

Enhanced oxygen reduction reaction performance of spinel lithium manganese oxide via proton exchange

Jiayi Li¹, Shengxi Zhao (✉)^{2,3}, Zhiwei Hu⁴, Xuepeng Zhong⁵, Nicolas Alonso-Vante⁶, Jiwei Ma (✉)¹

¹ Shanghai Key Laboratory for R & D and Application of Metallic Functional Materials, Institute of New Energy for Vehicles, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China

² School of Chemical and Biological Engineering, Guilin University of Technology, Guilin 541006, China

³ Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, School of Chemical and Bioengineering, Guilin University of Technology, Guilin 541004, China

⁴ Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany

⁵ Department of Chemistry, Technical University Berlin, 10623 Berlin, Germany

⁶ College of Smart Energy, Shanghai Jiao Tong University, Shanghai 200241, China

HIGHLIGHTS

- Protonated LiMn_2O_4 achieves a high ORR half-wave potential of 0.81 V with excellent cycling stability.
- Proton exchange induces lattice contraction and increases the average oxidation state of Mn.
- Enhanced surface hydroxylation improves oxygen adsorption capacity and reaction kinetics.
- Optimized electronic structure reduces the energy barrier for the rate-determining step.

Keywords:

Proton exchange
Spinel lithium manganese oxide
Oxygen reduction reaction
Electrocatalyst

ABSTRACT

The development of low-cost platinum-free electrocatalysts for the oxygen reduction reaction (ORR) is essential for the sustainable energy technologies. In this work, spinel-type LiMn_2O_4 was chemically modified via proton exchange to systematically investigate the effects of protonation on crystal structure, electronic configuration, and ORR performance. Experimental results reveal that proton exchange not only regulates the lattice parameters and Mn oxidation states, but also enhances surface hydrophilicity and oxygen adsorption capacity, leading to a significant improvement in ORR activity with at a half-wave potential of 0.81 V for pure Mn-based oxide. Physical characterizations and theoretical calculations reveal that protonation optimizes the surface electronic structure by mitigating the over-stabilization of oxygen intermediates on LiMn_2O_4 , thus facilitating the rate-determining step $^*\text{OH}$ adsorption and improving reaction kinetics. This work establishes proton exchange as a versatile strategy for the construction of Mn-based oxide electrocatalysts containing alkali metals, offering valuable insights for the rational design of non-precious metal catalysts in energy conversion applications.

© Higher Education Press 2026

1 Introduction

As global energy demands continue to rise and environmental concerns intensify, the development of efficient energy conversion and storage technologies has become a central focus in contemporary research. The oxygen reduction reaction (ORR), a key process in energy devices such as metal-air batteries and fuel cells, plays a significant role in determining both the energy conversion efficiency and operational lifespan of these systems [1–4]. Currently, platinum group metal (PGM) electrocatalysts are widely employed for their excellent ORR activity [5–8]. However, their limited availability

and high cost hinder commercial application [9,10]. Consequently, the design of highly efficient, low-cost, and PGM-free electrocatalysts has emerged as a key research focus in this field [11–15].

Among the various alternatives, transition metal oxides, especially Mn-based oxides, have received great attention due to their natural abundance, affordable cost, and excellent electrochemical stability [2,16,17]. Spinel-type Mn-based oxide has emerged as a promising PGM-free ORR electrocatalyst due to its abundant availability, low cost, unique crystal structure, and tunable electronic properties [18]. However, the intrinsic electrocatalytic activity of Mn-based oxides for ORR is generally limited

✉ Corresponding authors. E-mails: zhaosx@glut.edu.cn (S. Zhao); jiwei.ma@tongji.edu.cn (J. Ma)

by several factors. The insufficient electrical conductivity of Mn-based oxides leads to inefficient charge transport [19,20]. Moreover, the relatively low density of surface-active sites restricts the adsorption and conversion of reaction intermediates [21,22]. Additionally, Mn-based oxides are prone to structural degradation or dissolution during electrocatalytic processes, leading to the practical application being limited by these unstable Mn sites [23].

To address these limitations, recent studies have focused on the modification of Mn-based oxides by composition optimization [24–27], doping [28–30], defect engineering [20,31], and other strategies [32–36] to improve electrocatalytic performance. However, for a more precise understanding of the structure-performance relationship, it is desirable to adopt an optimization strategy that not only stabilizes Mn itself, but also keeps the components unchanged. In this context, proton exchange has been recognized as a simple yet effective chemical modification technique [37,38]. This approach can modulate the crystal lattice and electronic structure of the electrocatalysts, thereby shortening the internal transport pathways and facilitating oxygen diffusion. In addition, improvements in surface hydrophilicity and oxygen adsorption capacity further contribute to enhanced catalytic activity.

In the present study, spinel-type LiMn_2O_4 was modified via proton exchange, and the influence of protonation degree on its crystal structure, electronic configuration, and ORR performance was systematically investigated. The experimental results showed that proton exchange effectively regulated lattice parameters and Mn oxidation states of LiMn_2O_4 , while also enhancing surface hydrophilicity and oxygen adsorption capacity, thus significantly improving ORR activity. Furthermore, protonation on the surface electronic structure and electrocatalytic oxygen reaction mechanism was thoroughly explored by physical characterizations and theoretical calculations. This study offers a new perspective and practical approach for the development of efficient, stable, and platinum-free electrocatalysts, underscoring the potential of proton exchange as a powerful tool for advancing non-precious metal-based catalysts for energy technologies.

2 Results and discussion

2.1 Structural characterizations of as-prepared protonated LiMn_2O_4

Spinel-type protonated LiMn_2O_4 was synthesized via a combination of high-energy ball milling and low-temperature annealing, followed by acid pretreatment using H_2SO_4 solutions of varying concentrations. After wash-

ing and drying, a series of protonated LiMn_2O_4 samples with different degrees of protonation were obtained and labeled as 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO.

To characterize the crystal structure, X-ray diffraction (XRD) was employed. As shown in Fig. 1(a), both pristine and protonated samples retained the cubic $Fd\bar{3}m$ spinel structure, consistent with PDF#88-0589. However, as illustrated in Fig. 1(b), the XRD peaks shifted to higher angles with increasing levels of protonation, indicating a gradual contraction of the unit cell. Rietveld refinement further confirmed changes in lattice parameters, as summarized in Fig. S1 and Table S1. As depicted in Fig. 1(c), both lattice constant (a) and unit cell volume (V) decreased progressively with increasing protonation: lattice constant (a) decreased from 8.18 Å in LiMn_2O_4 to 8.17 Å (1-HLMO), 8.15 Å (2-HLMO), 8.12 Å (3-HLMO), and 8.04 Å (4-HLMO). This reduction was attributed to the partial substitution of Li^+ by H^+ during the proton exchange process.

X-ray absorption near edge structure (XANES) spectroscopy was performed to examine changes in the electronic structure of Mn. As shown in Fig. 1(d), the Mn K -edge shifted to higher energies following protonation, indicating an increase in the Mn oxidation state that intensified with deeper protonation. This shift was attributed to the partial solubility of Li^+ during acid treatment, which necessitated charge compensation. Fig. 1(e) shows the fitted Mn oxidation states using MnO , Mn_2O_3 , and MnO_2 references. The average Mn oxidation valence increased from $\text{Mn}^{3.51+}$ in LiMn_2O_4 , to $\text{Mn}^{3.82+}$ in 1-HLMO, $\text{Mn}^{3.83+}$ in 2-HLMO, $\text{Mn}^{3.85+}$ in 3-HLMO, and $\text{Mn}^{3.86+}$ in 4-HLMO, respectively.

To further examine the structural environment around Mn, extended X-ray absorption fine structure (EXAFS) analysis was conducted, as shown in Fig. 1(f). The Mn–O bond length, originally 1.50 Å in LiMn_2O_4 , shortened to 1.46 Å after protonation. This is in agreement with the lattice contraction observed via XRD, indicating enhanced covalence and structural stability after protonation. In addition, the coordination number of Mn–O increased with protonation, resulting in a more compact crystal structure [39, 40]. These structural modifications were expected to influence electron density distribution around Mn and its electronic structure, thus affecting the adsorption of ORR intermediates [41,42].

Cyclic voltammetry (CV) measurements provided further insight into Mn valence changes. As shown in Fig. S5, LiMn_2O_4 exhibited a typical oxidation peak corresponding to the $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ transition, and a reduction peak corresponding to $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$. In contrast, the typical 2-HLMO sample displayed no distinctive oxidation peak during the positive scan, indicating a reduced presence of Mn^{3+} for oxidation to Mn^{4+} . However, during the negative scan, a reduction process

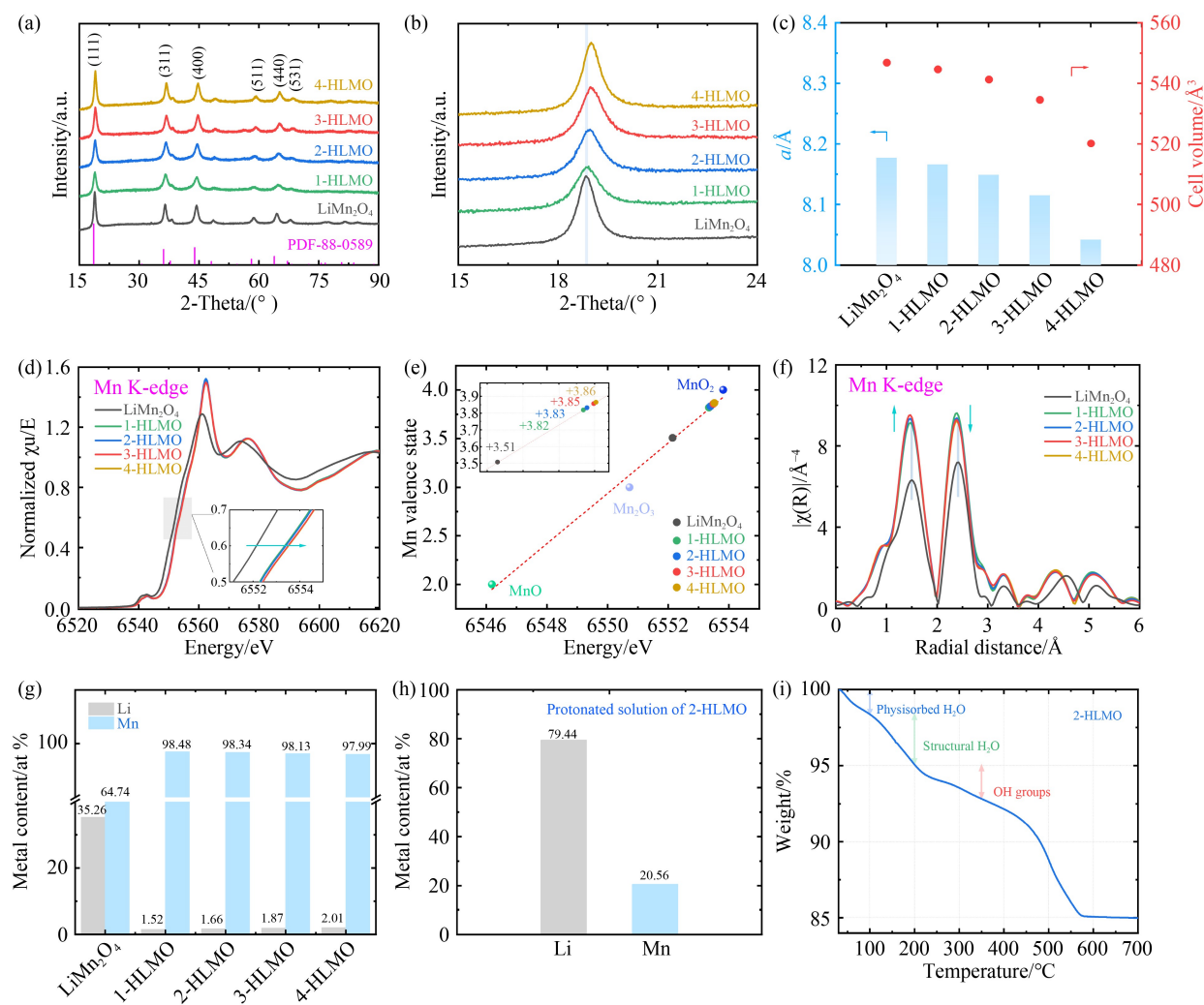


Fig. 1 Physical characterization of as-prepared protonated LiMn_2O_4 .

(a) XRD patterns of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO with standard LiMn_2O_4 (PDF#88-0589); (b) enlarged XRD patterns and 2-Theta from 15° to 24°; (c) lattice parameters and cell volumes from XRD by Rietveld refinement; (d) normalized Mn K-edge XANES spectra of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO; (e) fitted Mn valence states with XANES edge region with MnO , Mn_2O_3 , and Mn_2O_4 references; (f) Mn K-edge EXAFS spectra of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO; (g) content of Li and Mn measured by ICP-OES; (h) content of Li and Mn in protonated solution of 2-HLMO measured by ICP-MS; (i) TG analysis curve of 2-HLMO.

similar to that of Mn^{4+} to Mn^{3+} remained in LiMn_2O_4 . The CV curves implied a higher average Mn valence in 2-HLMO compared to LiMn_2O_4 .

To investigate the underlying causes of this valence change, elemental analysis was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES). As shown in Fig. 1(g), the Li content decreased significantly after protonation, from 35.26% in pristine LiMn_2O_4 to 1.52%, 1.66%, 1.87%, and 2.01%, in the protonated samples, respectively, while Mn content remained relatively stable. Elemental analysis of the acid solution, as shown in Fig. 1(h), confirmed that the amount of dissolved Li was approximately four times

higher than that of Mn, indicating significant Li leaching during protonation. This loss of Li was consistent with the observed Mn oxidation state increase, while the overall spinel structure remains intact.

To probe the incorporation of protons into the lattice, thermogravimetric (TG) analysis was performed on the representative 2-HLMO sample. As shown in Fig. 1(i), the TG curve showed three distinct stages of mass loss with increasing temperatures, corresponding to physisorbed water (25–100 °C), structural water (100–200 °C), and dehydroxylation OH groups (>200 °C), respectively [43]. The weight loss between 100 and 350 °C was calculated to be 5.54%, confirming the presence of H^+ in

2-HLMO. However, the amount of H^+ incorporated remained significantly lower than the amount of Li^+ leached, suggesting partial substitution and the formation of a protonated spinel phase.

2.2 ORR performance of as-prepared protonated LiMn_2O_4

The ORR performance of the synthesized samples was evaluated in O_2 -saturated 1 mol/L KOH solution, as shown in Fig. 2(a). Generally, Mn-based oxides exhibit low intrinsic electrical conductivity, which limit the electron transport efficiency inside and on the surface of catalyst [44–46]. However, the use of high-energy ball milling followed by low-temperature annealing in the synthesis of LiMn_2O_4 significantly improved its specific surface area, providing more accessible active sites for ORR and shortening the ion and electron transport pathways. As a result, the as-prepared LiMn_2O_4 demonstrated notable ORR performance, with a half-wave potential ($E_{1/2}$) of 0.75 V.

Following protonation via acid treatment, a further enhancement in ORR performance was observed, as illustrated in Fig. 2(b). Among all tested samples, 2-HLMO exhibited the best ORR activity, achieving an $E_{1/2}$

of 0.81 V with the highest limiting diffusion current, approaching the theoretical value. Compared with the Tafel slope of pristine LiMn_2O_4 (77.12 mV/dec), all protonated samples showed reduced Tafel slopes, indicating improved reaction kinetics after acid treatment, as shown in Fig. 2(c).

Durability, a critical metric for electrocatalyst evaluation, was assessed using 2-HLMO as a representative sample due to its superior performance. As shown in Fig. 2(d), the $E_{1/2}$ showed a minimal negative shift of only 4 mV after 20000 cycles in an accelerated durability test (ADT), highlighting exceptional long-term stability. Chronoamperometry (CA) was also performed at a constant potential of 0.8 V vs. RHE to further investigate catalytic stability. As shown in Fig. 2(e), 2-HLMO retained 85.14% of its initial current after 100 h of continuous operation, while LiMn_2O_4 retained only 60.16%, providing direct evidence of the enhanced stability compared to LiMn_2O_4 .

To elucidate the reaction pathway, rotating ring-disk electrode (RRDE) measurements were performed. As shown in Fig. S2, within the potential range of 0.2–0.8 V vs. RHE, 2-HLMO exhibited an electron transfer number exceeding 3.7, with a hydroperoxide (HO_2^-) yield of less

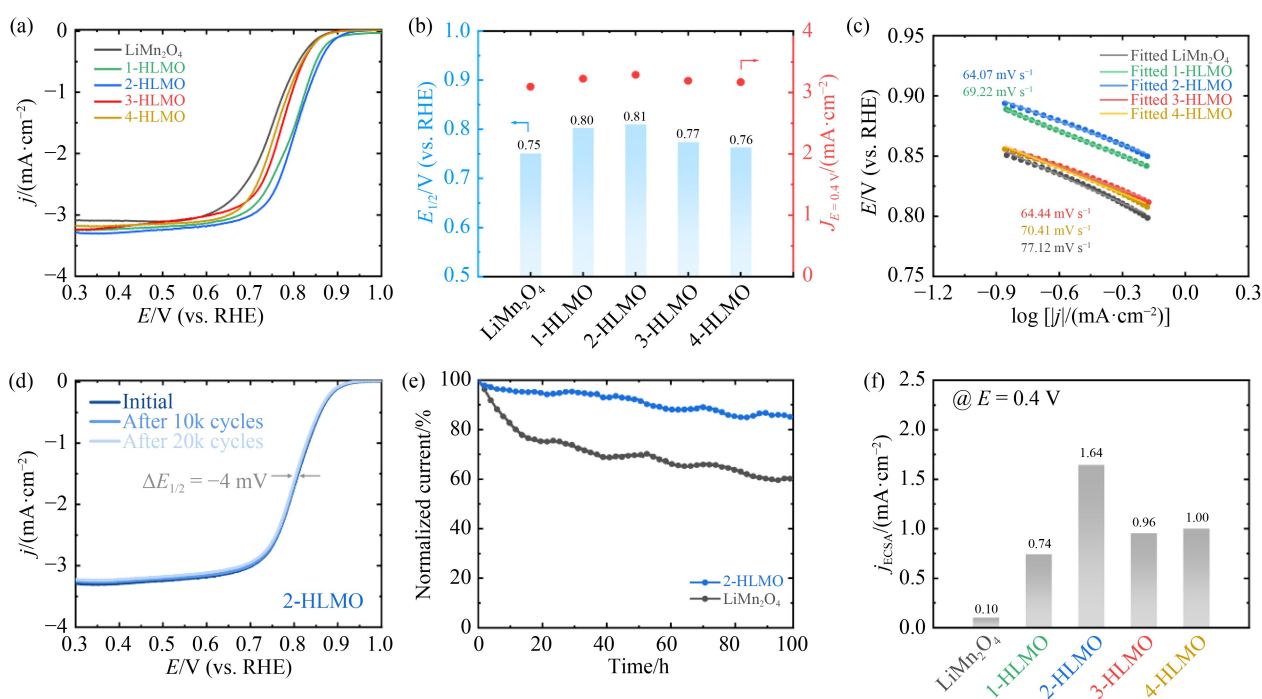


Fig. 2 ORR activity and stability of protonated LiMn_2O_4 .

(a) LSV curves of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO at 1600 r/min under O_2 -saturated 1 mol/L KOH solution; (b) half-wave potentials (left axis) and limiting diffusion current (right axis) of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO; (c) Tafel slopes of LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO. (d) LSV curves before and after accelerated durability testing (10k cycles, and 20k cycles) performed on 2-HLMO; (e) stability normalized current by CA test of LiMn_2O_4 and 2-HLMO; (f) current density normalized by electrochemical active surface area (ECSA) for LiMn_2O_4 , 1-HLMO, 2-HLMO, 3-HLMO, and 4-HLMO.

than 20%. This confirms that the dominant pathway for 2-HLMO follows a favorable four-electron transfer process.

The electrochemically active surface areas (ECSA) of these electrocatalysts were also estimated using CV at various scan rates in a non-Faradaic potential window, as shown in Fig. S3. The ECSA of pristine LiMn_2O_4 was 5.92 cm^2 , while the ECSA values of the different protonated HLMO samples exhibited lower values: 0.85 cm^2 (1-HLMO), 0.65 cm^2 (2-HLMO), 0.39 cm^2 (3-HLMO), and 0.62 cm^2 (4-HLMO), respectively (Fig. S4). After normalizing the diffusion-limited current at 0.4 V vs. RHE to the corresponding ECSA, 2-HLMO achieved a high area-specific current density (j_{ECSA}) of 1.64 mA/cm^2 , as shown in Fig. 2(f). The decrease in ECSA after protonation, combined with improved electrochemical performance, indicated that both the density and intrinsic

activity of the active sites per unit area had increased significantly.

2.3 Reasons for enhanced ORR performance

The enhanced ORR performance of LiMn_2O_4 was further elucidated by comparing the microstructural and electronic characteristics of the pristine LiMn_2O_4 and the best-performing 2-HLMO. SEM images revealed a substantial difference in particle morphology: LiMn_2O_4 exhibited irregular particle sizes and large flake-like aggregates (Fig. 3(a)), whereas 2-HLMO showed significantly reduced particle sizes, more uniform distribution and a rougher surface (Fig. 3(b)). Particle size (Fig. S6) confirmed a reduction in average particle diameter from approximately $70\text{--}80 \text{ nm}$ in LiMn_2O_4 to $30\text{--}40 \text{ nm}$ in 2-HLMO. This reduction was attributed to the chemical

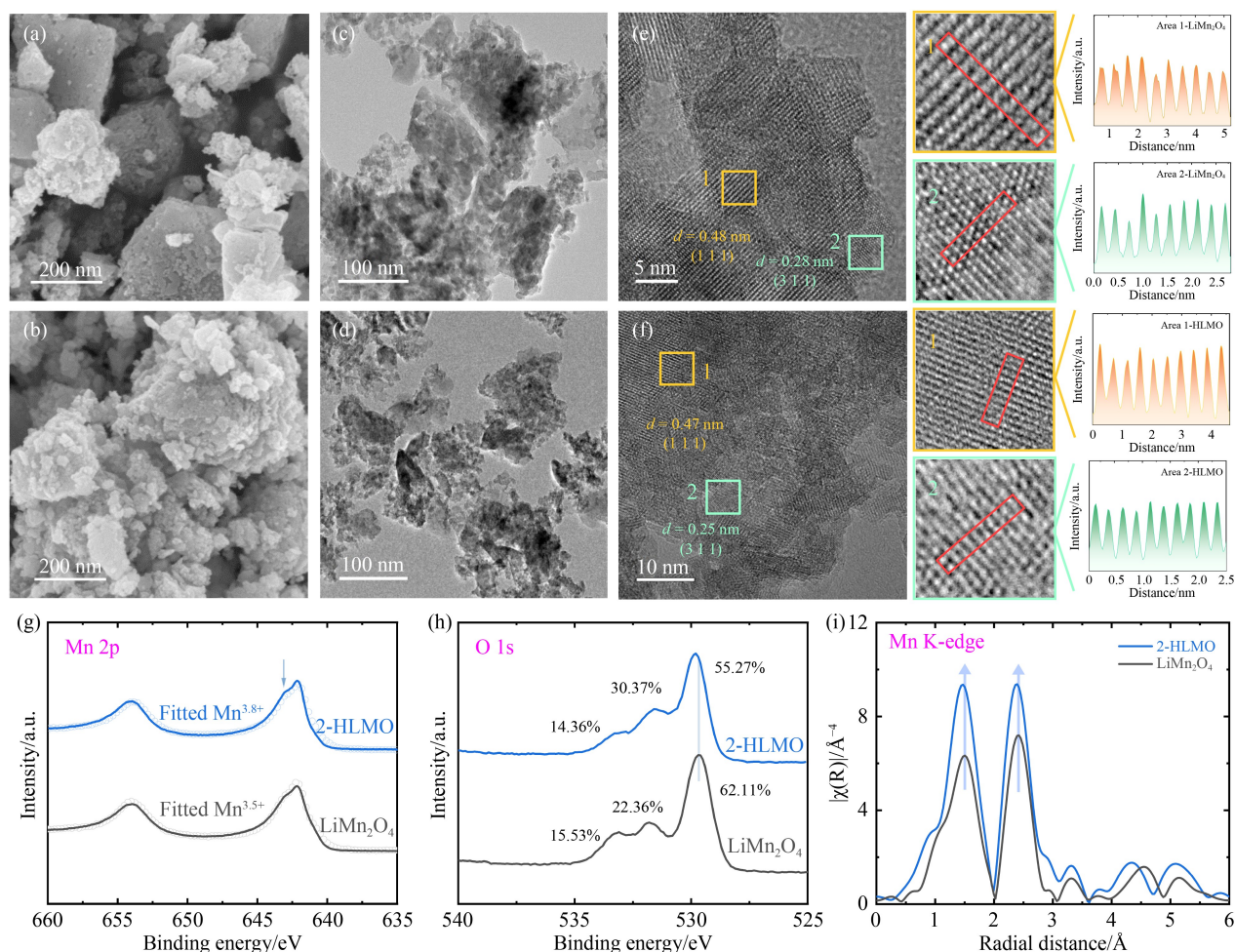


Fig. 3 Morphological and electronic changes between LiMn_2O_4 and 2-HLMO.

(a, b) SEM images of LiMn_2O_4 and 2-HLMO; (c, d) TEM images of LiMn_2O_4 and 2-HLMO; (e, f) HR-TEM images and interplanar spacings of LiMn_2O_4 and 2-HLMO; (g) Mn 2p XPS spectra; (h) O 1s XPS spectra; (i) Mn K-edge EXAFS spectra of LiMn_2O_4 and 2-HLMO.

grinding effect induced by acid leaching during the proton exchange process [38].

TEM images (Figs. 3(c) and 3(d)) showed that both LiMn_2O_4 and 2-HLMO maintained well-dispersed nanoparticles without forming aggregated clusters, with 2-HLMO exhibiting smaller particle sizes compared to LiMn_2O_4 . High-resolution TEM (HR-TEM) images (Figs. 3(e) and 3(f)), confirm the high crystallinity of both samples. In LiMn_2O_4 , the lattice spacings of 0.48 and 0.28 nm corresponded to the (111) and (311) crystal planes, respectively. For 2-HLMO, these spacings contracted slightly to 0.47 and 0.25 nm, consistent with the unit cell contraction observed from Rietveld refinement of XRD data.

Brunauer-Emmett-Teller (BET) surface area analysis revealed an increase from approximately $70.48 \text{ m}^2/\text{g}$ for LiMn_2O_4 (Fig. S7) to $93.43 \text{ m}^2/\text{g}$ for 2-HLMO (Fig. S8). The increase in specific surface area is related to the introduction of hydrogen species and the surface hydroxylation, which creates additional active sites for the ORR. To isolate the influence of specific surface area from catalytic activity, the currents of 2-HLMO and LiMn_2O_4 were normalized to both the catalyst mass activity and the BET-measured specific surface area, as shown in Fig. S9. Even after normalization, 2-HLMO still exhibited significantly enhanced performance, indicating improved intrinsic activity.

To elucidate changes in electronic structure, X-ray photoelectron spectroscopy (XPS) was performed on Mn 2p and O 1s regions. As shown in Fig. 3(g), the peak Mn 2p near 643.0 eV, characteristic of MnO_2 , became more pronounced in 2-HLMO compared to LiMn_2O_4 , indicating a higher average oxidation state of Mn in 2-HLMO than in pristine LiMn_2O_4 . Specifically, the average oxidation states of Mn in LiMn_2O_4 and 2-HLMO were determined to be $\text{Mn}^{3.5+}$ and $\text{Mn}^{3.8+}$, respectively, by fitting with the Mn_2O_3 and MnO_2 references (Figs. S10 and S11). These results were consistent with the Mn oxidation states obtained from XANES fitting.

Further insight into the oxygen environment was obtained from the O 1s XPS spectra (Fig. 3(h)). The overall O 1s binding energy of 2-HLMO showed an increase in binding energy, and the concentration of surface-adsorbed hydroxide species increased from 22.36% to 30.37% compared to LiMn_2O_4 . These changes were ascribed to the interaction between H^+ ions and surface oxygen atoms of LiMn_2O_4 during acid treatment, leading to protonation of some surface oxygen atoms and the formation of hydroxyl (-OH) groups. These surface -OH groups enhanced oxygen adsorption, promoted surface O_2 activation, and facilitated the ORR kinetics [47].

This result is also supported by the result of TG analysis. In addition, the acid treatment introduced more hydrophilic groups on the surface, such as hydroxyl

groups, improving the hydrophilicity of the material. The increased hydrophilicity improved electrolyte wetting and uniform distribution of the electrolyte on the surface of catalyst, which in turn facilitated the adsorption and diffusion of oxygen, thus stabilizing the ORR process. Deconvolution of the O 1s spectra identified contributions from lattice oxygen, surface hydroxyl/adsorbed water, and adsorbed oxygen species, further confirming the surface modifications.

The changes in surface oxygen after acid treatment were further investigated using the Mn K-edge EXAFS, as illustrated in Fig. 3(i). The Mn-O coordination number increased significantly after acid treatment, consistent with the rise in Mn valence state. In pristine LiMn_2O_4 , Mn is half $[\text{Mn-O}_4]$ and half $[\text{Mn-O}_6]$, whereas 2-HLMO showed an increase in $[\text{Mn-O}_6]$ octahedral environments. This transition toward more complete octahedral coordination implies a more stable and compact structure after protonation.

In summary, both microstructural (smaller nanoparticles providing more active sites) and electronic structure (optimized electronic structure offering better adsorption energy for intermediates) showed that the acid-treated LiMn_2O_4 exhibited improved ORR performance.

2.4 Structural characterization during ORR behavior

To investigate the structural evolution of protonated 2-HLMO during prolonged ORR, samples subjected to over 10000 cycles of cyclic voltammetry (CV) were characterized. First, scanning electron microscope (SEM) was used to observe changes in microstructures of 2-HLMO. As shown in Fig. 4(a), the morphology of 2-HLMO remained virtually unchanged after prolonged cycling, indicating good structural retention. TEM images (Fig. 4(b)) further confirmed this, with high-resolution (HR-TEM) imaging revealing distinctive lattice fringes. As shown in Fig. 4(c), the measured interplanar spacings of 0.25 nm corresponded to the (3 1 1) plane of the spinel structure, suggesting that the crystallographic integrity was preserved.

High-resolution XPS was subsequently performed to probe changes in electronic structure. As shown in Fig. 4(d), the Mn 2p XPS peaks showed a noticeable shift toward higher binding energies after cycling, indicating that Mn was further oxidized to higher valence states. The presence of more Mn^{4+} , compared to Mn^{3+} , was more stable due to the Jahn-Teller effect.

The Li 1s XPS spectra (Fig. 4(e)) showed an absence of detectable Li signal after CV, suggesting that Li was nearly completely absent from the spinel structure. As shown in Fig. S15, elemental analysis after cycling further revealed that the atomic ratio of Li was reduced to only 1.13%. Therefore, it can be concluded that the

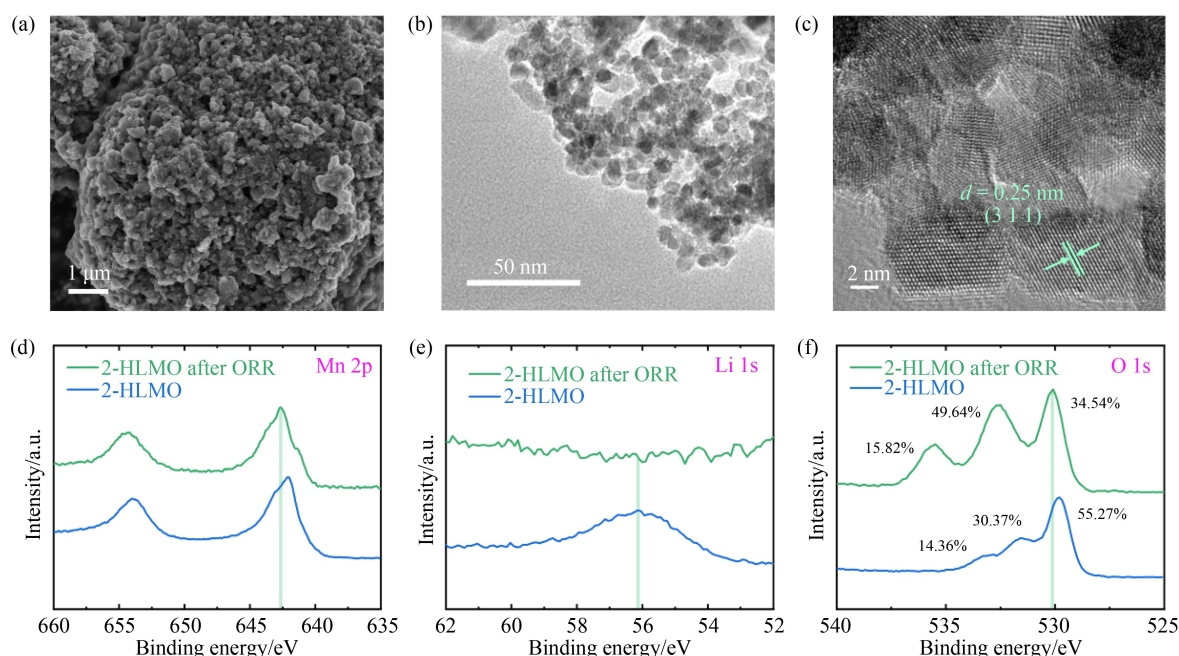


Fig. 4 Structural and electronic characterization after ORR

(a) SEM image of 2-HLMO after 10000 cycles; (b) corresponding TEM image of 2-HLMO after 10000 cycles; (c) HR-TEM image of 2-HLMO and corresponding interplanar spacing after 10000 cycles; High-resolution (d) Mn 2p, (e) Li 1s, (f) and O 1s XPS spectra of 2-HLMO after 10000 cycles.

dissolution of Li did not compromise the structural stability of 2-HLMO, while the increase in Mn valence states served to maintain charge balance.

Dissolution of Li and Mn species in the solution were also quantitatively analyzed (Fig. S16). The concentration of dissolved Mn was measured to be 155.37 $\mu\text{g/L}$, indicating some degree of Mn leaching, although not sufficient to disrupt the overall spinel framework. In addition, changes in oxygen species within 2-HLMO were also examined. As shown in Fig. 4(f), the content of surface hydroxyl groups or adsorbed water increased from 30.37% to 49.64%. This increased surface hydroxylation likely contributed to enhanced hydrophilicity and may facilitate sustained ORR activity by promoting oxygen adsorption.

XRD patterns demonstrated that the crystal structure remained as the spinel structure after the stability test, without evidence of phase transformation or amorphization (Fig. S17).

In summary, throughout the cycling process, the microstructure of 2-HLMO remained virtually unchanged, and surface hydroxylation was enhanced as the reaction progressed.

2.5 Theoretical investigations of ORR enhancement mechanism

To further investigate the effect of protonated spinel-type

lithium manganate on ORR activity, density functional theory (DFT) calculations were performed. The most stable configurations for pristine LiMn_2O_4 and protonated 2-HLMO were first constructed, as shown in Figs. 5(a) and 5(b), which presents the crystal structure models of LiMn_2O_4 and 2-HLMO, respectively. For 2-HLMO, the modeling was designed based on the experimentally determined atomic ratios of Li and Mn obtained via ICP analysis. Bader charge revealed that the surface Mn atoms in LiMn_2O_4 and 2-HLMO lost 0.976 and 1.012 eV of electrons, respectively (Figs. 5(c) and 5(d)), indicating a higher oxidation state of Mn in 2-HLMO. This result is in good agreement with the findings from XAS and XPS measurements.

The electron localization function (ELF) plots for LiMn_2O_4 and 2-HLMO are presented in Fig. S18. The protonated lithium manganite showed certain distortions to maintain stability, along with higher electron localization on the surface, which explains its better intrinsic ORR activity. Charge differential density (CDD) analysis revealed distinct $^*\text{O}$ intermediate adsorption behavior between LiMn_2O_4 and 2-HLMO. On the LiMn_2O_4 surface (Fig. 5(c)), excessive electron transfer led to over-stabilization of the $^*\text{O}$ intermediate, kinetically hindering subsequent $^*\text{OH}$ adsorption and resulting in a substantially higher activation energy barrier. In contrast, 2-HLMO (Fig. 5(d)) exhibited more balanced adsorption, facilitating improved ORR kinetics.

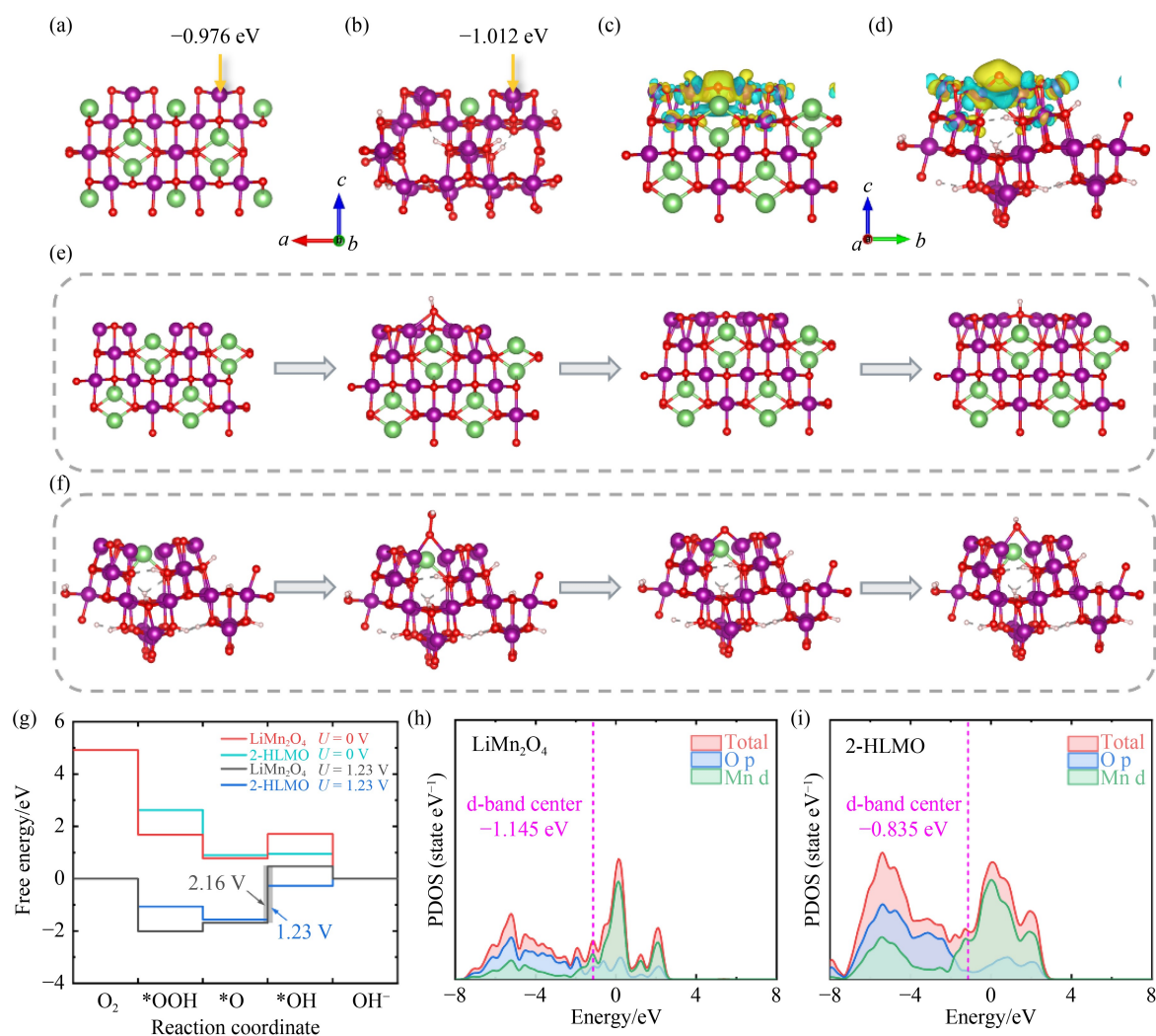


Fig. 5 Theoretical considerations of electronic structures and ORR enhancement mechanisms of LiMn_2O_4 and 2-HLMO.

(a, b) Structural model and Bader charge of LiMn_2O_4 and 2-HLMO; (c, d) charge density difference (CDD) of LiMn_2O_4 and 2-HLMO; (e, f) proposed alkaline ORR mechanism on LiMn_2O_4 and 2-HLMO; (g) ORR free-energy diagrams at $U = 0$ V and $U = 1.23$ V for LiMn_2O_4 and 2-HLMO; (h, i) projected density of states (PDOS) of LiMn_2O_4 and 2-HLMO.

The full four-electron ORR pathway was subsequently stimulated, with Mn acting as the principal active site for oxygen intermediate adsorption. Figures 5(e) and 5(f) present the adsorption configurations of O_2 , *OOH , *O , and *OH species on both LiMn_2O_4 and 2-HLMO. As shown in Fig. 5(g), a comparison was made between the ORR pathways of LiMn_2O_4 and typical 2-HLMO. In the initial step of O_2 adsorption, both processes occurred spontaneously. However, in LiMn_2O_4 , the free energy of spontaneous adsorption was excessively high, which could hinder subsequent desorption steps. In the fourth step, which involves the adsorption of *OH oxygen intermediates, LiMn_2O_4 required an overpotential of 2.16 V to proceed, which was considerably higher than the theoretical overpotential of 1.23 V for 2-HLMO. This

step was the rate-determining step (RDS) for both materials. These results indicated that protonation facilitated a reduction in the external voltage required for the RDS, which was consistent with experimental results.

Further insight was gained by analyzing the electronic structure. The d-band center of Mn atoms in LiMn_2O_4 , Fig. 5(h), and 2-HLMO, Fig. 5(i), relative to the Fermi level (E_f) were -1.145 and -0.835 eV, respectively. The d-band center of 2-HLMO was closer to the E_f , indicating that the protonated lithium manganite exhibited higher adsorption capacity toward oxygen intermediates and was more favorable for the interactions between the adsorbates and the electrocatalyst surface. In addition, the projected density of states (PDOS) revealed that 2-HLMO exhibited a broader total density of states near the E_f com-

pared to pristine, for Mn d electrons. This suggests that 2-HLMO can readily participate in electron transfer during ORR, thus accelerating the rate-determining step (RDS) involving electron-coupled *O to *OH conversion.

In summary, DFT calculations confirmed that protonation of LiMn_2O_4 modifies the electronic environment of Mn, optimizes the adsorption energy of ORR intermediates, and reduces the overpotential required for the rate-limiting step. These insights support the experimental findings and validate proton exchange as an effective strategy for improving ORR catalytic performance in Mn-based spinel oxides.

3 Conclusions

This study systematically demonstrated that protonation effectively enhanced the ORR performance of spinel-type LiMn_2O_4 through precise structural and electronic engineering. Comprehensive characterizations revealed that protonation induced lattice contraction (from 8.18 Å in LiMn_2O_4 to 8.04 Å in 4-HLMO) and increased the average oxidation state of Mn (from $\text{Mn}^{+3.51}$ to $\text{Mn}^{+3.86}$), accompanied by shortening of Mn–O bond lengths (from 1.50 to 1.46 Å) and an increase in Mn coordination numbers. These structural modifications optimized the surface electronic configuration, as evidenced by the shift of the Mn d-band center toward the Fermi level, which strengthened oxygen intermediate adsorption while reducing *O over-stabilization. The synergistic effects collectively contributed to exceptional ORR activity, with an $E_{1/2}$ of 0.81 V and outstanding durability, less than 4 mV shift after 20000 cycles. Theoretical calculations rationalized the improved performance at the atomic level: the optimized electronic structure of protonated HLMO reduced the rate-determining step energy barrier (*OH adsorption) by facilitating charge transfer, ultimately reducing the theoretical overpotential from 2.16 to 1.23 V. This work establishes proton exchange as a general methodology for enhancing ORR performance in Li-intercalated oxides and offers a promising approach for the rational design of other transition metal oxide electrocatalysts. It provides a robust framework for advancing next-generation, platinum-free electrocatalysts in sustainable energy conversion technologies.

Acknowledgements The work was supported by the Scientific Research Innovation Capability Support Project for Young Faculty (Grant No. ZYGXQNJSKYCXNLZCXM-E10), the National Natural Science Foundation of China (Grant No. 22179098), and Xiaomi Young Talents Program to J. Ma. The support from the Max Planck-POSTECH-Hsinchu Center for Complex Phase Materials is also acknowledged.

Competing Interests The authors declare that they have no competing interest.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s11708-026-1039-3> and is accessible for authorized users.

References

- Goswami C, Hazarika K K, Bharali P. Transition metal oxide nanocatalysts for oxygen reduction reaction. *Materials Science for Energy Technologies*, 2018, 1(2): 117–128
- Ge X, Sumboja A, Wu D, et al. Oxygen reduction in alkaline media: From mechanisms to recent advances of catalysts. *ACS Catalysis*, 2015, 5(8): 4643–4667
- Huang J, Sementa L, Liu Z, et al. Experimental sabatier plot for predictive design of active and stable Pt-alloy oxygen reduction reaction catalysts. *Nature Catalysis*, 2022, 5(6): 513–523
- Bai J, Lian Y, Deng Y, et al. Simultaneous integration of Fe clusters and NiFe dual single atoms in nitrogen-doped carbon for oxygen reduction reaction. *Nano Research*, 2024, 17(4): 2291–2297
- Hou J, Yang M, Ke C, et al. Platinum-group-metal catalysts for proton exchange membrane fuel cells: From catalyst design to electrode structure optimization. *EnergyChem*, 2020, 2(1): 100023
- Kodama K, Nagai T, Kuwaki A, et al. Challenges in applying highly active Pt-based nanostructured catalysts for oxygen reduction reactions to fuel cell vehicles. *Nature Nanotechnology*, 2021, 16(2): 140–147
- Bai J, Sun Z, Zhang H, et al. Modulating the local coordination environment of M-N_x single-atom site for enhanced electrocatalytic oxygen reduction. *Advanced Functional Materials*, 2025, 35(11): 2417013
- Yuan Z H, Wang T J, Sun B, et al. Recent advances in platinum group metallenes: From synthesis to energy-related electrocatalytic application. *Applied Catalysis B. Environment and Energy*, 2025, 366: 125041
- Nie Y, Li L, Wei Z. Recent advancements in Pt and Pt-free catalysts for oxygen reduction reaction. *Chemical Society Reviews*, 2015, 44(8): 2168–2201
- Firouzjaie H A, Mustain W E. Catalytic advantages, challenges, and priorities in alkaline membrane fuel cells. *ACS Catalysis*, 2020, 10(1): 225–234
- Serov A, Artyushkova K, Niangar E, et al. Nano-structured non-platinum catalysts for automotive fuel cell application. *Nano Energy*, 2015, 16: 293–300
- Lei H, Yang X, Chen Z, et al. Multiscale understanding of anion exchange membrane fuel cells: Mechanisms, electrocatalysts, polymers, and cell management. *Advanced Materials*, 2025, 37(8): 2410106
- Zhang H, Osmieri L, Park J H, et al. Standardized protocols for evaluating platinum group metal-free oxygen reduction reaction electrocatalysts in polymer electrolyte fuel cells. *Nature Catalysis*, 2022, 5(5): 455–462
- Chung H T, Cullen D A, Higgins D, et al. Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst. *Science*, 2017, 357(6350): 479–484

15. Bai J, Lin Y, Xu J, et al. PGM-free single atom catalysts for the oxygen reduction reaction in proton exchange membrane fuel cells. *Chemical Communications*, 2024, 60(56): 7113–7123
16. Bundschu C R, Ahmadi M, Méndez-Valderrama J F, et al. Oxygen reduction pathway for spinel metal oxides in alkaline media: an experimentally supported *ab initio* study. *Journal of the American Chemical Society*, 2024, 146(7): 4680–4686
17. Zhuang Q, Ma N, Yin Z, et al. Rich surface oxygen vacancies of MnO_2 for enhancing electrocatalytic oxygen reduction and oxygen evolution reactions. *Advanced Energy and Sustainability Research*, 2021, 2(8): 2100030
18. Huang J J, Yang Y, Weinstock D, et al. Multimodal *in situ* X-ray mechanistic studies of a bimetallic oxide electrocatalyst in alkaline media. *Nature Catalysis*, 2025, 8(2): 116–125
19. Ge C, Li Z J, Chang Y N, et al. The manipulation of Ni/MnO heterostructures within carbon hierarchical superstructures as bifunctional oxygen electrocatalysts for enhanced Zn-air batteries. *Rare Metals*, 2025, 44(5): 3107–3118
20. Zhang Y, Wang C, Fu J, et al. Fabrication and high ORR performance of MnO_x nanopyramid layers with enriched oxygen vacancies. *Chemical Communications*, 2018, 54(69): 9639–9642
21. Yang Z, Lai F, Mao Q, et al. Breaking the mutual-constraint of bifunctional oxygen electrocatalysis via direct O—O coupling on high-valence Ir single-atom on MnO. *Advanced Materials*, 2025, 37(3): 2412950
22. Zhu H, Zhang S, Huang Y X, et al. Monodisperse $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ (M = Fe, Cu, Co, Mn) nanoparticles and their electrocatalysis for oxygen reduction reaction. *Nano Letters*, 2013, 13(6): 2947–2951
23. Zhou Q, Hou S, Cheng Y, et al. Interfacial engineering Co and MnO within N,S co-doped carbon hierarchical branched superstructures toward high-efficiency electrocatalytic oxygen reduction for robust Zn-air batteries. *Applied Catalysis B: Environmental*, 2021, 295: 120281
24. Wang W, Liu E, Hu Y, et al. Understanding the ORR electrocatalysis on Co–Mn oxides. *Journal of Physical Chemistry C*, 2021, 125(46): 25470–25477
25. Li H., Xu J, Yang L, et al. Advancing Mn-based electrocatalysts: Evolving from Mn-centered octahedral entities to bulk forms. *eScience*, 2024, 5(4): 100368
26. Zhao W, Chen J, Liu X, et al. Prokaryote-inspired and derived oxygen reduction electrocatalysts for ultra-long-life Zn-air batteries. *Advanced Energy Materials*, 2025, 15(20): 2405594
27. Meng X, Liu T, Qin M, et al. Carbon-free, binder-free $\text{MnO}_2@\text{Mn}$ catalyst for oxygen reduction reaction. *ACS Applied Materials & Interfaces*, 2023, 15(16): 20110–20119
28. Chen G, Zhang X, Gu Y, et al. Efficiently re-utilizing the high-value metals in the spent $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ for the trifunctional electrocatalysts by a novel one-pot method. *Small*, 2025, 21(10): 2411337
29. Huang L, Wu Y. Spinel Ni-doped LiMn_2O_4 cathode material with high oxygen reduction catalytic performance for low temperature solid ceramic fuel cells. *Ceramics International*, 2024, 50(3): 5150–5159
30. Li J, Liu L, Wu J, et al. Synergistic effect to unlock the activity and stability for oxygen evolution reaction in spinel LiMn_2O_4 via d-block metal substitution. *Applied Catalysis B: Environmental*, 2024, 357: 124331
31. Choi J H, Chun H, Kim D W, et al. Zeolitic imidazolate framework-derived bifunctional $\text{CoO-Mn}_3\text{O}_4$ heterostructure cathode enhancing oxygen reduction/evolution via dynamic O-vacancy formation and healing for high-performance Zn-air batteries. *Energy Storage Materials*, 2025, 75: 104040
32. Cheng F, Su Y, Liang J, et al. MnO_2 -based nanostructures as catalysts for electrochemical oxygen reduction in alkaline media. *Chemistry of Materials*, 2010, 22(3): 898–905
33. Hughes L, Roy A, Downing C, et al. Surface reduced manganese states as a source of oxygen reduction activity in BaMnO_3 . *Advanced Functional Materials*, 2023, 33(24): 2214883
34. Zeng R, Li H, Shi Z, et al. Origins of enhanced oxygen reduction activity of transition metal nitrides. *Nature Materials*, 2024, 23(12): 1695–1703
35. Cheng Y, Wang H, Song H, et al. Design strategies toward transition metal single atom catalysts for the oxygen reduction reaction—A review. *Nano Research Energy*, 2023, 2: e9120082
36. Su Z, Huang Q, Guo Q, et al. Metal-organic framework and carbon hybrid nanostructures: Fabrication strategies and electrocatalytic application for the water splitting and oxygen reduction reaction. *Nano Research Energy*, 2023, 2: e9120078
37. Tang J, Liu X, Xiong X, et al. Ruthenium single-atom modulated protonated iridium oxide for acidic water oxidation in proton exchange membrane electrolyzers. *Advanced Materials*, 2024, 36(41): 2407394
38. Zhong X, Oubla M, Wang X, et al. Boosting oxygen reduction activity and enhancing stability through structural transformation of layered lithium manganese oxide. *Nature Communications*, 2021, 12(1): 3136
39. He H, Shen R, Yan Y, et al. Double enhancement of protonation and conjugation in donor–imine–donor covalent organic frameworks for photocatalytic hydrogen evolution. *Chemical Science*, 2024, 15(47): 20002–20012
40. Dong P, Xu X, Wu T, et al. Stepwise protonation of three-dimensional covalent organic frameworks for enhancing hydrogen peroxide photosynthesis. *Angewandte Chemie International Edition*, 2024, 63(30): e202405313
41. Sun K, Dong J, Sun H, et al. $\text{Co}(\text{CN})_3$ catalysts with well-defined coordination structure for the oxygen reduction reaction. *Nature Catalysis*, 2023, 6(12): 1164–1173
42. Zhu P, Song P, Feng W, et al. Tailoring the selectivity and activity of oxygen reduction by regulating the coordination environments of carbon-supported atomically dispersed metal sites. *Journal of Materials Chemistry. A, Materials for Energy and Sustainability*, 2022, 10(35): 17948–17967
43. Ma J, Reeves K G, Porras Gutierrez A G, et al. Layered lepidocrocite type structure isolated by revisiting the sol–gel chemistry of anatase TiO_2 : A new anode material for batteries. *Chemistry of Materials*, 2017, 29(19): 8313–8324
44. Li H, Kelly S, Guevarra D, et al. Analysis of the limitations in the oxygen reduction activity of transition metal oxide surfaces.

- Nature Catalysis, 2021, 4(6): 463–468
45. Song J, Wei C, Huang Z F, et al. A review on fundamentals for designing oxygen evolution electrocatalysts. Chemical Society Reviews, 2020, 49(7): 2196–2214
 46. Rittirum M, Buapin P, Saelee T, et al. First-principles calculation on effects of oxygen vacancy on α -MnO₂ and β -MnO₂ during oxygen reduction reaction for rechargeable metal-air batteries. Journal of Alloys and Compounds, 2022, 926: 166929
 47. Yuan H, Li J, Yang W, et al. Oxygen vacancy-determined highly efficient oxygen reduction in NiCo₂O₄/hollow carbon spheres. ACS Applied Materials & Interfaces, 2018, 10(19): 16410–16417