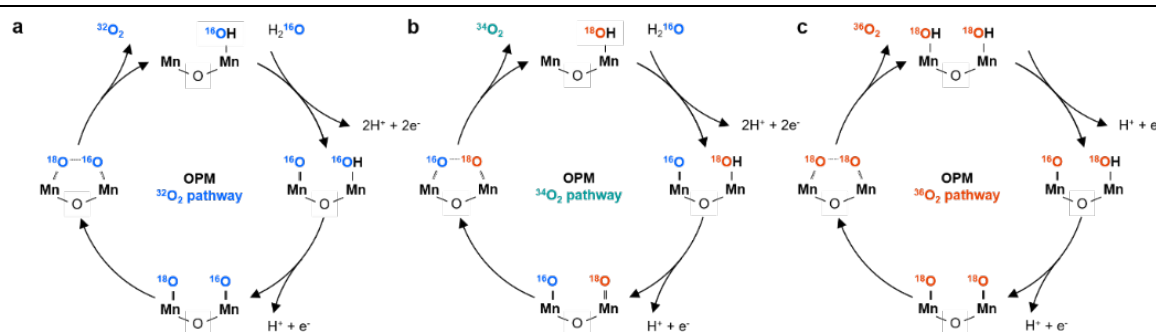
[Lines 295 to 310 in the revised manuscript]

To further probe the proposed oxygen-participating mechanism, we performed *in situ* differential electrochemical mass spectrometry (DEMS) using ^{18}O -labelled $\gamma\text{-MnO}_2$ and NMO-0.2 catalysts in ^{16}O -containing 0.5 M H_2SO_4 . In an OPM-type pathway, catalyst-associated ^{18}O species can participate in O–O bond formation together with oxygen species supplied from H_2^{16}O . Thus, the detection of isotope-labelled oxygen products at $m/z = 34$ and $m/z = 36$, corresponding to $^{34}\text{O}_2$ ($^{18}\text{O}^{16}\text{O}$) and $^{36}\text{O}_2$ ($^{18}\text{O}^{18}\text{O}$), respectively, provides evidence for the involvement of catalyst-associated oxygen species during OER (Supplementary Figs. 39, 40).

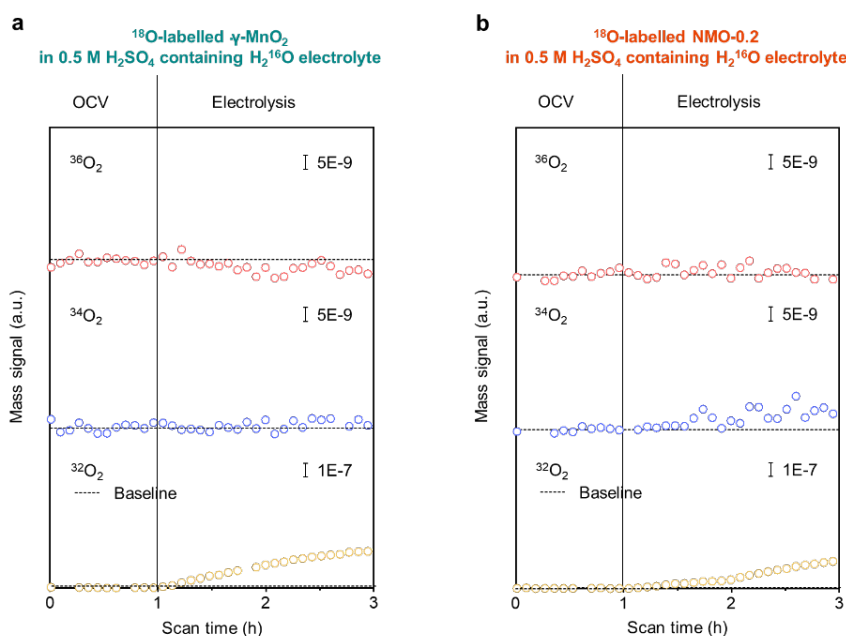
Compared with $\gamma\text{-MnO}_2$, NMO-0.2 exhibited more pronounced isotope-labelled oxygen signals during OER, with detectable $m/z = 32, 34$, and 36 signals corresponding to $^{32}\text{O}_2$, $^{34}\text{O}_2$, and $^{36}\text{O}_2$, respectively (Supplementary Fig. 41). The appearance of mixed-isotope oxygen products supports the participation of catalyst-associated oxygen species in the O–O coupling process on NMO-0.2. Together with the *in situ* Raman observation of the earlier formation of labile $^*\text{O}$ species, the isotope-labelling DEMS results support an OPM-like pathway in which surface or near-surface oxygen intermediates participate in O–O bond formation while the Mn–O framework is largely preserved (Fig. 3c).



Supplementary Fig. 39 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 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. 40 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. 41 *In situ* DEMS analysis of ^{18}O -labelled $\gamma\text{-MnO}_2$ and NMO-0.2 during acidic OER. *In situ* DEMS profiles of ^{18}O -labelled (a) $\gamma\text{-MnO}_2$ and (b) NMO-0.2 measured in H_2^{16}O -containing $0.5\text{ M H}_2\text{SO}_4$ 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.

[Lines 491 to 493 in the revised manuscript]

In situ XAS, Raman, and DEMS analyses collectively show that Nd doping stabilizes Jahn–Teller–active Mn^{3+} centers, suppresses Mn overoxidation and dissolution, and promotes a predominantly OPM-like pathway.

[Lines 200 to 217 in Supplementary Information]

***In situ* differential electrochemical mass spectrometry (DEMS) measurement with isotope ^{18}O -labelling**

In situ DEMS measurements with isotope labelling were conducted to probe the involvement of catalyst-associated oxygen species during OER. The DEMS system was connected to an electrochemical cell operated at ambient pressure, allowing the gaseous OER products generated at the working electrode to be continuously transferred to the mass spectrometer for real-time analysis. For isotope labelling, the catalyst-coated electrodes were electrochemically treated at a constant current density of 50 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ prepared with H_2^{18}O , allowing ^{18}O -labelled oxygen species to be incorporated onto or exchanged with the catalyst surface. After labelling, the electrodes were thoroughly rinsed with H_2^{16}O to remove physically adsorbed H_2^{18}O , while chemically incorporated or surface-bound ^{18}O species remained on the catalyst. The *in situ* DEMS measurements were then performed under a constant current density of 50 mA cm^{-2} in a three-electrode configuration using H_2^{16}O -containing H_2SO_4 . During OER, the gaseous O_2 products were continuously monitored by mass spectrometry. The signals at $m/z = 32, 34$, and 36 were assigned 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. Before each measurement, the electrolyte was purged with high-purity Ar to remove dissolved oxygen. The isotope-labelled oxygen signals were used to evaluate the participation of catalyst-associated oxygen species in O–O bond formation during acidic OER.

R1–5. It is recommended to compare the calculated adsorption energies of OER intermediates, which helps validate the theoretical model. Besides, the DFT energy profile for the whole OER pathway will also claim the of feasibility the OPM mechanism.

Response: We thank the reviewer for this valuable suggestion. In response, we calculated the full Gibbs free energy profiles of both AEM and OPM pathways for pristine and Nd-doped Mn-oxide slabs, including the adsorption energetics of key OER intermediates.

The additional calculations show that the OER pathway is phase-dependent rather than universally OPM-dominant. Pristine $\alpha\text{-Mn}_2\text{O}_3$ (111), $\beta\text{-MnO}_2$ (110), and R-MnO_2 (100) preferentially follow the conventional AEM pathway, with the $^*\text{OH}$ -to- $^*\text{O}$ step as the rate-determining step (RDS). Upon Nd doping, the OER barriers decrease in all phases. Notably, only Nd- $\alpha\text{-Mn}_2\text{O}_3$ favors the OPM pathway, consistent with the activity-promoting role of the $\alpha\text{-Mn}_2\text{O}_3$ -rich reference observed experimentally, whereas Nd- $\beta\text{-MnO}_2$ and Nd-R- MnO_2

remain AEM-dominant. These results indicate that Nd doping facilitates OER through phase-dependent pathways, with structural Mn^{3+} in Nd- α - Mn_2O_3 promoting OPM and electronically induced Mn^{3+} in Nd- β /R- MnO_2 improving AEM energetics.

We have added the complete AEM/OPM Gibbs free energy diagrams and corresponding discussion to the revised manuscript and Supplementary Information, as shown below.

[Lines 43 to 45 in the revised manuscript]

Phase-enriched reference experiments and density functional theory calculations show that Nd-doped α - Mn_2O_3 promotes OPM through structural Mn^{3+} motifs, whereas β /R- MnO_2 -rich domains provide structural robustness.

[Lines 92 to 96 in the revised manuscript]

Density functional theory (DFT) calculations further reveal phase-dependent OER pathways, with Nd-doped α - Mn_2O_3 favoring an OPM pathway and Nd-doped β /R- MnO_2 remaining adsorbate evolution mechanism (AEM)-dominant with reduced OER barriers. Nd doping also stabilizes Jahn–Teller-active Mn^{3+} centers while enhancing Mn–O covalency through $4f$ – $2p$ – $3d$ orbital coupling.

[Lines 414 to 427 in the revised manuscript]

To clarify the phase-dependent role of Nd doping in OER, we compared the Gibbs free energy diagrams of AEM and OPM for pristine and Nd-doped Mn-oxide slabs (**Figs. 4d–g and Supplementary Figs. 54–57**). Pristine α - Mn_2O_3 (111), β - MnO_2 (110), and R- MnO_2 (100) preferentially follow the conventional AEM pathway (**Supplementary Fig. 54**), whereas Nd doping lowers the OER barriers in all three phases (**Supplementary Figs. 55–57**). Notably, only Nd- α - Mn_2O_3 favors the OPM pathway (**Fig. 4d and Supplementary Fig. 55**), consistent with activity-promoting role of α - Mn_2O_3 -rich references observed experimentally. In contrast, Nd- β - MnO_2 and Nd-R- MnO_2 remain AEM-dominant, indicating that Nd doping improves their activity mainly by facilitating the conventional adsorbate-mediated OER steps rather than by inducing dual-site OPM activation. These results suggest that Nd doping accelerates OER through phase-dependent pathways (**Fig. 4g**): structural Mn^{3+} in Nd- α - Mn_2O_3 promotes OPM, whereas electronically induced Mn^{3+} in Nd- β - MnO_2 and Nd-R- MnO_2 enhances AEM. This highlights that the catalytic role of Mn^{3+} is governed not only by oxidation state but also by its structural environment.

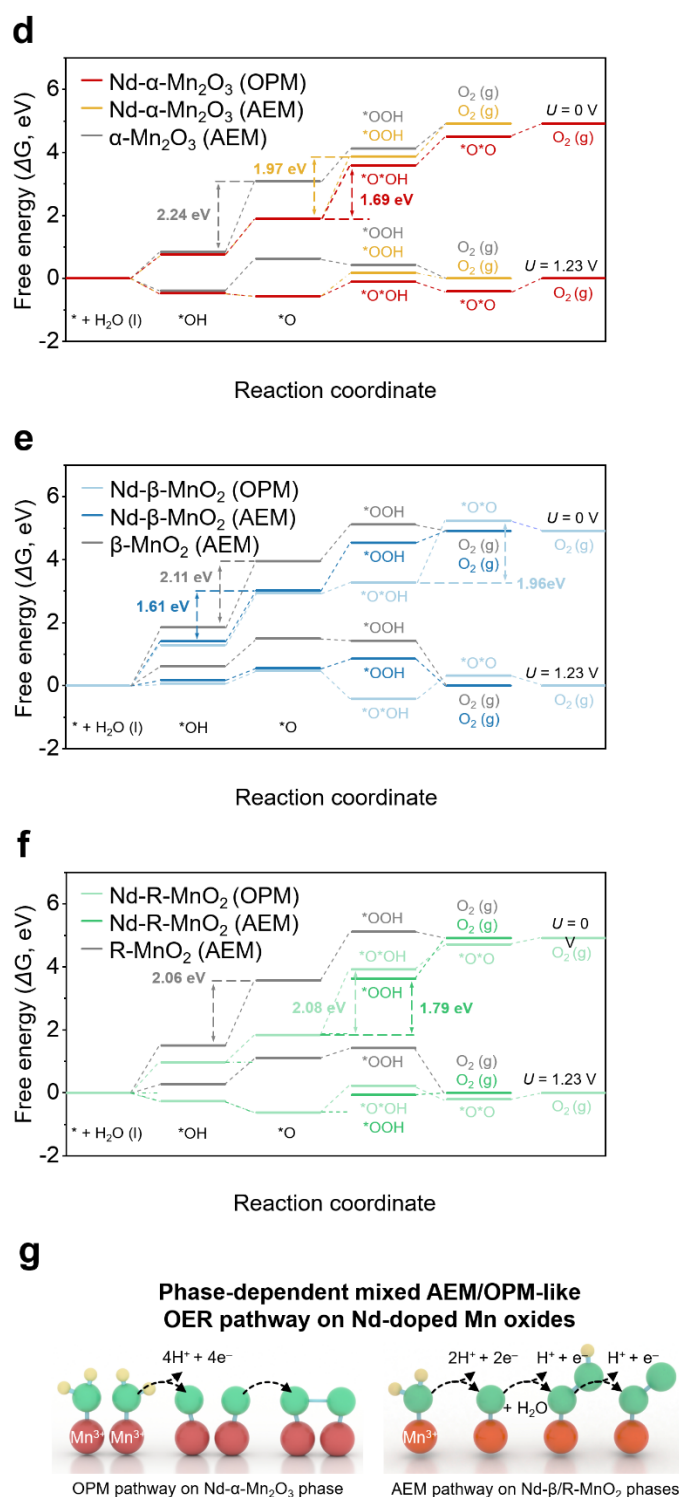
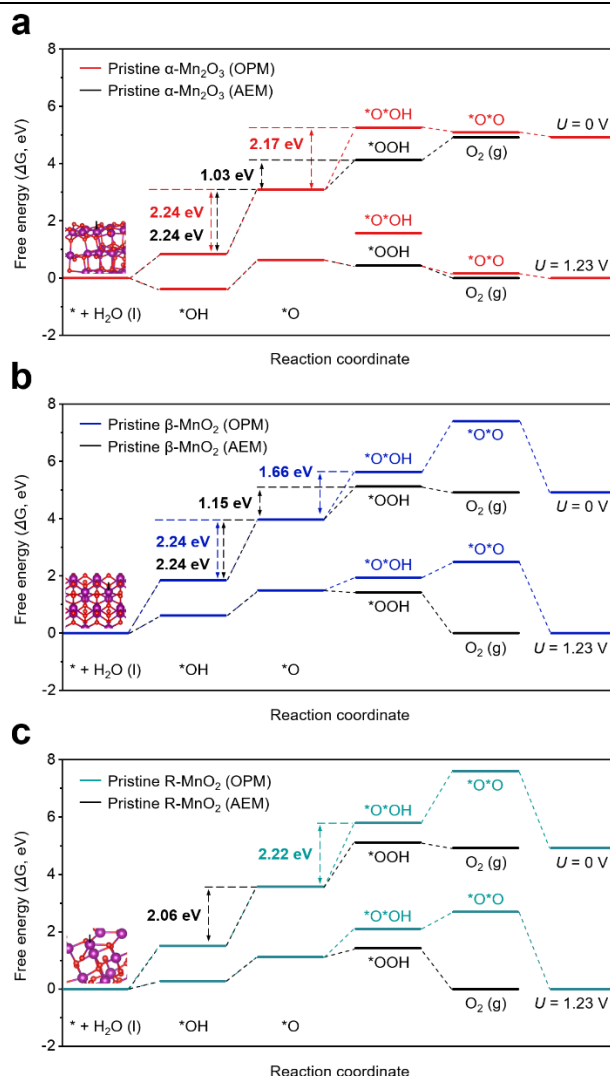


Fig. 4 Nd-induced electronic reconstruction and phase-dependent OER mechanisms in Mn oxides. **d–g** Gibbs free energy diagrams of AEM and OPM pathways on pristine and Nd-doped Mn-oxide slabs, showing an OPM-favored pathway in Nd- α -Mn₂O₃ (111) and AEM-dominant pathways in Nd- β -MnO₂ (110) and Nd-R-MnO₂ (100). **g** Schematic illustration of phase-dependent OER pathways, in which structural Mn³⁺ in Nd- α -Mn₂O₃ favors OPM, whereas electronically induced Mn³⁺ enhances AEM.



Supplementary Fig. 54 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.

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.

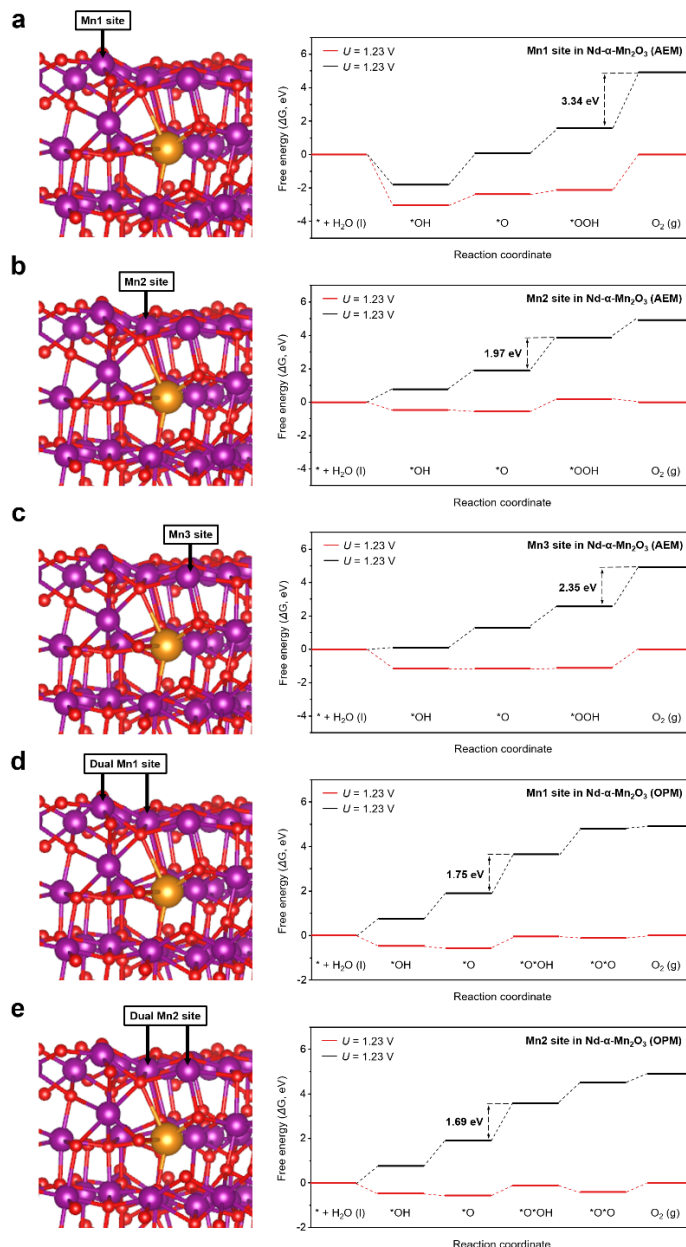
For pristine α - Mn_2O_3 , both AEM and OPM share the same rate-determining step (RDS), namely the $^*\text{OH}$ -to- $^*\text{O}$ conversion, with a ΔG value of 2.24 eV (Supplementary Fig. 54a). However, the subsequent $^*\text{O}$ -to- $^*\text{OOH}$ step in the AEM requires a lower energy barrier (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 - MnO_2 (Supplementary Fig. 54b). The $^*\text{OH}$ -to- $^*\text{O}$ step is the RDS for both pathways with a ΔG value of 2.24 eV, whereas the subsequent AEM step requires a lower energy barrier of 1.15 eV than the corresponding OPM pathway (1.66 eV). Therefore, pristine β - MnO_2 also favors the conventional AEM pathway.

For pristine R-MnO_2 , the AEM pathway is likewise energetically preferred (Supplementary

Fig. 54c). The RDS is the $\ast\text{OH}$ -to- $\ast\text{O}$ step with a ΔG value of 2.06 eV, whereas the OPM pathway is limited by the $\ast\text{O}$ -to- $\ast\text{O}^\ast\text{OH}$ step with a higher ΔG value of 2.22 eV.

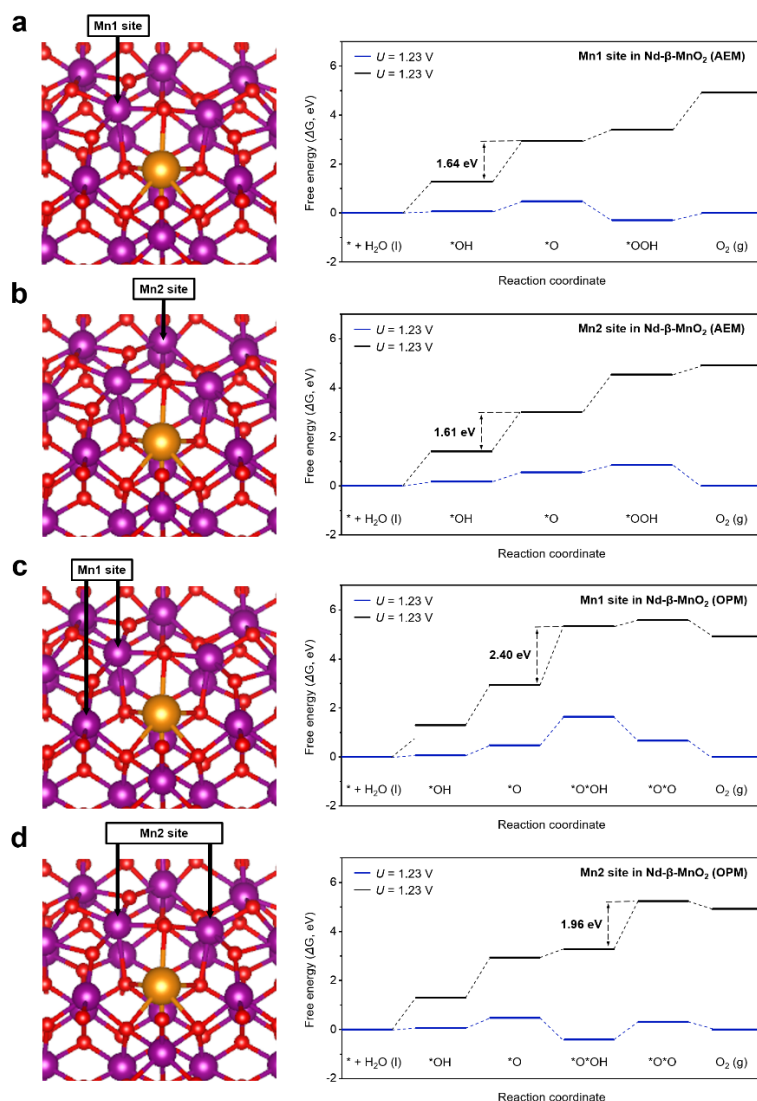
Overall, the calculated Gibbs free energy profiles demonstrate that all pristine Mn-oxide phases preferentially follow the conventional AEM pathway rather than the OPM pathway.



Supplementary Fig. 55 Gibbs free energy profiles comparing AEM and OPM pathways at different surface Mn sites of Nd-doped $\alpha\text{-Mn}_2\text{O}_3$ (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.

Supplementary Note 13 The Gibbs free energy profiles of the AEM and OPM pathways were calculated at different surface Mn sites in Nd- $\alpha\text{-Mn}_2\text{O}_3$. For the AEM pathway, Mn1, Mn2, and Mn3 sites were evaluated (Supplementary Figs. 55a–c). The RDSs are the $\ast\text{OOH}$ -to- O_2 step at the Mn1 site ($\Delta\text{G} = 3.34$ eV), the $\ast\text{O}$ -to- $\ast\text{OOH}$ step at the Mn2 site ($\Delta\text{G} = 1.97$

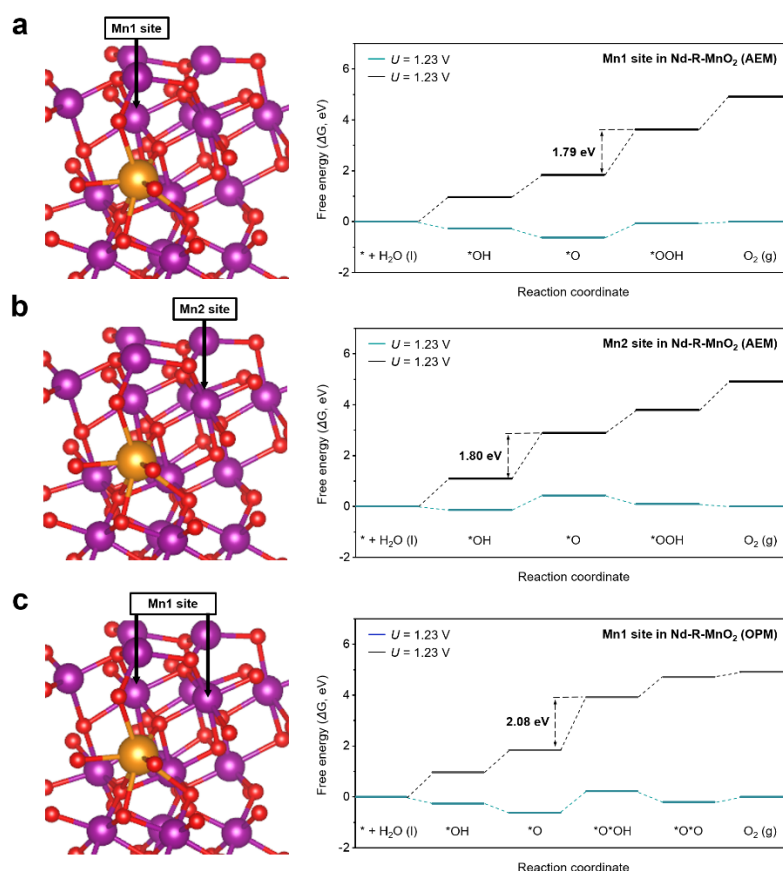
eV), and the $^*\text{OOH}$ -to- O_2 step at the Mn3 site ($\Delta G = 2.35$ eV). For the OPM pathway, Mn1 and Mn2 sites were considered (Supplementary Figs. 55d–e), where the $^*\text{O}$ -to- $^*\text{O}^*\text{OH}$ step is the RDS with ΔG values of 1.75 and 1.69 eV, respectively. Among the examined reaction sites and pathways, the Mn2-site OPM pathway exhibits the lowest RDS energy barrier of 1.69 eV, suggesting that Nd-doped α - Mn_2O_3 preferentially favors the OPM route.



Supplementary Fig. 56. 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.

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. 56a–b). The $^*\text{OH}$ -to- $^*\text{O}$ 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. 56c–d). The RDSs are the $^*\text{O}$ -to- $^*\text{O}^*\text{OH}$ step at the Mn1 site ($\Delta G = 2.40$ eV) and the $^*\text{O}^*\text{OH}$ -to- O_2 step at the Mn2 site ($\Delta G = 1.96$ 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 -

MnO₂ preferentially follows the AEM route.



Supplementary Fig. 57. 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.

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. 57a–b). The RDSs are the $\ast\text{O}$ -to- $\ast\text{OOH}$ step at the Mn1 site ($\Delta G = 1.79 \text{ eV}$) and the $\ast\text{OH}$ -to- $\ast\text{O}$ step at the Mn2 site ($\Delta G = 1.80 \text{ eV}$). For the OPM pathway, the $\ast\text{O}$ -to- $\ast\text{O}^\ast\text{OH}$ step is identified as the RDS with $\Delta G = 2.08 \text{ eV}$ (Supplementary Fig. 57c). 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.

[Lines 493 to 496 in the revised manuscript]

DFT calculations further reveal that Nd-derived 4f–2p–3d orbital coupling enhances Mn–O covalency and induces a phase-dependent OER mechanism: Nd-doped α -Mn₂O₃ preferentially follows the OPM pathway, whereas Nd-doped β -MnO₂ and R-MnO₂ remain AEM-dominant with reduced OER barriers.

Reviewers' Comments:

Reviewer #2

This manuscript presents a promising strategy for enhancing the acidic oxygen evolution reaction (OER) performance of Mn-based catalysts through Nd doping. The topic is of high interest for proton-exchange membrane water electrolysis, and the reported improvements in activity and stability are noteworthy. However, several key issues require clarification and additional experimental support before the work can be considered suitable for publication. The following points should be addressed to strengthen the conclusions and ensure the robustness of the study.

Response: We sincerely thank reviewer for the positive assessment of our work and the constructive comments. We have carefully considered all of the reviewer's suggestions and revised the manuscript and Supplementary Information accordingly by adding new control experiments, additional analyses, and expanded discussions. We believe these revisions have significantly strengthened the manuscript and addressed the reviewer's concerns.

R2–1. The study investigates α -Mn₂O₃, β -MnO₂, and R-MnO₂ but does not thoroughly explore potential synergistic effects between these phases in the catalytic system. It is important to clarify whether the observed performance arises from a specific phase or from interactions between multiple phases.

Response: We thank the reviewer for raising this important point. We agree that the original manuscript did not sufficiently clarify whether the improved performance of NMO-0.2 originates from a specific phase or from the coexistence of multiple phases.

To address this point, we prepared phase-enriched Mn oxide reference catalysts using the same thermal-decomposition platform and compared their OER activity and stability in 0.5 M H₂SO₄. Although complete phase purity could not be achieved because Mn oxide polymorphs inherently coexist during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. The α -Mn₂O₃-rich reference exhibited higher OER activity, whereas the β /R-MnO₂-rich references showed better stability under acidic OER conditions. Nd incorporation further improved the activity and/or stability of these phase-enriched references.

These results indicate that the enhanced performance of NMO-0.2 is not attributable to a single isolated phase. Rather, α -Mn₂O₃ provides activity-promoting Mn³⁺-rich motifs, while the β /R-MnO₂-rich framework contributes structural robustness. Nd doping further stabilizes

and electronically modulates these Mn environments, resulting in the improved activity–stability balance of NMO-0.2.

In addition, we added work-function analysis to discuss the possible role of mixed-phase domain boundaries in interphase charge redistribution and local Mn^{3+} stabilization, without assigning the improved performance to a specific idealized interface mechanism.

The corresponding experimental data, work-function analysis, and revised discussion have been incorporated into the revised manuscript and Supplementary Information, as shown below.

[Lines 43 to 45 in the revised manuscript]

Phase-enriched reference experiments and density functional theory calculations show that Nd-doped $\alpha\text{-Mn}_2\text{O}_3$ promotes OPM through structural Mn^{3+} motifs, whereas $\beta/\text{R-MnO}_2$ -rich domains provide structural robustness.

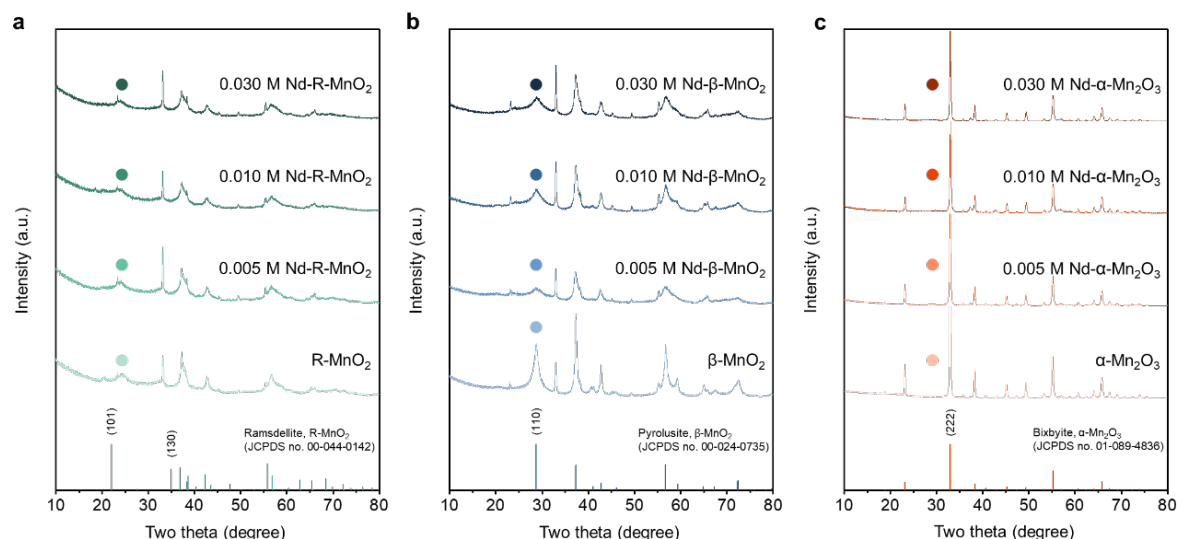
[Lines 89 to 94 in the revised manuscript]

Phase-enriched reference experiments reveal that $\alpha\text{-Mn}_2\text{O}_3$ -rich domains provide activity-promoting structural Mn^{3+} motifs, whereas $\beta/\text{R-MnO}_2$ -rich domains contribute structural robustness under acidic OER conditions. Density functional theory (DFT) calculations further reveal phase-dependent OER pathways, with Nd-doped $\alpha\text{-Mn}_2\text{O}_3$ favoring an OPM pathway and Nd-doped $\beta/\text{R-MnO}_2$ remaining adsorbate evolution mechanism (AEM)-dominant with reduced OER barriers.

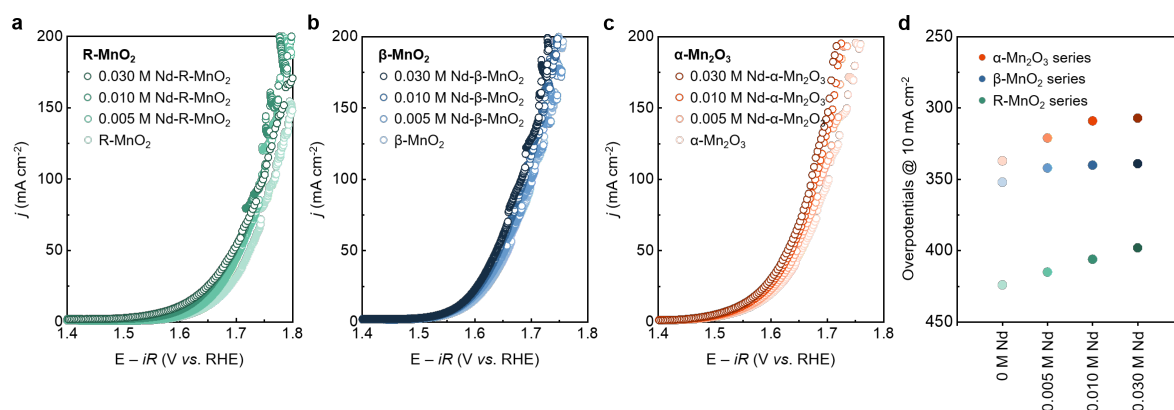
[Lines 344 to 358 in the revised manuscript]

To experimentally examine the role of each Mn oxide polymorph in the mixed-phase NMO catalyst, phase-enriched Mn oxide reference catalysts were prepared using the same thermal-decomposition platform (**Supplementary Fig. 44**). Although complete phase purity could not be achieved because of the inherent coexistence of Mn oxide polymorphs during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. Electrochemical measurements showed that the $\alpha\text{-Mn}_2\text{O}_3$ -rich reference exhibited the highest OER activity (**Supplementary Fig. 45**), whereas the $\beta/\text{R-MnO}_2$ -rich references displayed superior stability under acidic conditions (**Supplementary Fig. 46**). Nd incorporation further improved the activity and/or stability of all phase-enriched references. Therefore, the enhanced OER performance of NMO-0.2 is attributed to the combined contribution of minority $\alpha\text{-Mn}_2\text{O}_3$ -derived structural Mn^{3+} motifs and electronically induced

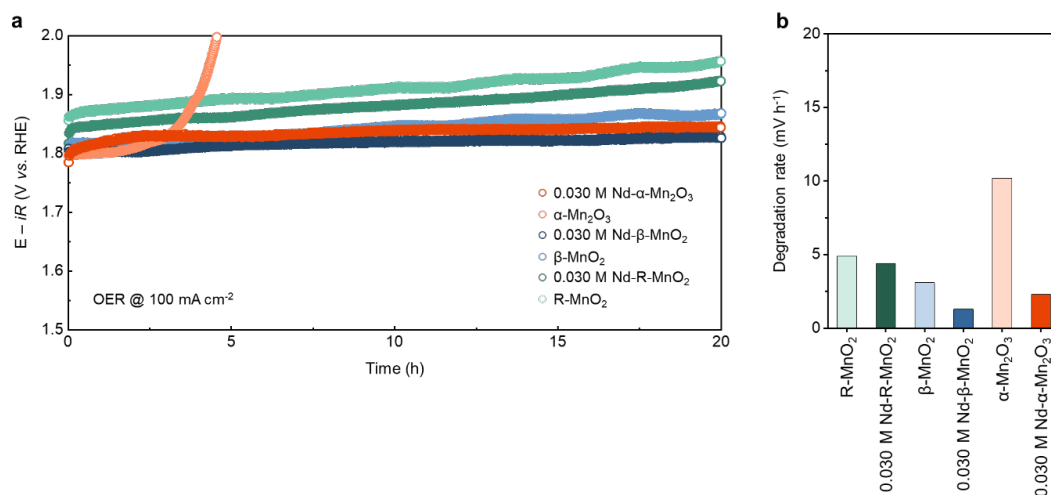
Mn^{3+} within the dominant MnO_2 -rich framework, rather than to an $\alpha\text{-Mn}_2\text{O}_3$ -dominant phase. These results provide the experimental basis for the phase-specific DFT analysis presented below, where each polymorph is modeled separately to clarify how Nd incorporation modifies its local structural and electronic properties.



Supplementary Fig. 44 Phase-controlled synthesis of Mn oxide reference catalysts. XRD patterns of (a) R-MnO_2 -rich, (b) $\beta\text{-MnO}_2$ -rich, and (c) $\alpha\text{-Mn}_2\text{O}_3$ reference catalysts prepared by thermal decomposition at different temperatures with varied Nd precursor concentrations. The characteristic reflections of R-MnO_2 (101), $\beta\text{-MnO}_2$ (110), and $\alpha\text{-Mn}_2\text{O}_3$ (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.



Supplementary Fig. 45 Phase-dependent OER activity of Nd-doped Mn oxide reference catalysts. Polarization curves of (a) R-MnO_2 -rich, (b) $\beta\text{-MnO}_2$ -rich, and (c) $\alpha\text{-Mn}_2\text{O}_3$ -rich catalysts with and without Nd dopants. (d) Comparison of the overpotential required to reach a current density of 10 mA cm^{-2} for the corresponding phase-rich Mn oxides as a function of Nd concentrations.



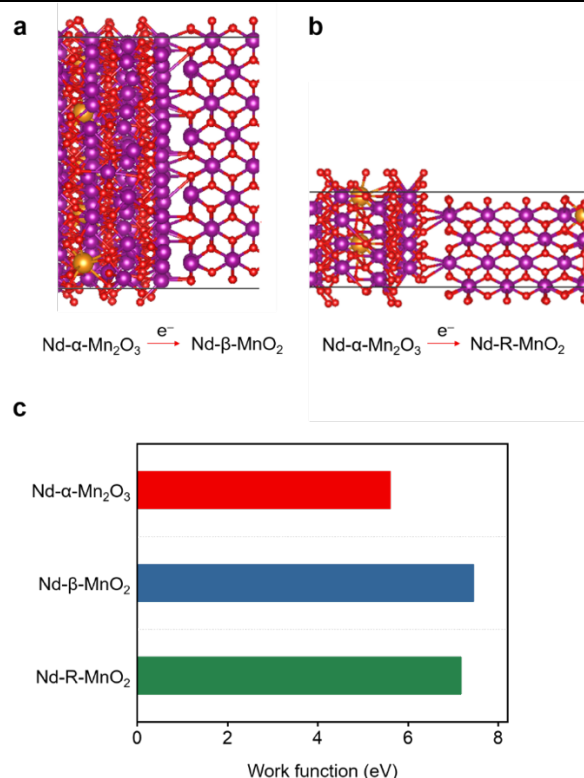
Supplementary Fig. 46 Phase-dependent OER stability of Nd-modified Mn oxide reference catalysts. (a) Chronopotentiometric stability curves of phase-controlled R- MnO_2 -rich, β - MnO_2 -rich, and α - Mn_2O_3 reference catalysts with and without Nd doping measured at 100 mA cm⁻² in 0.5 M H_2SO_4 . (b) Comparison of degradation rates derived from the chronopotentiometric stability tests.

[Lines 135 to 139 in the revised manuscript]

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) further revealed that NMO-0.2 formed a mixed-phase domain boundary composed of distinct α - Mn_2O_3 (Fig. 1b, R1) and R- MnO_2 (Fig. 1b, R2) phases, together with clear evidence of Nd incorporation into the Mn oxide lattice (Fig. 1c; Supplementary Figs. 9–13).

[Lines 435 to 437 in the revised manuscript]

Work-function calculations further suggest possible interphase charge redistribution between α - Mn_2O_3 and MnO_2 -rich domains, which may additionally modulate the local Mn–O electronic structure (Supplementary Fig. 58).



Supplementary Fig. 58 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. (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.

[Lines 586 to 594 in the revised Supplementary Information]

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 μL 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 μL of each mixed precursor solution was drop-cast onto carbon fiber paper and calcined at the corresponding temperature.

R2–2. The choice of Nd as a dopant needs clearer justification. Why was Nd selected over other rare-earth or transition metals? A comparative study involving other dopants (e.g., La, Ce, Pr, or non-rare-earth metals) would help establish whether the enhancement is unique to Nd or a more general phenomenon. Discussing the specific electronic or structural effects induced by Nd doping (e.g., charge redistribution, oxygen vacancy formation, or structural stabilization) is essential to support its selection.

Response: We thank the reviewer for this important comment. We agree that the rationale for selecting Nd as the dopant should be more clearly explained. Nd was selected because its stable trivalent state and partially occupied 4f orbitals were expected to effectively modulate the Mn–O framework through 4f–2p–3d orbital coupling, thereby stabilizing Jahn–Teller–active Mn^{3+} species and enhancing Mn–O covalency.

To examine whether the observed enhancement is specific to Nd or reflects a broader lanthanide effect, we performed additional lanthanide-control experiments using La-, Ce-, Pr-, and Nd-modified Mn oxide catalysts prepared under identical synthesis conditions. Although the exact incorporated amount of each lanthanide may differ because of differences in hydrolysis, decomposition, and lattice incorporation, the comparative provides a useful quantitative assessment of lanthanide-dependent trends. Among the tested lanthanides, Nd-modified Mn oxide exhibited the most favorable balance of OER activity and durability, as shown below.

[FIGURE REDACTED]

Fig. R1 (review-only data) Lanthanide dopant comparison for Mn oxide catalysts. **a** Polarization curves and **b** chronopotentiometric stability tests of pristine $\gamma\text{-MnO}_2$ and lanthanide-modified Mn oxide catalysts prepared with La, Ce, Pr, and Nd dopants. Nd-modified Mn oxide exhibits the most favorable activity–stability balance among the tested lanthanide dopants.

A comprehensive understanding of lanthanide-dependent effects requires systematic investigation of their electronic structures and structure–property relationships, which is beyond the scope of the present study and is currently being pursued in a separate project.

Therefore, these comparative data are provided here to justify the selection of Nd, but are not included in the revised manuscript.

R2–3. In Figure 2e, MnO₂ is tested on a carbon substrate, while Nd-doped catalysts are tested on a porous transport layer (PTL). Carbon corrosion and catalyst detachment under OER conditions may unfairly penalize the MnO₂ performance. To ensure a fair comparison, MnO₂ should also be tested on the same PTL substrate under identical conditions. This will isolate intrinsic catalytic differences from substrate-related artifacts.

Response: We thank the reviewer for this important comment. We agree that comparing γ -MnO₂ and NMO-0.2 on different electrode supports could lead to an unfair evaluation, because carbon fiber paper can undergo corrosion (Small Methods **2022**, 2201130) and catalyst detachment under strongly oxidative acidic OER conditions. To address this concern, we revised Fig. 2e and additionally tested γ -MnO₂ on the same Pt/Ti fiber felt substrate used for NMO-0.2 under identical conditions.

In the revised Fig. 2e, the stability data are now clearly separated by both catalyst and substrate: the upper row shows γ -MnO₂, the lower row shows NMO-0.2, the left column shows results on carbon fiber paper, and the right column shows results on Pt/Ti fiber felt. On carbon fiber paper, γ -MnO₂ rapidly deactivated within <30 h, whereas NMO-0.2 operated for ~100 h before deactivation, likely due to carbon corrosion and catalyst detachment. In contrast, when Pt/Ti fiber felt was used as a corrosion-resistant porous transport layer, γ -MnO₂ showed markedly improved stability for >300 h at 200 mA cm⁻². This confirms that the rapid decay of γ -MnO₂ on carbon fiber paper was largely influenced by the electrode/support configuration.

Importantly, under the same Pt/Ti fiber felt configuration, NMO-0.2 still exhibited superior durability, operating for >1000 h at 200 mA cm⁻² in 0.5 M H₂SO₄. Therefore, the revised comparison isolates substrate-related artifacts and confirms that NMO-0.2 retains higher high-current acidic OER stability than γ -MnO₂ under identical electrode conditions. We have revised results section in the manuscript, and the related discussion accordingly.

[Lines 237 to 251 in the revised manuscript]

Encouraged by these results, we further evaluated the high-current stability of γ -MnO₂ and NMO-0.2 on different electrode supports at 200 mA cm⁻² in 0.5 M H₂SO₄ (Fig. 2e). On carbon fiber paper, γ -MnO₂ rapidly deactivated within <30 h, whereas NMO-0.2 maintained operation for ~100 h before rapid deactivation, likely due to carbon corrosion and catalyst

detachment under strongly oxidative acidic conditions. To minimize support-related degradation, both catalysts were further tested on platinized titanium fiber felt (Pt/Ti), a corrosion-resistant porous transport layer commonly used in PEMWE systems (Supplementary Fig. 33). Under this configuration, γ -MnO₂ exhibited improved stability compared with that on carbon fiber paper, but its performance began to degrade rapidly after ~300 h, indicating that the Pt/Ti support mitigates support-related degradation but does not fully resolve the intrinsic instability of γ -MnO₂ under acidic OER condition. More importantly, NMO-0.2 showed further enhanced durability, operating stably for >1000 h at 200 mA cm⁻² under the same Pt/Ti fiber felt configuration. These results demonstrate that NMO-0.2 retains superior high-current durability on a practical corrosion-resistant support, surpassing the performance of most state-of-the-art Mn-based acidic OER catalysts (Fig. 2f; Supplementary Table 4).

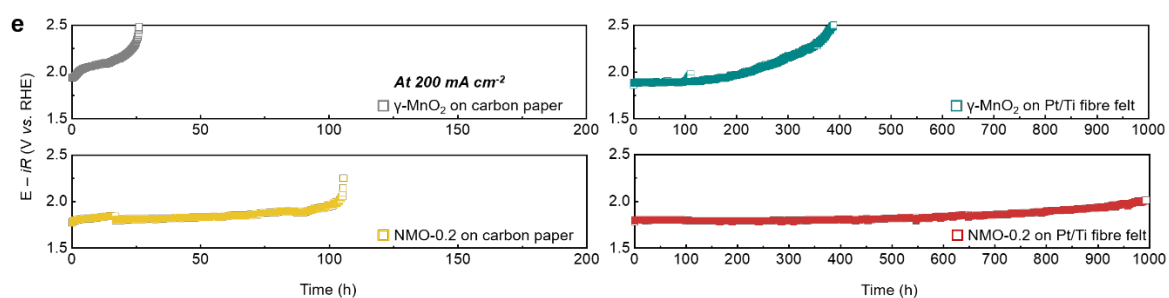


Fig. 2e Chronopotentiometric stability tests of γ -MnO₂ and NMO-0.2 at 200 mA cm⁻² in 0.5 M H₂SO₄. The right panels compare both catalysts on Pt/Ti fiber felt under identical conditions, whereas the left panels present the corresponding measurements on carbon fiber paper for comparison. These results demonstrate the superior durability of NMO-0.2.

R2–4. The Raman signals presented are exceptionally weak, raising concerns about signal-to-noise ratio and there liability of the phase identification. It is recommended to repeat the measurements with optimized experimental conditions (e.g., longer acquisition time, higher laser power, or alternative excitation wavelengths) or to supplement with additional techniques (e.g., FTIR or high-resolution TEM) to confirm the proposed phase composition.

Response: We thank the reviewer for this important comment. We agree that the Raman measurements should be optimized and supported by complementary structural analyses before being used for phase assignment.

To address this concern, we repeated the Raman measurements after systematically optimizing the acquisition conditions. We examined the effects of laser power, integration time, and accumulation number, and identified conditions that improved signal-to-noise ratio without

noticeable spectral distortion or laser-induced damage (Figs. R1 and R2, review-only data). Using these optimized conditions, we obtained clearer *ex situ* Raman spectra of γ -MnO₂ and NMO-0.2, including MnO₂-related features and α -Mn₂O₃-related signals in the Mn₂O₃-rich region of NMO-0.2.

[FIGURE REDACTED]

Fig. R2 (review-only data) Laser-power-dependent Raman spectra of γ -MnO₂. Ex situ Raman spectra of γ -MnO₂ measured using a 532 nm excitation laser with different laser powers.

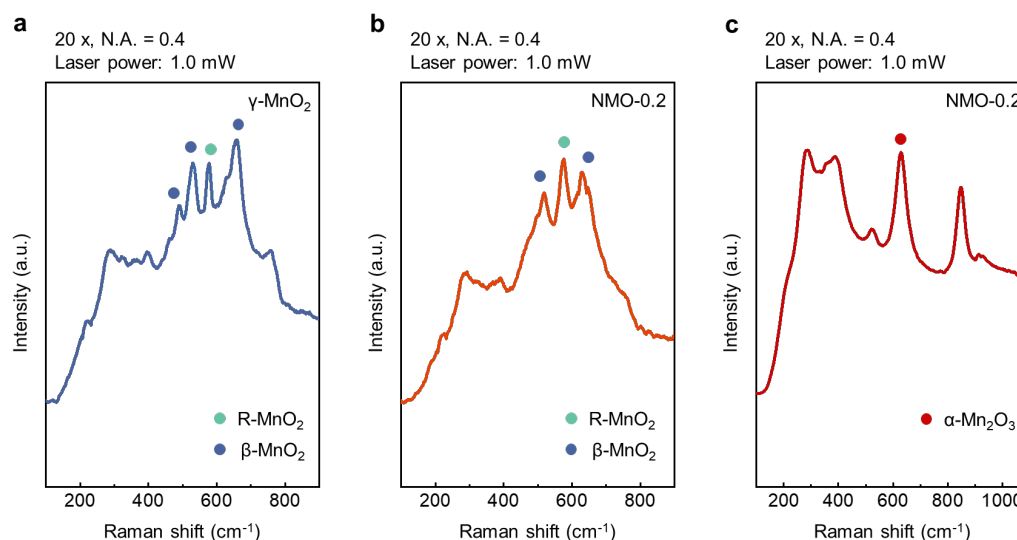
[FIGURE REDACTED]

Fig. R3 (review-only data) Optimization of Raman acquisition parameters for γ -MnO₂ and NMO-0.2. Ex situ Raman spectra of **a** γ -MnO₂ and **b** NMO-0.2 collected under different integration times and accumulation numbers using a fixed 532 nm excitation laser with 1 mW of laser power.

Importantly, we do not rely on Raman spectroscopy alone for phase identification. The optimized Raman results are consistent with the PXRD/Rietveld refinement, HRTEM, and EXAFS analyses, which provide the primary evidence for the mixed-phase composition of NMO-0.2. We have revised the Results section and Supplementary Information to include the optimized confocal Raman analysis and the corresponding acquisition conditions, as shown below.

[Lines 146 to 147 in the revised manuscript]

This mixed-phase assignment was further supported by confocal Raman spectroscopy (Supplementary Fig. 14).



Supplementary Fig. 14 Optimized confocal Raman analysis of Mn oxide phases. Raman spectra of (a) γ - 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 γ - MnO_2 -derived MnO_2 framework showed Raman features near ~ 570 and ~ 650 cm^{-1} , corresponding to R- MnO_2 - and β - 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 α - Mn_2O_3 -related Raman band near ~ 630 cm^{-1} , supporting the coexistence of MnO_2 and minority α - Mn_2O_3 phases.

R2–5. The authors propose an oxide path mechanism (OPM) for OER. To substantiate this claim, differential electrochemical mass spectrometry (DEMS) experiments should be conducted to directly monitor oxygen evolution and possible intermediate species. This would provide critical evidence to distinguish between OPM and alternative mechanisms such as the adsorbate evolution mechanism (AEM).

Response: We sincerely thank the reviewer for this valuable suggestion. We agree that DEMS analysis can provide important experimental evidence for evaluating the proposed OPM-like pathway and distinguishing it from conventional AEM.

To address this point, we performed additional *in situ* isotope-labelling DEMS measurements using ^{18}O -labelled γ - MnO_2 and NMO-0.2 catalysts in ^{16}O -containing 0.5 M H_2SO_4 electrolyte. The DEMS results show that NMO-0.2 exhibits more pronounced ^{18}O -labelled oxygen signals than γ - MnO_2 , supporting the participation of catalyst-associated oxygen species during OER. These results are consistent with the *in situ* Raman observation of earlier formation of labile $^*\text{O}$ species and provide additional support for the proposed OPM-

like pathway.

Accordingly, we have added the isotope-labelled DEMS results, AEM/OPM isotope-labelled O₂ formation schemes, and corresponding experimental details to the revised manuscript and Supplementary Information. Please also refer to our response to Reviewer #1, Comment 4 for a detailed discussion of the DEMS results.

R2–6. Figure 5a, b lacks a direct comparison with undoped MnO₂ in the same electrolyzer configuration. Including MnO₂ tested under identical conditions is necessary to objectively evaluate the improvement offered by Nd doping.

Response: We thank the reviewer for this important suggestion. We agree that a direct comparison with undoped γ -MnO₂ under the same PEMWE configuration is necessary to objectively evaluate the effect of Nd doping.

In response, we optimized the PEMWE cell configuration and performed additional PEMWE measurements using γ -MnO₂ or NMO as the anode catalyst under identical MEA fabrication and operating conditions. The NMO-0.2-based PEMWE cell exhibited lower cell voltages than the γ -MnO₂-based cell over the investigated current-density range, demonstrating the improved PEMWE performance enabled by Nd modification.

We further compared their durability under constant-current electrolysis at 100 mA cm⁻². The γ -MnO₂-based PEMWE cell showed a continuous increase in cell voltage, the NMO-0.2-based cell maintained substantially more stable operation for >600 h. In addition, NMO-0.2 sustained operation for >300 h at 200 mA cm⁻² and >60 h at 500 mA cm⁻². These results confirm that the NMO-0.2 shows higher PEMWE performance than γ -MnO₂ under identical cell conditions.

We have revised results section and the corresponding discussion in the manuscript accordingly.

[Lines 460 to 467 in the revised manuscript]

The NMO-0.2 catalyst was integrated into a membrane electrode assembly (MEA) for PEMWE operation. The MEA was fabricated by the catalyst-coated substrate (CCS) method using NMO-0.2 as the anode catalyst, Pt/C as the cathode catalyst, and Nafion[®] N117 as the PEM (Fig. 5a and Supplementary Fig. 59). The NMO-0.2-based PEMWE achieved a cell voltage of 1.88 V at 1 A cm⁻² (Fig. 5b) and maintained stable operation for >600 h at 100 mA cm⁻², outperforming γ -MnO₂ (Fig. 5c). Remarkably, it also operated for >300 h at 200

mA cm^{-2} and for >60 h at 500 mA cm^{-2} , demonstrating the PEMWE applicability of NMO-0.2 under high-current acidic OER conditions.

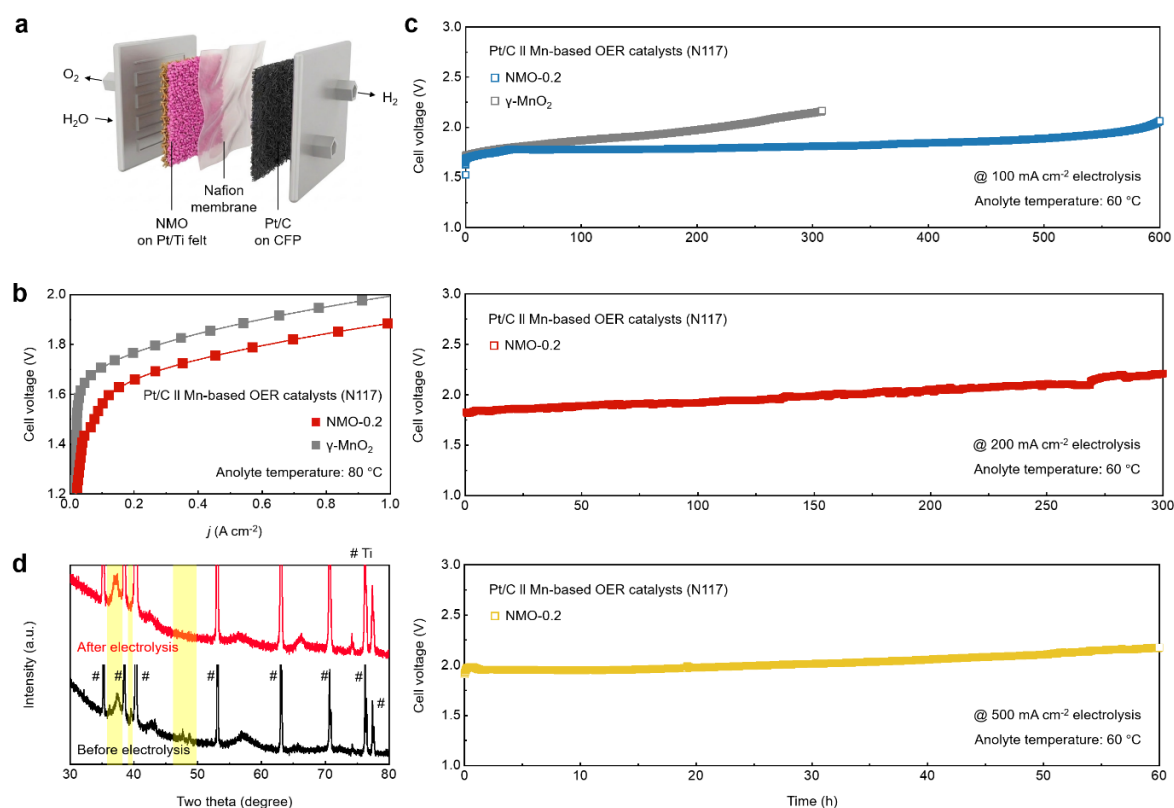


Fig. 5 Evaluation of PEMWE performance. **a** Schematic illustration of the PEMWE system with an MEA prepared by the CCS method. **b** Polarization curves of PEMWE cells employing γ -MnO₂ or NMO-0.2 as the anode catalysts. **c** Cell-voltage profiles of PEMWE cells employing γ -MnO₂ or NMO-0.2 as the anode catalyst at 100 mA cm^{-2} , together with NMO-0.2 based PEMWE operation at 200 and 500 mA cm^{-2} . **d** XRD patterns of NMO deposited on the Pt/Ti felt before and after electrolysis at 200 mA cm^{-2} . The # symbols indicate the Ti substrate features, while the yellow-shaded regions highlight diffraction peaks showing significant changes after electrolysis at 200 mA cm^{-2} .

R2–7. Figure 5c indicates noticeable performance degradation over time. The origin of this deactivation should be discussed in detail.

Response: We thank the reviewer for this important comment. During revision, we further optimized the PEMWEs and extended the durability tests up to 1000 h. Nevertheless, a gradual increase in cell voltage was still observed, indicating partial performance degradation during long-term PEMWE operation.

To examine the origin of this deactivation, we compared the XRD patterns of the NMO anode on Pt/Ti felt before and after electrolysis at 200 mA cm^{-2} (Revised Fig. 5d). After electrolysis, the diffraction features of pristine NMO became weakened, while additional features associated with the deactivated NMO phase appeared, indicating partial structural

reconstruction of the Mn oxide catalyst under acidic and oxidative PEMWE conditions.

These results suggest that the voltage increase during extended PEMWE operation is mainly associated with gradual structural reconstruction/deactivation of the NMO anode, rather than immediate failure of the MEA or complete catalyst removal. We have revised the Results section to include this deactivation discussion.

[Lines 468 to 483 in the revised manuscript]

Although the NMO-0.2-based PEMWE showed prolonged operation, a gradual increase in cell voltage was observed during extended electrolysis, indicating partial performance degradation. To clarify the origin of this deactivation, XRD patterns of the NMO anode on Pt/Ti felt were collected before and after electrolysis at 200 mA cm^{-2} (**Fig. 5d**). After electrolysis, the diffraction features corresponding to pristine NMO were weakened, while additional features associated with the deactivated NMO phase appeared, suggesting partial structural reconstruction of the Mn oxide catalyst under acidic and oxidative PEMWE conditions. The Ti substrate peaks remained clearly visible, confirming that the observed changes mainly originated from the NMO catalyst layer rather than the underlying substrate. These results indicate that the voltage increase during long-term operation is primarily associated with gradual structural reconstruction/deactivation of the NMO surface, rather than immediate failure of the MEA. Overall, the NMO-based PEMWE demonstrated promising efficiency and durability among reported non-noble-metal acidic OER catalysts (**Supplementary Fig. 60 and Supplementary Table 5**), while the post-electrolysis structural analysis further clarifies that partial reconstruction of the NMO anode is responsible for the remaining performance decay under high-current PEMWE operation.

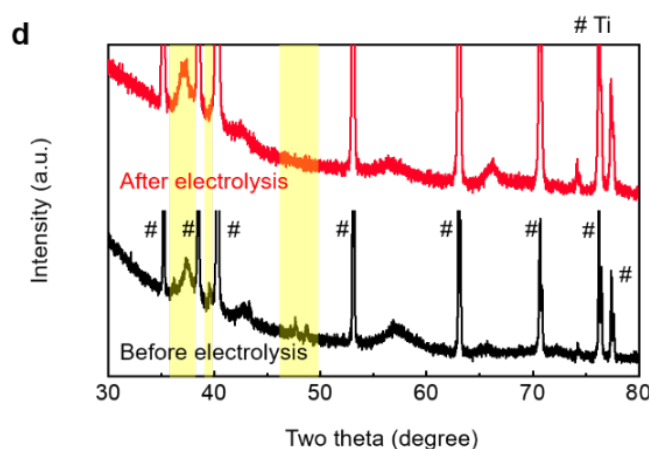


Fig. 5d XRD patterns of NMO deposited on the Pt/Ti felt before and after electrolysis at 200 mA cm^{-2} . The # symbols indicate the Ti substrate features, while the yellow-shaded regions highlight diffraction peaks showing significant changes after electrolysis at 200 mA cm^{-2} .

Reviewers' Comments:

Reviewer #3

This manuscript reported a Nd-doped Mn oxide (NMO) to stabilize Jahn–Teller–active Mn^{3+} centers, which showed a stable operation over 300 h at 200 mA cm^{-2} . A PEMWE with NMO as the anode also showed a stable operation for 160 h at 200 mA cm^{-2} . *In situ* Raman, *in situ* XAS, and DFT calculations have been used to reveal the working mechanism. The performance with 300 h operation at 200 mA cm^{-2} is good for noble-metal-free catalysts used in PEMWE. However, Mn based catalysts already showed much better catalytic performance for PEMWE, as reported in the literature (some of them in Fig. 2f). Especially, the Nd doped Mn oxide has been reported in a very similar paper in 2025 (DOI:10.1002/adfm.202423709), which labeled as Nd- γ - MnO_2 catalyst while in this work it is Nd-doped Mn oxide (NMO). The structures in these two papers revealed by XAS are also similar, which are mainly MnO_2 (Mn^{4+}) with a slight reduction of Mn to Mn^{3+} . The literature also showed that Nd-doping would result in optimized binding energy between the catalyst and the oxygen intermediates. Most importantly, the Nd- γ - MnO_2 catalyst showed a much better performance for over 700 h stability at 200 mA cm^{-2} and over 1000 h at 100 mA cm^{-2} (300 h at 200 mA cm^{-2} in this work). Considering the similar composition and structure but the much lower performance, I am not sure about the advancement of this work. There are also some other critical issues should be addressed:

Response: We sincerely thank the reviewer for this important comparison with the recent Nd- γ - MnO_2 work by Hu et al. (*Adv. Funct. Mater.* **2025**, 2423709). We agree that this report is highly relevant and revised the manuscript to explicitly discuss its relationship to the present study.

The key distinction is that our work focuses on improving the activity–stability balance through a mixed-phase Mn^{3+} stabilization strategy. While the reported Nd- γ - MnO_2 catalyst mainly involves Nd modification within a γ - MnO_2 framework, NMO-0.2 is a MnO_2 -rich mixed-phase oxide containing α - Mn_2O_3 , β - MnO_2 , and R- MnO_2 components. This structure provides both structural Mn^{3+} associated with the α - Mn_2O_3 component and electronically induced Mn^{3+} within the MnO_2 -rich framework.

In the revised manuscript, we extended the stability performance up to 1000 h at 200 mA cm^{-2} (Revised Fig. 2e) while achieving lower overpotentials than the previously reported Nd- γ - MnO_2 catalyst. As summarized in the revised benchmarking comparison (revised Fig. 2f), NMO-0.2 also exhibits superior high-current durability. In addition, the PEMWE evaluation was further optimized, demonstrating stable operation for >600 h at 100 mA cm^{-2} , >300 h at

200 mA cm⁻², and >60 h at 500 mA cm⁻².

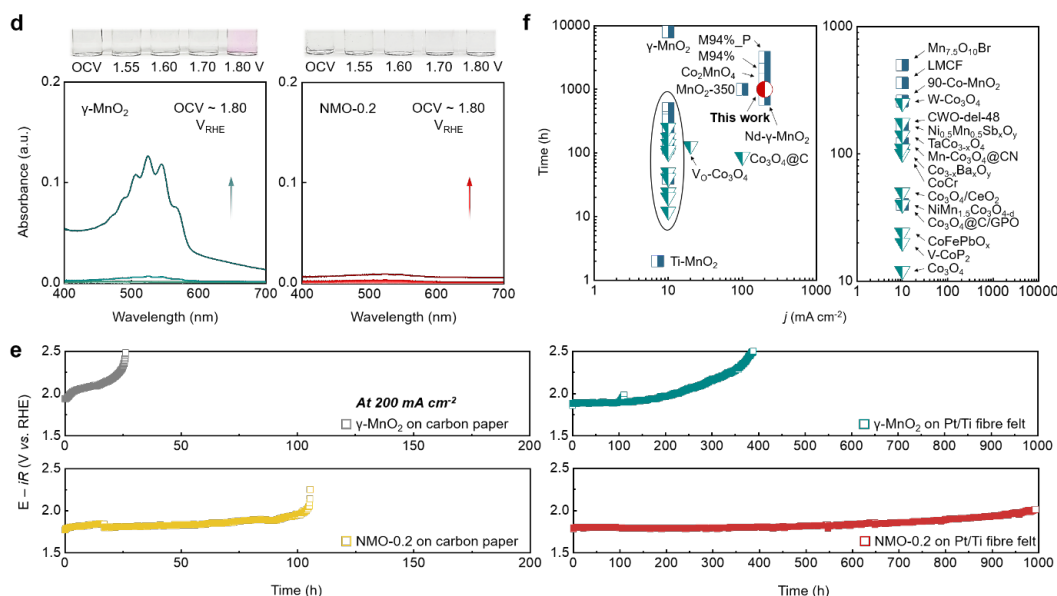


Fig. 2e Chronopotentiometric stability tests of γ -MnO₂ and NMO-0.2 at 200 mA cm⁻² in 0.5 M H₂SO₄. The right panels compare both catalysts on Pt/Ti fiber felt under identical conditions, whereas the left panels present the corresponding measurements on carbon fiber paper for comparison. These results demonstrate the superior durability of NMO-0.2. **f** Benchmarking plot showing stability of various reported non-noble-metal-based OER catalysts in acidic electrolytes, presenting current densities on a logarithmic scale over time. The red half-circle highlights the performance of this work. Blue semi-rectangular boxes represent previously reported Mn-based OER catalysts,^{15-18,27-35} while green inverted semi-triangles indicate non-Mn, non-noble-metal OER catalysts.³⁶⁻⁵¹

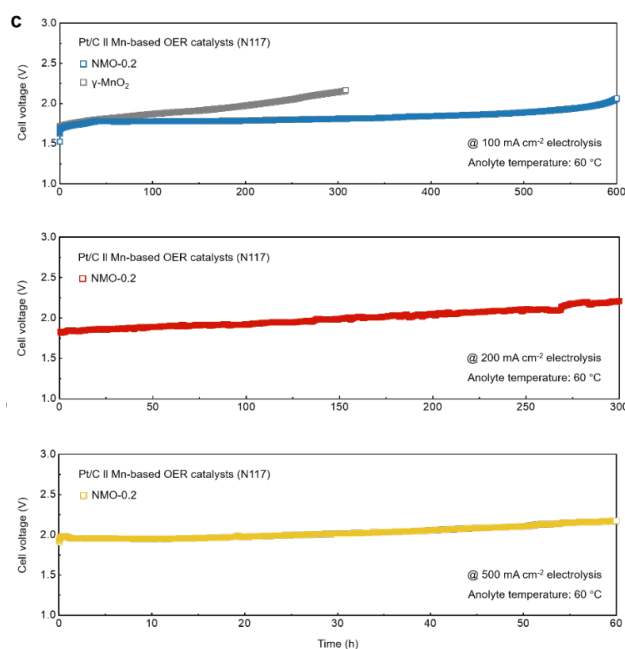


Fig. 5c Cell-voltage profiles of PEMWE cells employing γ -MnO₂ or NMO-0.2 as the anode catalyst at 100 mA cm⁻², together with NMO-0.2 based PEMWE operation at 200 and 500 mA cm⁻².

Therefore, our study does not simply repeat Nd doping of γ -MnO₂. Rather, it provides a complementary design strategy based on mixed-phase Mn³⁺ stabilization, supported by revised *in situ* Raman, isotope-labelling DEMS, *in situ* XAS, phase-enriched reference experiments, and DFT calculations. We have revised the manuscript to clarify this distinction and the advancement of the present work.

R3–1. In this work the authors emphasize the significant contribution of Mn³⁺ in Mn₂O₃ (from XRD), which is different from typical MnO₂. However, from the XAS data in Fig. 1d, it is mainly MnO₂ (Mn⁴⁺) with only a slight reduction, which is obviously different from the spectrum of Mn₂O₃. So the main content in NMO-0.2 should be MnO₂. The EXAFS spectra in Fig. 1e also confirm this conclusion.

Response: We thank the reviewer for this important clarification. We agree that NMO-0.2 should be described as a MnO₂-rich mixed-phase oxide rather than a Mn₂O₃-dominant catalyst. This is consistent with the XANES/EXAFS data in Fig. 1d, e and the Rietveld refinement in Fig. 1a, which shows that α -Mn₂O₃ is a minority phase while β -MnO₂ and R-MnO₂ remain dominant.

We have revised the manuscript to clarify that our claim is not that Mn₂O₃ is the major component. Rather, Nd incorporation produces two types of Mn³⁺-containing motifs within the MnO₂-rich mixed-phase oxide: structural Mn³⁺ associated with the minority α -Mn₂O₃ phase and electronically induced Mn³⁺ generated by partial reduction of Mn⁴⁺ within the MnO₂-rich framework. The red shift of the Mn K-edge XANES absorption edge of NMO-0.2 relative to γ -MnO₂ supports this partial reduction while retaining the overall MnO₂-like spectral character. Therefore, we do not attribute the enhanced OER performance solely to the minority α -Mn₂O₃ phase, but rather to the combined contribution of structural Mn³⁺ in the α -Mn₂O₃ component and electronically induced Mn³⁺ within the dominant MnO₂-rich framework.

We have revised the manuscript, accordingly, as shown below.

[Lines 89 to 94 in the revised manuscript]

Phase-enriched reference experiments reveal that α -Mn₂O₃-rich domains provide activity-promoting structural Mn³⁺ motifs, whereas β /R-MnO₂-rich domains contribute structural robustness under acidic OER conditions. Density functional theory (DFT) calculations further reveal phase-dependent OER pathways, with Nd-doped α -Mn₂O₃ favoring an OPM

pathway and Nd-doped β /R-MnO₂ remaining absorbate evolution mechanism (AEM)-dominant with reduced OER barriers.

[Lines 143 to 147 in the revised manuscript]

These results indicate that NMO-0.2 is not an α -Mn₂O₃-dominant catalyst, but rather a MnO₂-rich mixed-phase oxide containing a minority α -Mn₂O₃ phase. In this structure, the α -Mn₂O₃ phase may provide structural Mn³⁺ motifs, whereas the MnO₂-rich β /R framework constitutes the dominant structural component. This mixed-phase assignment was further supported by confocal Raman spectroscopy (Supplementary Fig. 14).

[Lines 165 to 170 in the revised manuscript]

Although the overall XANES line shape of NMO-0.2 remains closer to MnO₂ than to Mn₂O₃, the red-shifted absorption edge indicates that NMO-0.2 contains partially reduced Mn species within a MnO₂-rich framework. This mixed-valence character can be understood as arising from two Mn³⁺ contributions: structural Mn³⁺ associated with the minority α -Mn₂O₃ phase and electronically generated Mn³⁺ by partial reduction of Mn⁴⁺ within the MnO₂-rich framework.

[Lines 353 to 355 in the revised manuscript]

Therefore, the enhanced OER performance of NMO-0.2 is attributed to the combined contribution of minority α -Mn₂O₃-derived structural Mn³⁺ motifs and electronically induced Mn³⁺ within the dominant MnO₂-rich framework, rather than to an α -Mn₂O₃-dominant phase.

R3–2. The authors claim that “their catalytic activity and stability are limited by the instability of Jahn–Teller (J–T) active Mn³⁺ centers that readily disproportionate in acid and by their narrow potential window” and discuss this point in the introduction part. However, the related references for the importance of Jahn–Teller (J–T) active Mn³⁺ centers (Refs. 16–19) are ten years ago, while in recent years significant progress has been made in this research field, in which γ -MnO₂ with Mn⁴⁺ can even work for 1000 h at 200 mA cm^{–2} (DOI:10.1038/s41929-023-01091-3). I am not sure about the importance of Mn³⁺ in Mn₂O₃ for the PEMWE. Actually, the Nd- γ -MnO₂ catalyst with similar Mn reduction but without the presence of Mn₂O₃ showed a much better performance.

Response: We thank the reviewer for this important comment. We agree that recent γ -MnO₂-based acidic OER catalysts have achieved remarkable stability at high current densities, including the optimized γ -MnO₂ reported in *Nature Catalysis*. We have revised the Introduction to reflect this recent progress more clearly. Our intention is not to suggest that Mn⁴⁺-dominant γ -MnO₂ is intrinsically unsuitable for acidic OER. Rather, our objective is to improve the activity–stability balance of Mn oxide catalysts.

(1) Activity

As summarized in Figure below, NMO-0.2 exhibits a lower overpotential than representative Mn-based acidic OER catalysts reported in recent literature, supporting our motivation to stabilize highly active Mn³⁺-containing motifs within a MnO₂-rich framework.

[FIGURE REDACTED]

Fig. R4 (review-only data) Overpotential comparisons of Mn-based acidic OER catalysts (Co₂MnO₄, *Nat. Catal.* **2022**, 5, 109; M94%, *Nat. Catal.* **2024**, 7, 252; Nd- γ -MnO₂, *Adv. Funct. Mater.* **2025**, 36, 2423709)

(2) Durability

We also revised the stability comparison to avoid any ambiguity arising from electrode/support effects. In the original manuscript, the rapid decay of γ -MnO₂ within <30 h was observed on carbon fiber paper. To ensure a fairer comparison, we additionally tested γ -MnO₂ on the same Pt/Ti fiber felt substrate used for NMO-0.2. Under this configuration, γ -MnO₂ exhibited substantially improved stability, confirming that its rapid decay on carbon fiber paper was strongly affected by the electrode/support configuration. Nevertheless, NMO-0.2 still showed superior high-current durability under the same Pt/Ti fiber felt configuration, operating for 1000 h at 200 mA cm⁻².

(3) PEMWE performance

We further optimized and evaluated the practical applicability of NMO-0.2 in a PEM water electrolyzer. The NMO-0.2-based MEA achieved lower cell voltages than the γ -MnO₂-based MEA and operated stably for >600 h at 100 mA cm⁻², >300 h at 200 mA cm⁻², and >60 h at 500 mA cm⁻² (Fig. 5). These results demonstrate that the improved activity and durability of NMO-0.2 are maintained under practical PEMWE operating conditions.

In this context, Mn³⁺-containing motifs remain relevant because they can provide highly active Jahn–Teller–distorted coordination environments, but they are difficult to stabilize under acidic OER conditions. NMO-0.2 is designed to stabilize such Mn³⁺-containing motifs within a Mn oxide framework, thereby improving activity while retaining high-current durability.

We have revised the Introduction and Results sections and updated references by including recent papers about Jahn-Teller distortion in Mn oxides, accordingly, as shown below.

[Lines 63 to 77 in the revised manuscript]

In this context, Mn has garnered significant interest as a promising active element for acidic OER catalysts due to its low cost and abundance (**Supplementary Fig. 1**). Recent studies have shown that structurally optimized γ -MnO₂, including M94%-type γ -MnO₂ and Nd-modified γ -MnO₂, can exhibit high durability under acidic OER conditions.^{15,16} However, achieving both high activity and high-current durability remains challenging for Mn-based acidic OER catalysts. While MnO₂ can operate stably within a narrow potential window,¹⁷ highly active Mn³⁺ species are difficult to stabilize under acidic conditions. Mn³⁺, with a t_{2g}³ e_g¹ electronic configuration, can induce Jahn–Teller distortion and provide flexible Mn–O coordination environments that facilitate OER intermediate formation and conversion.¹⁸⁻²⁰ However, Jahn–Teller-active Mn³⁺ species can readily disproportionate into Mn²⁺ and Mn⁴⁺ in acid.²¹ Therefore, stabilizing Jahn–Teller-active Mn³⁺ motifs while maintaining the structural robustness of Mn oxides is a promising strategy to bridge the activity–stability gap of Mn-based OER catalysts under high-current-density acidic conditions. To date, however, very few Mn-based acidic OER catalysts have simultaneously achieved high activity together with long-term durability at current densities exceeding 100 mA cm⁻².

References)

15 Kong, S. *et al.* Acid-stable manganese oxides for proton exchange membrane water electrolysis. *Nat. Catal.* **7**, 252–261 (2024).

- 16 Hu, Q. *et al.* Tailor control of neodymium doping sites in γ - MnO_2 for stable oxygen evolution reaction in acidic electrolyte. *Adv. Funct. Mater.* **36**, 2423709–2423717 (2025).
- 18 Liu, J. *et al.* Triggering the dual-metal-site lattice oxygen mechanism with in situ-generated Mn^{3+} sites for enhanced acidic oxygen evolution. *J. Am. Chem. Soc.* **146**, 33276–33287 (2024).
- 19 Gaur, A., Sharma, J., Kaur, G., Mhin, S. & Han, H. Jahn–Teller effect: Impact of distortion on oxygen electrocatalysis. *Adv. Funct. Mat.* **36** (2025).
- 20 Singh, B. & Draksharapu, A. Jahn–Teller distortion in the oxygen evolution reaction: from fundamental insights to catalyst design. *J. Mater. Chem. A* **14**, 830–851 (2026).

[Lines 237 to 251 in the revised manuscript]

Encouraged by these results, we further evaluated the high-current stability of $\gamma\text{-MnO}_2$ and NMO-0.2 on different electrode supports at 200 mA cm^{-2} in $0.5\text{ M H}_2\text{SO}_4$ (**Fig. 2e**). On carbon fiber paper, $\gamma\text{-MnO}_2$ rapidly deactivated within $<30\text{ h}$, whereas NMO-0.2 maintained operation for $\sim 100\text{ h}$ before rapid deactivation, likely due to carbon corrosion and catalyst detachment under strongly oxidative acidic conditions. To minimize support-related degradation, both catalysts were further tested on platinized titanium fiber felt (Pt/Ti), a corrosion-resistant porous transport layer commonly used in PEMWE systems (**Supplementary Fig. 33**). Under this configuration, $\gamma\text{-MnO}_2$ exhibited improved stability compared with that on carbon fiber paper, but its performance began to degrade rapidly after $\sim 300\text{ h}$, indicating that the Pt/Ti support mitigates support-related degradation but does not fully resolve the intrinsic instability of $\gamma\text{-MnO}_2$ under acidic OER condition. More importantly, NMO-0.2 showed further enhanced durability, operating stably for $>1000\text{ h}$ at 200 mA cm^{-2} under the same Pt/Ti fiber felt configuration. These results demonstrate that NMO-0.2 retains superior high-current durability on a practical corrosion-resistant support, surpassing the performance of most state-of-the-art Mn-based acidic OER catalysts (**Fig. 2f**; **Supplementary Table 4**).

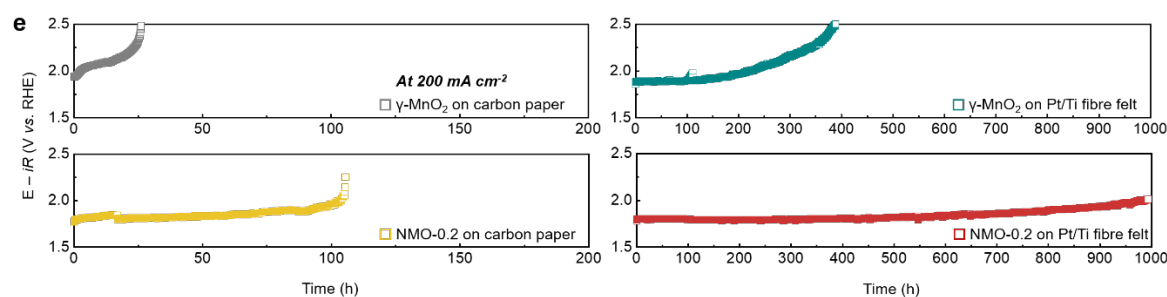


Fig. 2e Chronopotentiometric stability tests of $\gamma\text{-MnO}_2$ and NMO-0.2 at 200 mA cm^{-2} in $0.5\text{ M H}_2\text{SO}_4$. The right panels compare both catalysts on Pt/Ti fiber felt under identical

conditions, whereas the left panels present the corresponding measurements on carbon fiber paper for comparison. These results demonstrate the superior durability of NMO-0.2.

[Lines 460 to 467 in the revised manuscript]

The NMO-0.2 catalyst was integrated into a membrane electrode assembly (MEA) for PEMWE operation. The MEA was fabricated by the catalyst-coated substrate (CCS) method using NMO-0.2 as the anode catalyst, Pt/C as the cathode catalyst, and Nafion® N117 as the PEM (Fig. 5a and Supplementary Fig. S9). The NMO-0.2-based PEMWE achieved a cell voltage of 1.88 V at 1 A cm⁻² (Fig. 5b) and maintained stable operation for >600 h at 100 mA cm⁻² (Fig. 5c). Remarkably, it also operated for >300 h at 200 mA cm⁻² and for >60 h at 500 mA cm⁻², demonstrating the PEMWE applicability of NMO-0.2 under high-current acidic OER conditions.

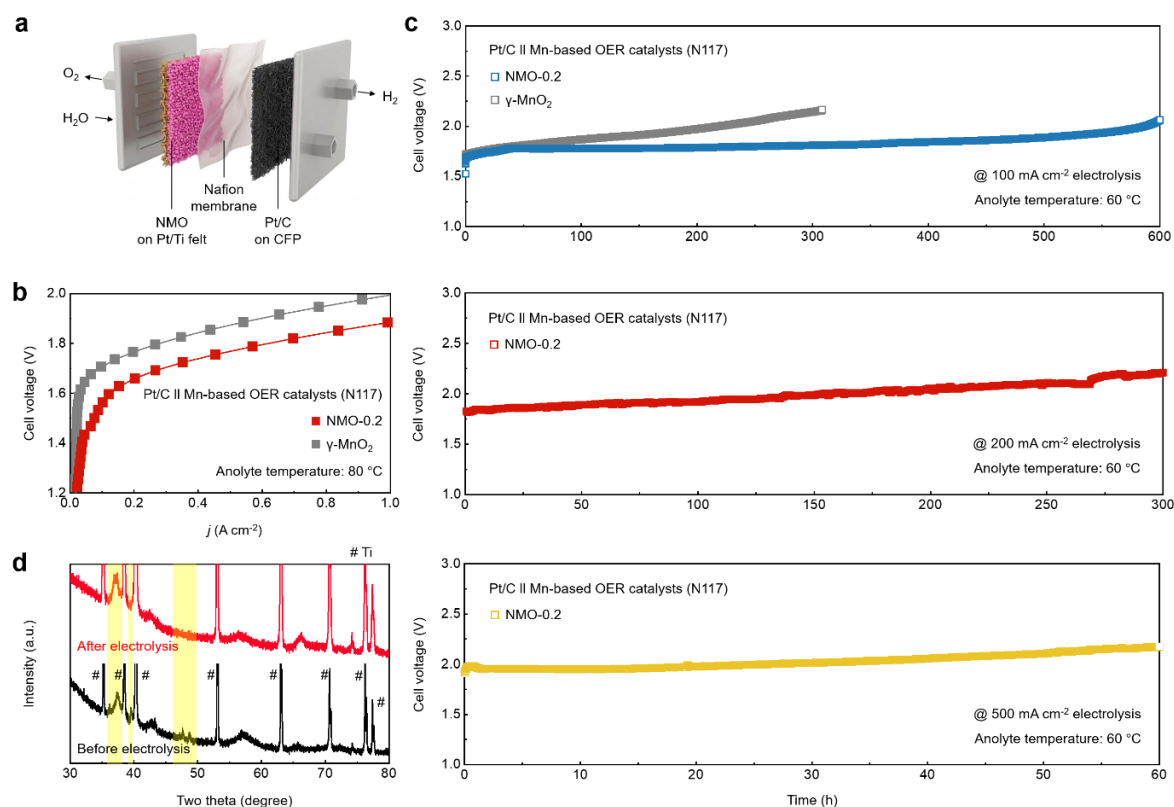


Fig. 5 Evaluation of PEMWE performance. **a** Schematic illustration of the PEMWE system with an MEA prepared by the CCS method. **b** Polarization curves of PEMWE cells employing γ -MnO₂ or NMO-0.2 as the anode catalysts. **c** Cell-voltage profiles of PEMWE cells employing γ -MnO₂ or NMO-0.2 as the anode catalyst at 100 mA cm⁻², together with NMO-0.2 based PEMWE operation at 200 and 500 mA cm⁻². **d** XRD patterns of NMO deposited on the Pt/Ti felt before and after electrolysis at 200 mA cm⁻². The # symbols indicate the Ti substrate features, while the yellow-shaded regions highlight diffraction peaks showing significant changes after electrolysis at 200 mA cm⁻².

R3–3. The authors have used *in situ* XAS to reveal the stability of NMO-0.2 in Fig. 3. Although the white line peak position for NMO-0.2 in Fig. 3e shows only slight changes, the EXAFS curves in Fig. 3h indicate that the Mn–O has become obviously shorter at 1.8 V, which normally means the increased chemical state of Mn. Another abnormal phenomenon is the *in situ* XAS spectra of γ -MnO₂ in Fig. 3g. The Mn–O bond of γ -MnO₂ should be shortened if the valence state of Mn increases. However, the Mn–O bond has become longer indicating a possible lower chemical state at high voltages. The authors should carefully check and explain the experimental data.

Response: We sincerely thank the reviewer for identifying this important inconsistency in the original *in situ* XAS analysis. We agree that the original EXAFS trend was not fully consistent with the corresponding XANES edge shifts, particularly the apparent Mn–O shortening in NMO-0.2 and Mn–O bond elongation in γ -MnO₂ at high potentials.

To address this issue, we re-examined the original dataset and concluded that the high-potential EXAFS spectra were likely affected by measurement-related artifact, including bubble-induced noise. Therefore, we newly performed *in situ* Mn K-edge XAS measurements under improved conditions, where the current densities remained below $\sim 50 \text{ mA cm}^{-2}$ and excessive O₂ gas evolution was minimized. The revised measurements were performed using Ar-degassed electrolyte, with the working electrode positioned on the front side of the *in situ* cell for fluorescence-mode EXAFS to reduce the electrolyte/X-ray path length. Bubbles were removed from the electrode surface after each measurement, and the measurements were repeated using independently prepared electrodes.

In the revised data, the XANES and EXAFS trends are now physically consistent. γ -MnO₂ shows a clear Mn K-edge blue shift with increasing applied potential, accompanied by Mn–O bond contraction and decreased Mn–O peak intensity, indicating Mn oxidation with local coordination changes. In contrast, NMO-0.2 shows only minor XANES edge shifts and largely preserved Mn–O EXAFS features, indicating better retention of the Mn oxidation state and local Mn–O coordination environment during OER.

Accordingly, we have revised Fig. 3, the corresponding Results section, and the Methods section based on the newly measured *in situ* XAS dataset, as shown below.

[Lines 321 to 329 in the revised manuscript]

The corresponding *in situ* Mn K-edge FT-EXAFS spectra further support this interpretation (Supplementary Fig. 43). For γ -MnO₂, the Mn–O feature in the first coordination shell

shifted to a shorter radial distance with increasing applied potential, accompanied by a decrease in Mn–O peak intensity (Figs. 3f, h). After returning to OCV after OER, the Mn–O feature did not fully recover to its initial state, indicating irreversible local coordination changes under acidic OER conditions. In contrast, NMO-0.2 maintained a nearly unchanged Mn–O radial distance and preserved Mn–O peak intensity throughout the potential sequence (Figs. 3g, h). The Mn–O feature also returned close to its initial state after OER, indicating that the local Mn–O coordination environment is largely preserved.

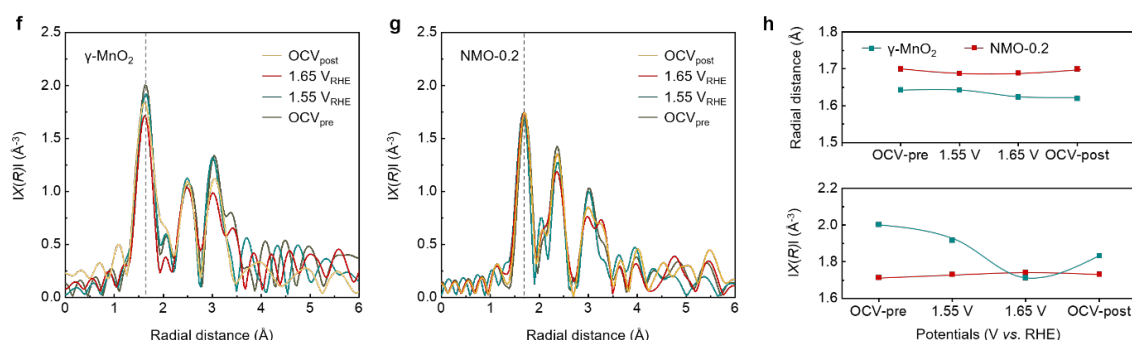


Fig. 3. f–h k^2 -weighted FT-EXAFS spectra of γ -MnO₂ and NMO-0.2 collected at OCV_{pre}, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV_{post}. **h** Potential-dependent changes in the Mn–O radial distance (upper box) and Mn–O peak intensity (lower box) extracted from the *in situ* EXAFS spectra.

R3–4. Differential electrochemical mass spectrometry (DEMS) data should be provided to confirm the OPM process.

Response: We sincerely thank the reviewer for this valuable suggestion. We agree that DEMS analysis can provide important experimental evidence for evaluating the proposed OPM-like pathway.

To address this point, we performed additional *in situ* isotope-labelling DEMS measurements using ¹⁸O-labelled γ -MnO₂ and NMO-0.2 catalysts in ¹⁶O-containing 0.5 M H₂SO₄ electrolyte. NMO-0.2 exhibited more pronounced ¹⁸O-labelled oxygen signals than γ -MnO₂, supporting the participation of catalyst-associated oxygen species during OER. These results are consistent with the *in situ* Raman observation of earlier formation of labile *O species and provide additional support for the proposed OPM-like pathway.

Accordingly, we have added the isotope-labelled DEMS results, AEM/OPM isotope-labelled O₂ formation schemes, and corresponding experimental details to the revised manuscript and Supplementary Information. Please also refer to our response to Reviewer #1, Comment 4 for a detailed discussion of the DEMS results.

R3–5. Why the stability test and LSV curves were measured in 0.5 M H₂SO₄ but the *in situ* and XAS were measured in 0.5 M HClO₄ solution?

Response: We thank the reviewer for pointing out this ambiguity. We apologize for the unclear description in the original manuscript. The *in situ* Raman and XAS measurements were conducted in different electrolytes, but this was not clearly stated.

Specifically, the *in situ* Raman measurements were conducted in 0.5 M HClO₄ to minimize Raman spectral interference from SO₄²⁻ species, which appear near 980 and 1050 cm⁻¹ and can overlap with or obscure weak signals from oxygenated intermediates, particularly *O–O* radical-coupled intermediates around 1050 cm⁻¹ (*J. Am. Chem. Soc.* **2025**, 147, 10678). In contrast, HClO₄ only mainly shows a ClO₄⁻ band near 955 cm⁻¹, allowing us to monitor the 1050 cm⁻¹ region without electrolyte interference. Therefore, 0.5 M HClO₄ was used only for *in situ* Raman spectroscopy (Figs. 3a and 3b).

In situ XAS measurements were conducted in 0.5 M H₂SO₄, consistent with the LSV and stability tests. Since XAS is not affected by vibrational bands from electrolyte anions, H₂SO₄ was used for the XAS measurements to match the electrochemical testing conditions.

We have revised the Results and Methods sections to clearly specify the electrolyte used for each *in situ* measurement, as shown below.

[Lines 281 to 283 in the revised manuscript]

In situ Raman measurement was conducted to probe reaction intermediates under applied potentials ranging from open circuit voltage (OCV) to 1.95 V_{RHE} in 0.5 M HClO₄ (**Figs 3a, b and Supplementary Fig. 37**).

[Lines 311 to 313 in the revised manuscript]

In situ XAS analysis was performed in 0.5 M H₂SO₄ electrolyte to examine the potential-dependent changes in the Mn oxidation state and local coordination environment during acidic OER (**Supplementary Fig. 42**).

[Lines 160 to 171 in the revised Supplementary Information]

***In situ* Raman spectroscopy**

In situ Raman spectroscopy was performed using a custom-designed *in situ* electrochemical cell equipped with an immersion objective lens (50×, N.A. = 0.8). The working electrode was prepared on carbon fiber paper, with a Pt wire and an Ag/AgCl electrode used as the counter and reference electrodes, respectively. A 0.5 M HClO₄ solution served as the electrolyte.

R3–6. In Table 3 the fitted bond length for NMO-0.2 shows too many decimal places.

Response: We thank the reviewer for pointing this out. We have revised Supplementary Table 3 by rounding the fitted Mn–O bond lengths to an appropriate level number of significant digits.

[In the revised Supplementary Information]						
Supplementary Table 3 Fitting parameters of the Mn K-edge EXAFS spectra for γ -MnO ₂ 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		

R3–7. The XAS spectra (both XANES and EXAFS) after reaction should be provided to check if the electronic structure can recover.

Response: We thank the reviewer for this important suggestion. In response, we have added the post-OER reaction XAS spectra collected after returning to OCV to both the XANES and EXAFS analyses in Fig. 3.

The revised Mn K-edge XANES spectra show that γ -MnO₂ undergoes a pronounced absorption-edge blue shift under applied potentials, and the edge position does not fully recover after returning to OCV after OER. In contrast, NMO-0.2 shows only minor edge shifts during OER, and the edge position is largely restored after returning to OCV.

The corresponding EXAFS spectra show the same trend. For γ -MnO₂ the Mn–O radial distance and peak intensity do not fully recover after OER, indicating irreversible local coordination change. In contrast, the EXAFS features of NMO-0.2 remain close to the initial state, demonstrating that the local Mn–O coordination environment is largely preserved.

These post-OER XAS results support that NMO-0.2 can preserve both the Mn oxidation state and local Mn–O framework during acidic OER. We have revised the Results section accordingly to include this post-OER XANES/EXAFS analysis.

[Lines 311 to 336 in the revised manuscript]

In situ XAS analysis was performed in 0.5 M H₂SO₄ electrolyte to examine the potential-dependent changes in the Mn oxidation state and local coordination environment during acidic OER (**Supplementary Fig. 42**). In the Mn K-edge XANES spectra, γ -MnO₂ exhibited a clear blue shift of the absorption edge with increasing applied potential, indicating progressive Mn oxidation under OER conditions (**Fig. 3d**). At OCV after OER, the absorption edge of γ -MnO₂ did not fully recover to its initial position, suggesting irreversible structural/electronic changes in the MnO₂ framework. In contrast, NMO-0.2 showed only minor absorption-edge shifts during OER, and the edge position was restored after returning to OCV (**Fig. 3e**). This reversible behavior indicates that NMO-0.2 better preserves the Mn oxidation state and local electronic structure under acidic OER conditions.

The corresponding *in situ* Mn K-edge FT-EXAFS spectra further support this interpretation (**Supplementary Fig. 43**). For γ -MnO₂, the Mn–O feature in the first coordination shell shifted to a shorter radial distance with increasing applied potential, accompanied by a decrease in Mn–O peak intensity (**Figs. 3f, h**). After returning to OCV after OER, the Mn–O feature did not fully recover to its initial state, indicating irreversible local coordination changes under acidic OER conditions. In contrast, NMO-0.2 maintained a nearly unchanged Mn–O radial distance and preserved Mn–O peak intensity throughout the potential sequence (**Figs. 3g, h**). The Mn–O feature also returned close to its initial state after OER, indicating that the local Mn–O coordination environment is largely preserved.

Taken together, the *in situ* XAS results show that γ -MnO₂ undergoes irreversible Mn oxidation and local structural degradation under acidic OER conditions, whereas NMO-0.2 exhibits largely reversible oxidation-state and coordination responses. This behavior supports that Nd incorporation helps preserve the Mn oxidation state and local Mn–O framework during OER, supporting the stabilization of Mn³⁺-containing motifs in the mixed-phase NMO structure (**Fig. 3i**). Such structural and electronic robustness contributes to the enhanced acidic OER activity and durability of NMO-0.2.

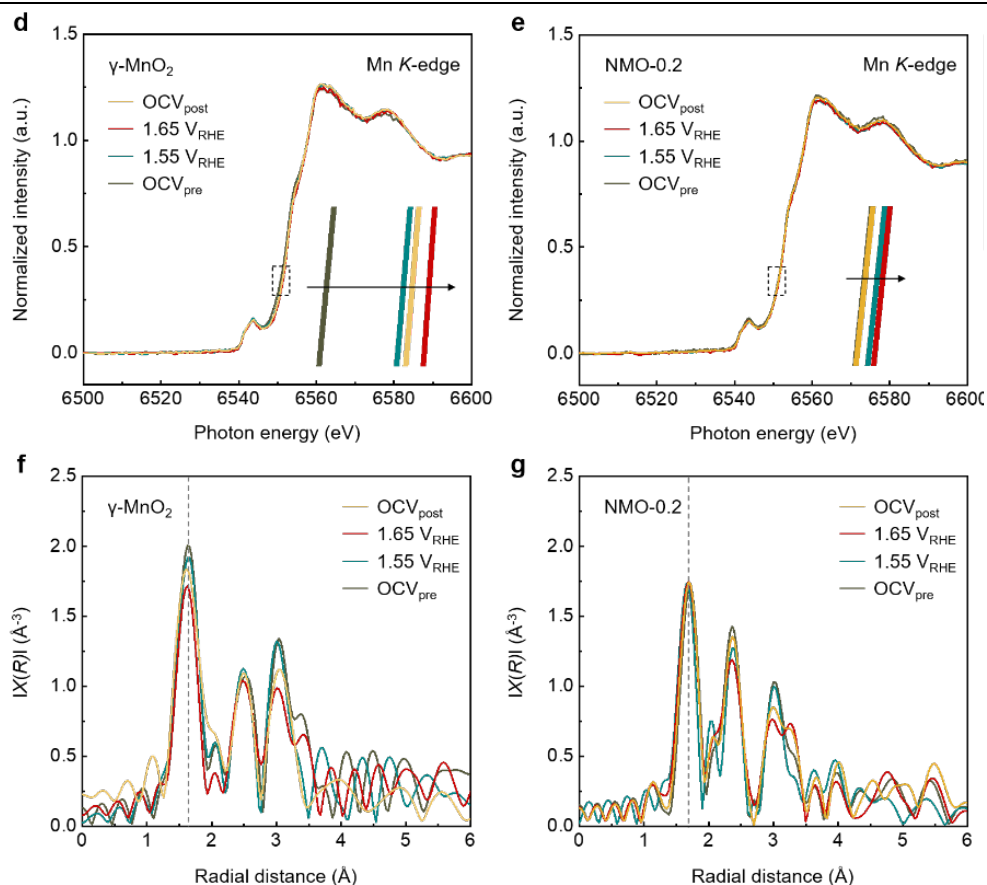


Fig. 3. d, e *In situ* Mn K-edge XANES spectra of γ -MnO₂ and NMO-0.2 measured at OCV before OER (OCV_{pre}), 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV after OER (OCV_{post}). The magnified absorption-edge regions show the potential-dependent changes in the average Mn oxidation state. **f, g** k²-weighted FT-EXAFS spectra of γ -MnO₂ and NMO-0.2 collected at OCV_{pre}, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV_{post}.

Reviewers' Comments:

Reviewer #4

The manuscript reported the construction of Nd doped γ -MnO₂ (NMO) to achieve durable acidic water oxidation. Combined DFT studies and spectroscopic analysis, the authors attributed the facilitated OER kinetics of NMO to enhanced Mn–O covalency through 4f–2p–3d orbital coupling and the stabilization of J–T–active Mn³⁺ site. (1) However, from my point of view, this work falls short as the performance characterization in some case exhibit an opposite conclusion compared to recent key study on γ -MnO₂ (Nat. Catal. 7, 252–261 (2024)). (2) Moreover, the experimental evidence provided does not sufficiently support the proposed mechanism. (3) Critical aspects, including surface electronic structure evolution and catalyst reconstruction under operating conditions, are inadequately addressed. (4) The manuscript could be strengthened by providing more compelling discussion, particularly the individual contributions of different crystal phases. Therefore, in its current form, the novelty and systematic rigor are insufficient for publication in Nature Communications.

Response: We sincerely thank the reviewer for the critical and constructive assessment of our manuscript. We understand the reviewer's concerns regarding the comparison with recent γ -MnO₂ studies, the sufficiency of mechanistic evidence, catalyst reconstruction under operating conditions, and the phase-specific contributions within NMO-0.2.

In response, we have substantially revised the manuscript and added new experimental and theoretical analyses. First, we clarified that our γ -MnO₂ reference is a thermally prepared catalyst and that the rapid decay originally observed on carbon fibre paper was strongly affected by the electrode/support configuration. We therefore added a direct γ -MnO₂/NMO-0.2 comparison on the same Pt/Ti fibre felt substrate.

Second, we strengthened the mechanistic evidence by adding isotope-labelling DEMS and ¹⁸O-labelling *in situ* Raman experiments, which support catalyst-associated oxygen participation and the assignment of Mn–oxo-related intermediates. We also newly performed *in situ* XAS measurements under improved conditions to better evaluate potential-dependent Mn oxidation and local coordination changes while minimizing bubble-induced artifacts.

Third, we clarified the phase-dependent role of NMO-0.2. Phase-enriched reference experiments and revised DFT analysis indicate that α -Mn₂O₃-rich components contribute activity-promoting Mn³⁺ motifs, whereas the β /R-MnO₂-rich framework provides structural robustness and electronically modulated Mn sites.

Overall, the revised manuscript no longer presents NMO-0.2 as simply outperforming

optimized γ -MnO₂ benchmarks in absolute lifetime. Rather, it establishes Nd doping as a complementary strategy for stabilizing Mn³⁺-containing motifs and improving the activity–stability balance of thermally synthesized Mn oxide catalysts under acidic OER conditions.

R4–1. The confusing aspect is about the OER performance of pristine γ -MnO₂. Recent key study has already demonstrated that γ -MnO₂ exhibited robust OER activity under acidic conditions *Nat. Catal.* 7, 252–261 (2024). In contrast, the current manuscript claims that pristine γ -MnO₂ undergoes rapid activity decay within less than 30 h. This discrepancy is not adequately explained and raises concerns regarding the novelty of experimental design.

Response: We thank the reviewer for pointing out this important issue. We agree that our original manuscript of γ -MnO₂ stability could be potentially confusing. The rapid decay of γ -MnO₂ within <30 h was observed on carbon fiber paper, where carbon corrosion and catalyst detachment can accelerate apparent deactivation under acidic OER conditions (*Small Methods* **2022**, 6, 2201130; *Nat. Commun.* **2022**, 13, 2294).

To ensure a fairer comparison, we additionally evaluated γ -MnO₂ and NMO-0.2 on Pt/Ti fiber felt as in the previous study. Under this revised configuration, γ -MnO₂ exhibited substantially improved stability (for >300 h at 200 mA cm⁻²) compared with that on carbon fiber paper, confirming that the original rapid decay was strongly influenced by the electrode/support configuration. Nevertheless, NMO-0.2 still showed superior durability under the same Pt/Ti fiber felt configuration, demonstrating that the Nd-modified catalyst retain an improved activity-stability balance relative to our thermally prepared γ -MnO₂ reference.

The difference from the recently reported highly stable γ -MnO₂ catalyst in *Nat. Catal.* **2024** can be attributed to differences in catalyst synthesis, structural optimization, and electrode configuration. That study used an optimized electrodeposited/annealed γ -MnO₂ catalyst on Pt/Ti mesh, whereas our γ -MnO₂ reference was thermally prepared and used as the direct undoped counterpart to NMO-0.2. Therefore, our conclusion is not that γ -MnO₂ is universally unstable, but that Nd doping improves the activity–stability balance of our Mn oxide catalyst system under identical testing conditions.

We have revised Fig. 2e and the corresponding Results section to clarify the substrate effect and to include the direct γ -MnO₂/NMO-0.2 comparison on Pt/Ti fiber felt, as shown below.

[Lines 237 to 251 in the revised manuscript]

Encouraged by these results, we further evaluated the high-current stability of γ -MnO₂ and

NMO-0.2 on different electrode supports at 200 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ (Fig. 2e). On carbon fiber paper, $\gamma\text{-MnO}_2$ rapidly deactivated within $<30 \text{ h}$, whereas NMO-0.2 maintained operation for $\sim 100 \text{ h}$ before rapid deactivation, likely due to carbon corrosion and catalyst detachment under strongly oxidative acidic conditions. To minimize support-related degradation, both catalysts were further tested on platinized titanium fiber felt (Pt/Ti), a corrosion-resistant porous transport layer commonly used in PEMWE systems (Supplementary Fig. 33). Under this configuration, $\gamma\text{-MnO}_2$ exhibited improved stability compared with that on carbon fiber paper, but its performance began to degrade rapidly after $\sim 300 \text{ h}$, indicating that the Pt/Ti support mitigates support-related degradation but does not fully resolve the intrinsic instability of $\gamma\text{-MnO}_2$ under acidic OER condition. More importantly, NMO-0.2 showed further enhanced durability, operating stably for $>1000 \text{ h}$ at 200 mA cm^{-2} under the same Pt/Ti fiber felt configuration. These results demonstrate that NMO-0.2 retains superior high-current durability on a practical corrosion-resistant support, surpassing the performance of most state-of-the-art Mn-based acidic OER catalysts (Fig. 2f; Supplementary Table 4).

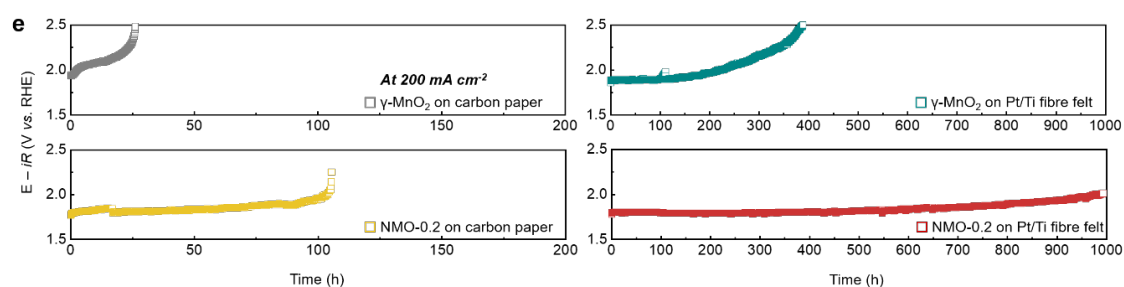


Fig. 2e Chronopotentiometric stability tests of $\gamma\text{-MnO}_2$ and NMO-0.2 at 200 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$. The right panels compare both catalysts on Pt/Ti fiber felt under identical conditions, whereas the left panels present the corresponding measurements on carbon fiber paper for comparison. These results demonstrate the superior durability of NMO-0.2.

R4-2. “Operando” XAS characterization section is questionable.

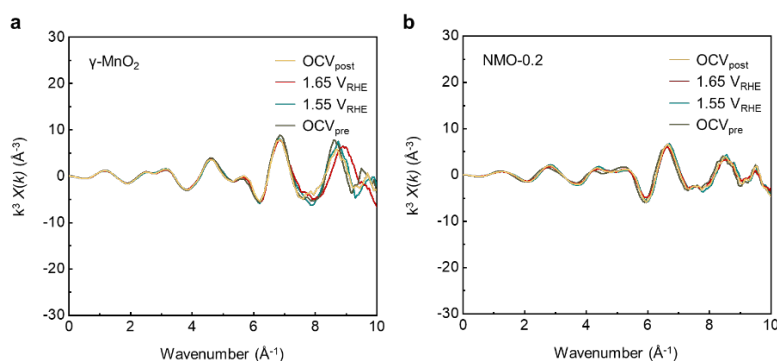
(1) The authors provided only Mn K-edge XANES and FT-EXAFS spectra, without showing the corresponding K-space spectra. In general, the observed backscattering signals in FT-EXAFS spectra are strongly affected by noise. Without showing the K-space data, the FT-EXAFS spectra presented in the manuscript are not convincing. (2) In addition, the experimental details of the electrochemical XAS measurements are insufficiently described, including the electrochemical cell configuration, electrode preparation, catalyst loading, and the time resolution of the XAS measurements. Critical questions remain to be addressed, such as: (3) How many spectra were collected at each applied potential? (4) Was beam damage

assessed? (5) How were gas bubble formation issues mitigated? (6) What changes in the spectra were observed when gas bubbles formed? The lack of such essential information renders the operando XAS results unconvincing and unacceptable.

Response: We sincerely thank the reviewer for this critical and constructive comment. We agree that the reliability of *in situ* XAS analysis requires corresponding *k*-space EXAFS data and sufficient experimental details. To address these concerns, and also in response to Comment 3 regarding possible bubble-induced artifacts, we newly performed *in situ* Mn K-edge XAS measurements under improved experimental conditions and revised Fig.3 accordingly.

(1) Regarding EXAFS reliability

We added the corresponding *k*-space EXAFS oscillations from the newly acquired *in situ* XAS dataset to Supplementary Information. The revised *k*-space data show well-preserved oscillation features over the measured potential range, supporting the reliability of the corresponding FT-EXAFS spectra, as shown below.



Supplementary Fig. 43 k^3 -weighted EXAFS oscillations of Mn K-edge. The k^3 -weighted EXAFS oscillations of (a) γ -MnO₂, and (b) NMO-0.2, respectively.

[FIGURE REDACTED]

Fig. R5 (review-only data) *In situ* Mn K-edge EXAFS data in the original manuscript. (a, b)

Original k^2 -weighted FT-EXAFS spectra and corresponding k^3 -weighted EXAFS oscillations of γ -MnO₂. (c, d) Original k^2 -weighted FT-EXAFS spectra and corresponding k^3 -weighted EXAFS oscillations of NMO-0.2.

(2) Experimental details

We revised the Methods section to provide additional experimental details, including the electrochemical cell configuration, electrode preparation, electrode geometry, electrolyte condition, catalyst loading, gas-bubble mitigation procedure, and XAS data processing, as shown below.

[Lines 173 to 198 in the revised Supplementary Information]

***In situ* XAS measurement**

In situ Mn K-edge XAS measurements, including XANES and EXAFS, were conducted in fluorescence mode using a custom-designed electrochemical cell equipped with polyimide film windows to allow efficient X-ray transmission while minimizing absorption and scattering. The catalyst-coated working electrode was mounted on the front side of the cell to reduce the effective electrolyte/X-ray path length and minimize bubble-induced scattering during fluorescence-mode measurements. The catalyst-coated working electrodes were prepared by drop-casting a precursor solution of 3 M Mn(NO₃)₂·4H₂O and 0.2 M Nd(NO₃)₃·6H₂O onto hydrophilic carbon fiber paper. The electrodes were then annealed in air at 350 °C for 6 h to directly form a binder-free catalyst layer on the carbon fiber paper through a self-supporting thermal-decomposition process.

Electrochemical measurements were carried out in a three-electrode configuration using the catalyst-coated electrode as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. Prior to *in situ* XAS measurements, the catalyst-coated electrodes were pretreated by electrolysis in 0.5 M H₂SO₄ for 1 h. Ar-degassed 0.5 M H₂SO₄ was used as the electrolyte. XAS spectra were collected at OCV before OER, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV after OER, with chronoamperometry performed during each acquisition. At each applied potential, XAS spectra were collected with an acquisition time of approximately 25 min per scan. After each spectrum was collected, gas bubbles attached to the electrode surface were physically removed before proceeding to the next potential. The measurements were repeated using independently prepared electrodes to confirm reproducibility.

The acquired XAS spectra were processed by subtracting the pre-edge background and

normalizing the post-edge region. EXAFS analysis was performed by Fourier transformation of the k^2 -weighted EXAFS oscillations, and k^3 -weighted EXAFS oscillations were also examined to assess the high- k data quality.

(3) Number of spectra and reproducibility

The revised measurements were performed at OCV before OER, 1.55 V_{RHE} , 1.65 V_{RHE} , and OCV after OER. The measurements were repeated at least twice using independently prepared electrodes, and the same potential-dependent trends were reproduced.

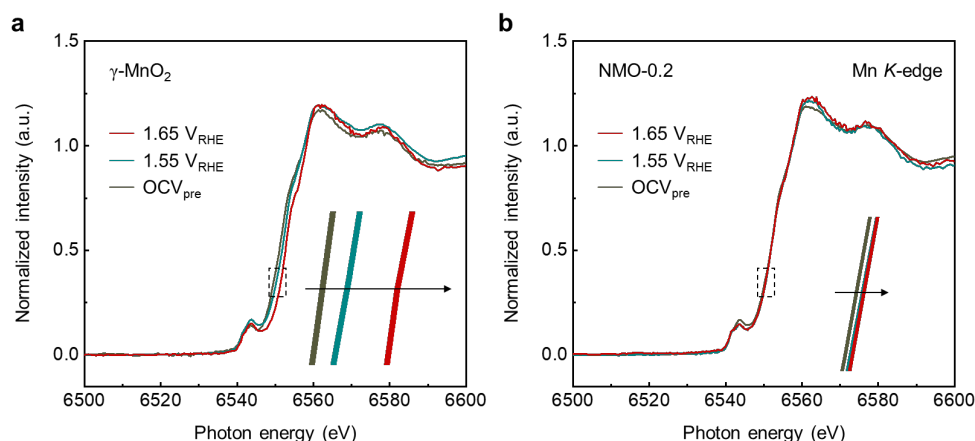


Fig. R6 (review-only data) Repeated *in situ* Mn K-edge XANES spectra of (a) γ - MnO_2 and (b) NMO-0.2 measured at OCV_{pre} , 1.55 V_{RHE} , 1.65 V_{RHE} , and OCV_{post} using independently prepared electrodes. The repeated measurements reproduce the same trend observed in Fig. 3, confirming the reliability of the potential-dependent XANES changes.

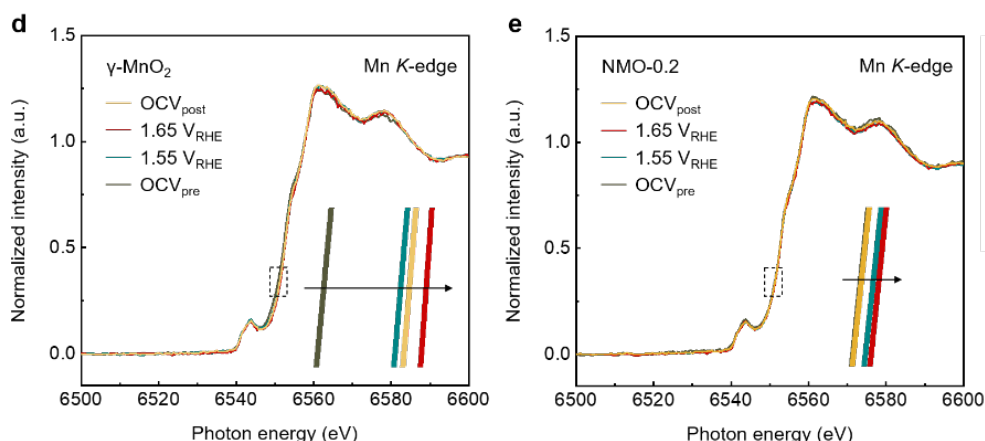


Fig. 3d, e *In situ* Mn K-edge XANES spectra of γ - MnO_2 and NMO-0.2 measured at OCV before OER (OCV_{pre}), 1.55 V_{RHE} , 1.65 V_{RHE} , and OCV after OER (OCV_{post}). The magnified absorption-edge regions show the potential-dependent changes in the average Mn oxidation state.

[FIGURE REDACTED]

Fig. R7 (review-only data) Repeated *in situ* Mn K-edge EXAFS measurements. (a, b) Repeated k^2 -weighted FT-EXAFS spectra and corresponding (b, d) k -space EXAFS oscillations of γ -MnO₂ and NMO-0.2 measured at OCV_{pre}, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV_{post} using independently prepared electrodes. The repeated measurements reproduce the trends observed in Fig. 3, confirming the reliability of the potential-dependent local structural changes.

(4) Beam damage assessment

Beam damage was assessed by comparing the spectra before and after OER under the same measurement configuration. The near recovery of the Mn K-edge edge and Mn–O EXAFS features after returning to OCV indicates that the observed changes are mainly potential-induced rather dominated by than beam damage (Figs. 3e and 3g).

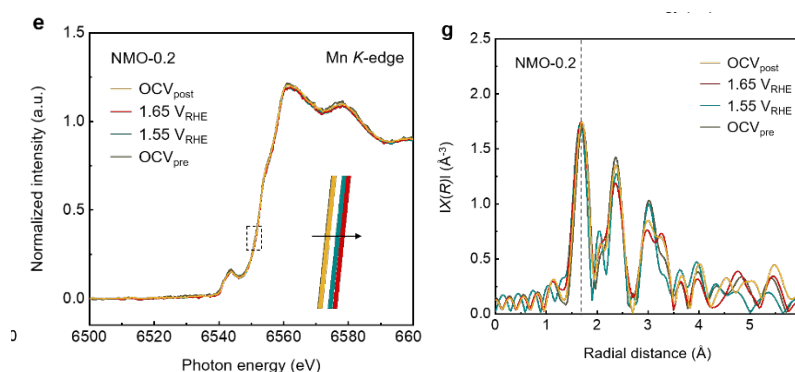


Fig. 3e *In situ* Mn K-edge XANES spectra of NMO-0.2 measured at OCV before OER (OCV_{pre}), 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV after OER (OCV_{post}). The magnified absorption-edge regions show the potential-dependent changes in the average Mn oxidation state. **g** k^2 -weighted FT-EXAFS spectra of γ -MnO₂ and NMO-0.2 collected at OCV_{pre}, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV_{post}.

(5) Gas-bubble mitigation

(6) Spectral changes caused by bubbles

To address this concern, we re-examined the original *in situ* XAS dataset and found that the spectra collected at 1.7 and 1.8 V_{RHE} showed abnormal damping and increased noise in the high-k EXAFS region, consistent with bubble-induced artifacts.

We therefore replaced these data with newly measured *in situ* XAS spectra under improved conditions at OCV before OER, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV after OER, where the current densities remained below ~50 mA cm⁻² and excessive O₂ gas evolution was minimized. The revised measurements were performed using Ar-degassed electrolyte, with the working electrode positioned on the front side of the *in situ* cell for fluorescence-mode EXAFS to reduce the electrolyte/X-ray path length. Bubbles were removed from the electrode surface after each measurement, and the measurements were repeated using independently prepared electrodes.

The revised measurements reproduce the same potential-dependent trends while exhibiting substantially improved XANES and EXAFS data quality. Accordingly, Fig. 3, the manuscript has been revised based on the newly acquired XAS dataset, as shown below.

[Lines 311 to 336 in the revised manuscript]

In situ XAS analysis was performed in 0.5 M H₂SO₄ electrolyte to examine the potential-dependent changes in the Mn oxidation state and local coordination environment during acidic OER (**Supplementary Fig. 42**). In the Mn K-edge XANES spectra, γ -MnO₂ exhibited a clear blue shift of the absorption edge with increasing applied potential, indicating progressive Mn oxidation under OER-relevant conditions (**Fig. 3d**). At OCV after OER, the absorption edge of γ -MnO₂ did not fully recover to its initial position, suggesting irreversible structural/electronic changes in the MnO₂ framework. In contrast, NMO-0.2 showed only minor absorption-edge shifts during OER, and the edge position was restored after returning to OCV (**Fig. 3e**). This reversible behavior indicates that NMO-0.2 better preserves the Mn oxidation state and local electronic structure under acidic OER conditions.

The corresponding *in situ* Mn K-edge FT-EXAFS spectra further support this interpretation (**Supplementary Fig. 43**). For γ -MnO₂, the Mn–O feature in the first coordination shell shifted to a shorter radial distance with increasing applied potential, accompanied by a decrease in Mn–O peak intensity (**Figs. 3f, h**). After returning to OCV after OER, the Mn–O feature did not fully recover to its initial state, indicating irreversible

local coordination changes under acidic OER conditions. In contrast, NMO-0.2 maintained a nearly unchanged Mn–O radial distance and preserved Mn–O peak intensity throughout the potential sequence (Figs. 3g, h). The Mn–O feature also returned close to its initial state after OER, indicating that the local Mn–O coordination environment is largely preserved.

Taken together, the *in situ* XAS results show that γ -MnO₂ undergoes irreversible Mn oxidation and local structural degradation under acidic OER conditions, whereas NMO-0.2 exhibits largely reversible oxidation-state and coordination responses. This behavior supports that Nd incorporation helps preserve the Mn oxidation state and local Mn–O framework during OER, supporting the stabilization of Mn³⁺-containing motifs in the mixed-phase NMO structure (Fig. 3i). Such structural and electronic robustness contributes to the enhanced acidic OER activity and durability of NMO-0.2.

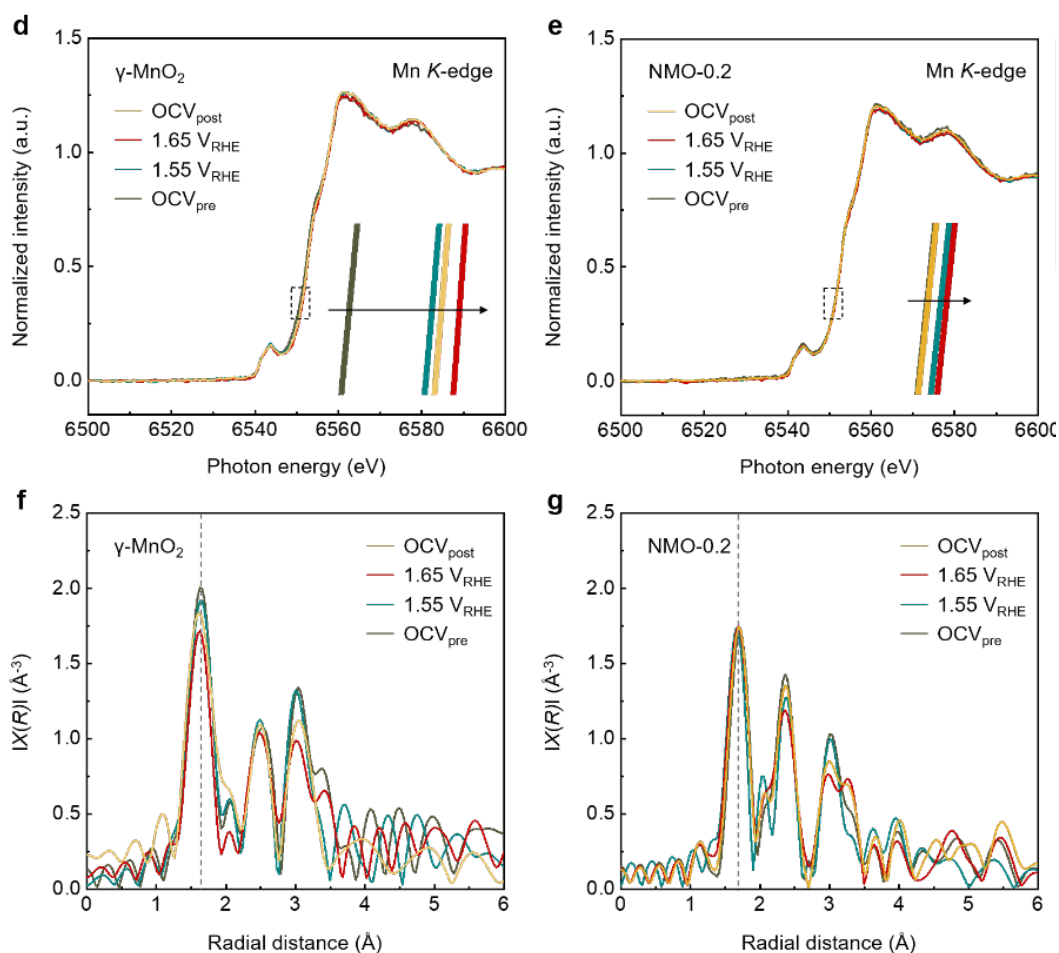


Fig. 3. d, e *In situ* Mn K-edge XANES spectra of γ -MnO₂ and NMO-0.2 measured at OCV before OER (OCV_{pre}), 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV after OER (OCV_{post}). The magnified absorption-edge regions show the potential-dependent changes in the average Mn oxidation state. **f, g** *k*²-weighted FT-EXAFS spectra of γ -MnO₂ and NMO-0.2 collected at OCV_{pre}, 1.55 V_{RHE}, 1.65 V_{RHE}, and OCV_{post}.

R4-3. From the electrochemical data (Figure 2), both γ -MnO₂ and NMO are expected to deliver current densities higher than 200 mA cm⁻² at 1.8 V vs. RHE. This means that under such a condition, substantial gas evolution is inevitable. Gas bubble formation can drastically distort spectroscopic signals. However, no such effects are apparent in the operando and XAS data shown in Fig. 3, raising concerns about the validity of the measurements.

Response: We thank the reviewer for this important comment. We agree that O₂ bubble formation at high current densities can distort *in situ* XAS measurements. To address this concern, we repeated the *in situ* XAS measurements under improved experimental conditions by limiting the applied potentials to <1.65 V_{RHE}, where the current densities remained below ~50 mA cm⁻², thereby minimizing excessive gas evolution. Details regarding gas-bubble mitigation, and data validity are also provided in our response to Comment 2.

R4-4. In Figure 3a,b, isotropic ¹⁸O labelling experiments should be conducted to confirm the assignment of signatures at 750 cm⁻¹ to Mn⁴⁺=O.

Response: We thank the reviewer for this important suggestion.

To verify the assignment of the Raman feature in the ~750–780 cm⁻¹ region observed under acidic OER conditions, we performed additional *in situ* Raman measurements using ¹⁸O-containing 0.5 M H₂SO₄ electrolyte prepared with H₂¹⁸O. In H₂¹⁶O electrolyte, the Raman band appeared at ~780 cm⁻¹, whereas it shifted to ~730 cm⁻¹ in H₂¹⁸O electrolyte, corresponding to a negative isotope shift of ~50 cm⁻¹. This shift to lower Raman frequency is consistent with the increased reduced mass of the Mn–O oscillator after substitution of ¹⁶O by ¹⁸O, supporting the assignment of this band to an oxygen-containing Mn–oxo intermediate, such as Mn⁴⁺=O. Similar isotope-dependent shifts have been used to identify Mn=O (Angew. Chem. Int. Ed. **2021**, 60, 4673) or Mn–OOH intermediates (Nat. Commun. **2022**, 13, 2294) in previous *in situ* Raman studies of Mn-based OER catalysts.

Therefore, the additional ¹⁸O-labelling Raman result supports that the potential-dependent feature in the ~750–780 cm⁻¹ region originates from an oxygen-containing Mn-oxo intermediate rather than from a non-oxygen lattice vibration or electrolyte-derived signal. We have added the ¹⁸O-labelling Raman result to the revised manuscript and Supplementary Information and updated the Method section, accordingly, as shown below.

[Lines 281 to 294 in the revised manuscript]

In situ Raman measurement was conducted to probe reaction intermediates under applied

potentials ranging from open circuit voltage (OCV) to 1.95 V_{RHE} in 0.5 M HClO₄ (**Figs. 3a, b and Supplementary Fig. 37**). The peaks at ~510/~650, ~580, and ~930 cm⁻¹ are attributed to out-of-plane symmetric Mn–O stretching, in-plane Mn–O stretching along the octahedral chains, and ClO₄⁻ species, respectively.^{22, 53, 54} With increasing applied potential, a new band corresponding to oxygen-containing Mn–oxo intermediates, such as surface terminal Mn⁴⁺=O, emerged at ~750 cm⁻¹. This assignment is supported by the isotope-induced red shift from ~780 cm⁻¹ in 0.5 M H₂SO₄ containing H₂¹⁶O electrolyte to ~730 cm⁻¹ in 0.5 M H₂SO₄ containing H₂¹⁸O electrolyte (**Supplementary Fig. 38**). NMO-0.2 exhibited this Mn⁴⁺=O feature at a lower potential than γ-MnO₂ (1.65 and 1.75 V_{RHE}, respectively), indicating faster kinetics of the intermediate transition from M–*OH to M–*O species facilitated by Mn³⁺ and O_v in NMO-0.2. It is also noteworthy that γ-MnO₂ displayed a peak at ~835 cm⁻¹ corresponding to dissolved high-valent MnO₄⁻ species at >1.75 V_{RHE}, whereas no such feature was observed for NMO-0.2 even at 1.95 V_{RHE}.

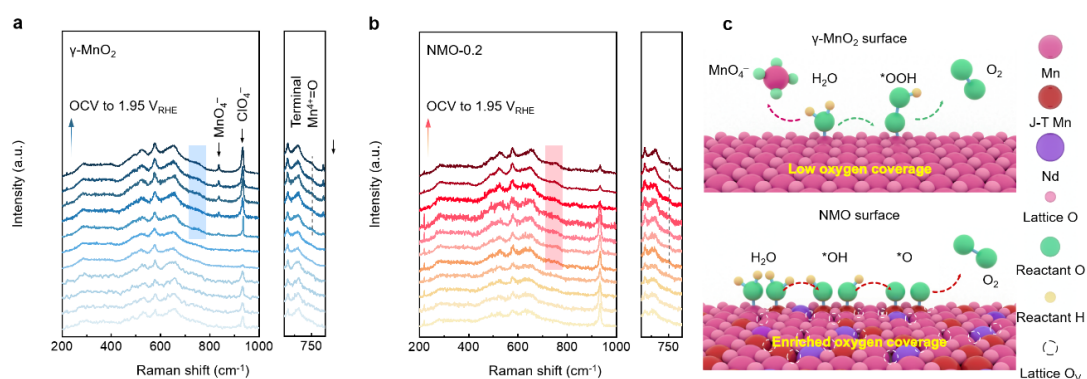
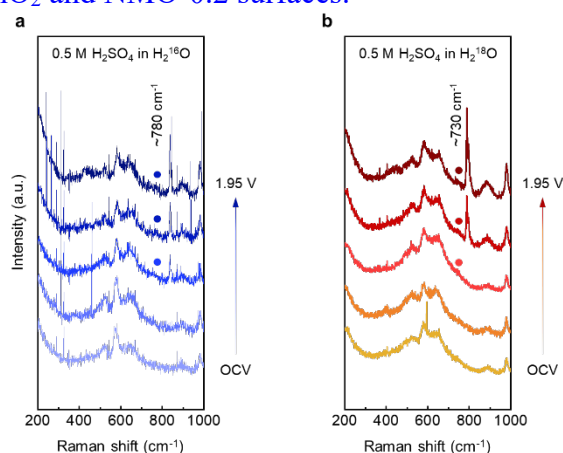


Fig. 3a, b *In situ* Raman spectra of γ-MnO₂ and NMO-0.2 collected under applied potentials, with magnified views of the 550–850 cm⁻¹ region. **c** Schematic illustration of the proposed OER pathways on γ-MnO₂ and NMO-0.2 surfaces.



Supplementary Fig. 38 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*.

[Lines 38 to 48 in the revised Supplementary Information]

Reagents and materials

All chemical reagents were used as received without further purification. $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%), MnO (99%), Mn_2O_3 (99.9%), Mn_3O_4 (97%), MnO_2 (99%), Nd_2O_3 (99.9%), RuO_2 (99.9%), H_2SO_4 (95–98%), H_2O_2 (30 wt.%), $\text{C}_2\text{H}_5\text{OH}$ (99.9%), CH_3OH (99.9%), tetramethylammonium chloride (TMACl, 98%), isotope-labelled H_2^{18}O water (97 atomic % ^{18}O) were purchased from Sigma-Aldrich. Nafion[®] ionomer (D520) was purchased from DuPont Co. Carbon fiber paper (TGP-H-060) was purchased from Fuel Cell Earth Co. Platinized titanium (Pt/Ti) fiber felt, titanium fiber felt, and platinum on carbon black (Pt/C, 20 wt%) were obtained from Fuel Cell Store. Nafion[®] 117 polymer membrane (N117) was purchased from Nara Cell Tech Co. Milli-Q ultrapure water (18.2 M Ω ·cm) was used throughout all experiments.

[Lines 160 to 171 in the revised Supplementary Information]

***In situ* Raman spectroscopy**

In situ Raman spectroscopy was performed using a custom-designed *in situ* electrochemical cell equipped with an immersion objective lens (50 $\times$, N.A. = 0.8). The working electrode was prepared on carbon fiber paper, with a Pt wire and an Ag/AgCl electrode used as the counter and reference electrodes, respectively. A 0.5 M HClO_4 solution served as the electrolyte. To prevent electrolyte leakage, an additional hydrophobic carbon fiber paper was placed beneath the working electrode and affixed to a conductive Tantalum (Ta) ring. Electrochemical potentials were applied using an SP–150 potentiostat. All Raman spectra were acquired at a laser power of 1 mW and 30 accumulations per spectrum. For isotope– ^{18}O labelling *in situ* Raman measurements, 0.5 M H_2SO_4 electrolyte was prepared using isotope-labelled H_2^{18}O water (97 atom% ^{18}O) as the solvent. The Raman spectra were collected under the same electrochemical and optical conditions and compared with those measured in H_2^{16}O electrolyte.

R4–5. The DFT calculations suggest that Nd doping may induce the formation of multiple crystal phases, including α - Mn_2O_3 , β - MnO_2 , and R- MnO_2 . However, it remains unclear which phase contributes most significantly to the observed OER activity. Additional experimental studies (electrochemical characterizations) involving Nd doping in these individual MnO_2 phases are necessary to provide deeper mechanistic insights.

Response: We thank the reviewer for raising this important point. We agree that the original manuscript did not sufficiently clarify whether the improved performance of NMO-0.2 originates from a specific phase or from the coexistence of multiple phases.

To address this point, we prepared phase-enriched Mn oxide reference catalysts using the same thermal-decomposition platform and compared their OER activity and stability in 0.5 M H₂SO₄. Although complete phase purity could not be achieved because Mn oxide polymorphs inherently coexist during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. The α -Mn₂O₃-rich reference exhibited higher OER activity, whereas the β /R-MnO₂-rich references showed better stability under acidic OER conditions. Nd incorporation further improved the activity and/or stability of these phase-enriched references.

These results indicate that the enhanced performance of NMO-0.2 is not attributable to a single isolated phase. Rather, α -Mn₂O₃ provides activity-promoting Mn³⁺-rich motifs, while the β /R-MnO₂-rich framework contributes structural robustness. Nd doping further stabilizes and electronically modulates these Mn environments, resulting in the improved activity–stability balance of NMO-0.2.

In addition, we added work-function analysis to discuss the possible role of mixed-phase domain boundaries in interphase charge redistribution and local Mn³⁺ stabilization, without assigning the improved performance to a specific idealized interface mechanism.

The corresponding experimental data, work-function analysis, and revised discussion have been added to the revised manuscript and Supplementary Information, as shown below.

[Lines 43 to 45 in the revised manuscript]

Phase-enriched reference experiments and density functional theory (DFT) calculations show that Nd-doped α -Mn₂O₃ promotes OPM through structural Mn³⁺ motifs, whereas β /R-MnO₂-rich domains provide structural robustness.

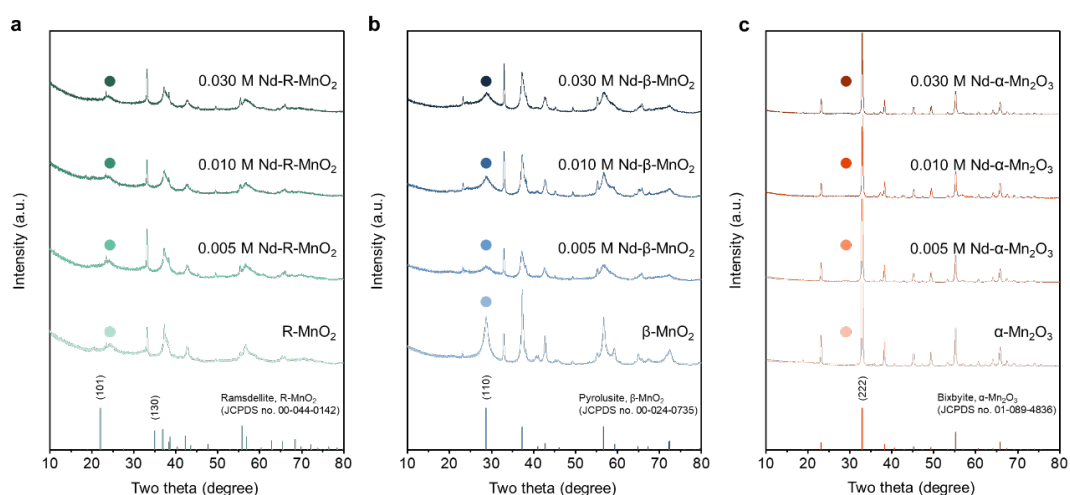
[Lines 89 to 94 in the revised manuscript]

Phase-enriched reference experiments reveal that α -Mn₂O₃-rich domains provide activity-promoting structural Mn³⁺ motifs, whereas β /R-MnO₂-rich domains contribute structural robustness under acidic OER conditions. Density functional theory (DFT) calculations further reveal phase-dependent OER pathways, with Nd-doped α -Mn₂O₃ favoring an OPM

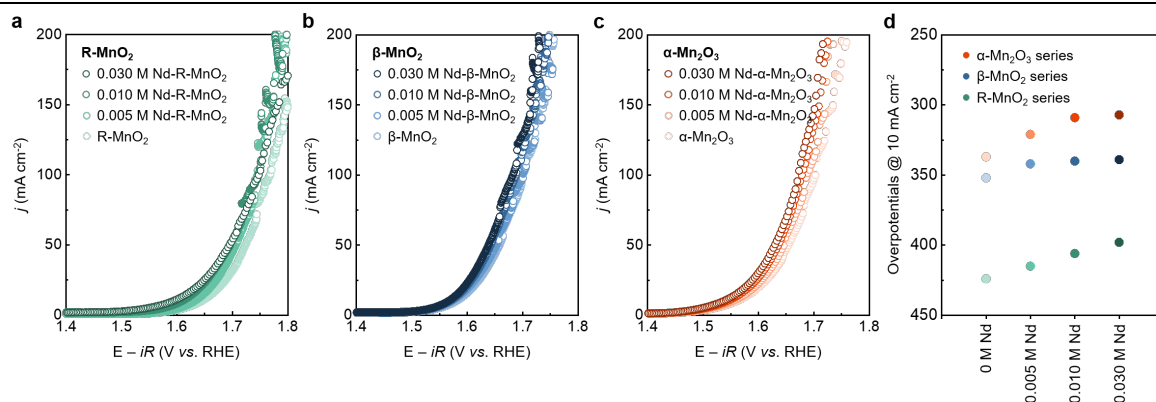
pathway and Nd-doped β /R-MnO₂ remaining absorbate evolution mechanism (AEM)-dominant with reduced OER barriers.

[Lines 344 to 358 in the revised manuscript]

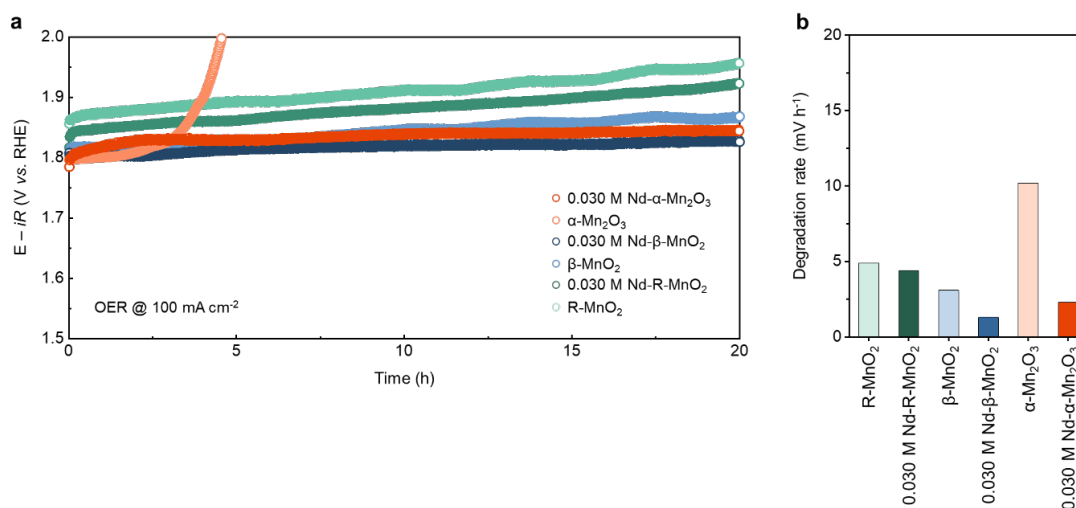
To experimentally examine the role of each Mn oxide polymorph in the mixed-phase NMO catalyst, phase-enriched Mn oxide reference catalysts were prepared using the same thermal-decomposition platform (**Supplementary Fig. 44**). Although complete phase purity could not be achieved because of the inherent coexistence of Mn oxide polymorphs during thermal decomposition, the dominant phase was systematically tuned by controlling the synthesis conditions. Electrochemical measurements showed that the α -Mn₂O₃-rich reference exhibited the highest OER activity (**Supplementary Fig. S45**), whereas the β /R-MnO₂-rich references displayed superior stability under acidic conditions (**Supplementary Fig. S46**). Nd incorporation further improved the activity and/or stability of all phase-enriched references. Therefore, the enhanced OER performance of NMO-0.2 is attributed to the combined contribution of minority α -Mn₂O₃-derived structural Mn³⁺ motifs and electronically induced Mn³⁺ within the dominant MnO₂-rich framework, rather than to an α -Mn₂O₃-dominant phase. These results provide the experimental basis for the phase-specific DFT analysis presented below, where each polymorph is modeled separately to clarify how Nd incorporation modifies its local structural and electronic properties.



Supplementary Fig. 44 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.



Supplementary Fig. 45 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 dopants. (d) Comparison of the overpotential at 10 mA cm⁻² for the corresponding phase-rich Mn oxides as a function of Nd concentrations.



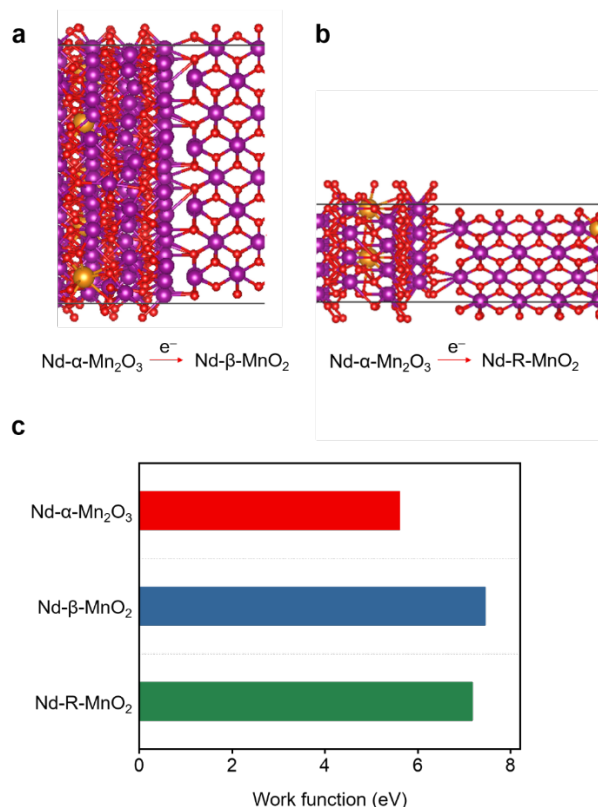
Supplementary Fig. 46 Phase-dependent OER stability of Nd-modified Mn oxide reference catalysts. (a) Chronopotentiometric stability curves of phase-controlled R-MnO₂-rich, β -MnO₂-rich, and α -Mn₂O₃ reference catalysts with and without Nd doping measured at 100 mA cm⁻² in 0.5 M H₂SO₄. (b) Comparison of degradation rates derived from the chronopotentiometric stability tests.

[Lines 135 to 139 in the revised manuscript]

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) further revealed that NMO-0.2 formed a mixed-phase domain boundary composed of distinct α -Mn₂O₃ (Fig. 1b, R1) and R-MnO₂ (Fig. 1b, R2) phases, together with clear evidence of Nd incorporation into the Mn oxide lattice (Fig. 1c; Supplementary Figs. 9–13).

[Lines 435 to 437 in the revised manuscript]

Work-function calculations further suggest possible interphase charge redistribution between α -Mn₂O₃ and MnO₂-rich domains, which may additionally modulate the local Mn–O electronic structure (Supplementary Fig. 58).



Supplementary Fig. 58 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. (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.

[Lines 587 to 595 in the revised Supplementary Information]

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, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor solutions (0.005, 0.010, or 0.030 M) were added to the 3 M $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution. Subsequently, 60 μL of each mixed precursor solution was drop-cast onto carbon fiber paper and calcined at the corresponding temperature.

R4–6. In Supplementary Table S3, the author should also provide the key fitting parameter of S_0^2 . Moreover, the σ^2 for NMO-0.2 appears unrealistically small. Typically, a smaller σ^2 corresponds to lower structural disorder and smaller coordination numbers, implying a highly ordered structure. This observation contradicts the central claims of structural distortion in the current study and therefore requires careful reassessment.

Response: We thank the reviewer for this important comment. We agree that the amplitude reduction factor, S_0^2 , is an essential EXAFS fitting parameter and should be explicitly provided. We also appreciate the reviewer's careful observation regarding σ^2 value of NMO-0.2, as an anomalously small σ^2 could lead to an incorrect interpretation of the local structural disorder.

In response, we carefully re-examined the Mn K-edge EXAFS fitting and updated the fitting parameters in Supplementary Table S3. The updated table now includes S_0^2 values for both $\gamma\text{-MnO}_2$ and NMO-0.2. After reassessment, the σ^2 value of NMO-0.2 was revised to 0.0103 $\text{\AA}^2$, which is larger than that of $\gamma\text{-MnO}_2$. This revised trend is physically reasonable and consistent with the increased local structural disorder and Mn–O coordination distortion induced by Nd incorporation.

The revised fitting also maintains acceptable fitting quality, as reflected by the corresponding R-factors. Therefore, the updated EXAFS fitting parameters now consistent with our conclusion that Nd doping modifies the local Mn–O coordination environment and induces structural distortion around Mn centers. We have updated Supplementary Table S3 accordingly, as shown below.

[FIGURE REDACTED]

[FIGURE REDACTED]

Fig. R8 (review-only data) Artemis EXAFS fitting log for (top) γ -MnO₂ and (bottom) NMO-0.2.

[Updated Supplementary Table 3]

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

R4–7. It is expected that rare earth element underwent oxidation and leached into the electrolyte, resulting structural amorphization (<https://doi.org/10.1038/s41929-025-01476-6>). In such a case, how to precisely model the investigated catalysts based on DFT calculations?

Response: We thank the reviewer for this important comment. We agree that rare-earth dopant leaching and surface reconstruction can occur under acidic OER conditions and should be considered when interpreting DFT models.

In our system, post-OER analyses indicate that Nd dissolution and structural amorphization are limited under the operating conditions examined in this study. ICP-OES analysis of the electrolyte after long-term electrolysis showed only minor Nd dissolution, and post-OER XRD/TEM analyses confirmed that the bulk mixed-phase structure of NMO-0.2 was largely retained without severe amorphization. These results suggest that Nd leaching does not dominate the structural evolution of NMO-0.2 within the experimental time scale of this work.

More generally, atomistic DFT modelling of amorphous or dynamically reconstructed oxide surfaces is challenging because such structures lack a unique periodic atomic model and can contain a broad distribution of local coordination environments, defects, and surface terminations (JACS Au **2021**, 1, 12, 2224; Small Sci. **2021**, 1, 2100011). Therefore, our DFT calculations were designed to elucidate the intrinsic electronic and structural effects of Nd incorporation in the experimentally observed crystalline Mn oxide framework, rather than to describe a fully reconstructed long-term operating surface.

Accordingly, our DFT calculations are intended to describe the intrinsic electronic and structural effects of Nd incorporation in the experimentally observed crystalline Mn oxide framework, rather than a fully reconstructed or amorphized long-term operating surface. The calculated trends—Nd-derived electron donation, Mn-centered distortion, enhanced Mn–O covalency, and altered OER energetics—are consistent with the XANES, EXAFS, XPS, and post-OER structural analyses.