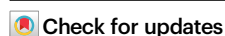


Ir-O-Mn embedded in porous nanosheets enhances charge transfer in low-iridium PEM electrolyzers

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Using metal oxides to disperse iridium (Ir) in the anode layer proves effective for lowering Ir loading in proton exchange membrane water electrolyzers (PEMWE). However, the reported low-Ir-based catalysts still suffer from unsatisfying electrolytic efficiency and durability under practical industrial working conditions, mainly due to insufficient catalytic activity and mass transport in the catalyst layer. Herein we report a class of porous heterogeneous nanosheet catalyst with abundant Ir-O-Mn bonds, achieving a notable mass activity of 4 A mg_{Ir}⁻¹ for oxygen evolution reaction at an overpotential of 300 mV, which is 150.6 times higher than that of commercial IrO₂. Ir-O-Mn bonds are unraveled to serve as efficient charge-transfer channels between in-situ electrochemically-formed IrO_x clusters and MnO_x matrix, fostering the generation and stabilization of highly active Ir³⁺ species. Notably, Ir/MnO_x-based PEMWE demonstrates comparable performance under 10-fold lower Ir loading (0.2 mg_{Ir} cm⁻²), taking a low cell voltage of 1.63 V to deliver 1 A cm⁻² for over 300 h, which positions it among the elite of low Ir-based PEMWEs.

The proton exchange membrane water electrolyzers (PEMWE) have emerged as one of the most significant techniques for the green hydrogen synthesis^{1–4}. However, the large amount of iridium (Ir) used in current PEMWE devices (400 kg GW⁻¹) has been widely considered as the main impediment to the large-scale and sustainable deployment of PEMWEs^{5–9}. Cooperating iridium and metal oxide-based support materials serves as an effective strategy for the elevated atomic utilization of Ir to enhance the activity and stability of oxygen evolution reaction (OER) with the decrease of Ir loading^{10–13}. Though efficient supported Ir catalysts have been reported, realizing both satisfactory activity and durability under industrially high current density with a low Ir loading (<0.3 mg_{Ir} cm⁻²) still remains a big challenge because the limited number of active sites with insufficient intrinsic activity usually necessitate higher electrolytic voltage for achieving industrial current density, leading to the conversion of Ir into a more readily dissolvable

higher oxidation state^{14–18}. Furthermore, the practical PEMWE devices appeal harsher demands to OER catalysts with the capacity of rapid gas-liquid mass transfer and good interface conductivity^{19,20}.

Herein we report an in-situ reduction and phase-separation method for synthesizing the Ir/MnO_x catalyst with Ir nanoclusters embedded within two-dimensional porous MnO_x matrix. We reveal that the abundant Ir-O-Mn bonds near the reconstructed IrO_x/MnO_x interfaces, confirmed by in-situ X-ray absorption fine structures (XAFS) and surface-enhanced Raman spectroscopy (SERS), can provide efficient charge transfer channels for the generation and stabilization of active Ir³⁺ species. Because of the optimal d-band structure of low-valence Ir state, the IrO_x/MnO_x exhibits comparable OER activity and stability, with a notable mass activity of 4 A mg_{Ir}⁻¹ at the overpotential of 300 mV, which is 150.6 times higher than that of IrO₂ and a comparable S-number of 6.8 × 10⁵ in all the reported Ir-metal-based

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catalysts. Notably, the PEMWE device utilizing Ir/MnO_x as anodic catalyst layer with a low 0.2 mg_{Ir} cm⁻² loading achieves a high mass activity of 6.69 A mg_{Ir}⁻¹ @ 1.7 V and a stable operation for 300 h at a current density of 1 A cm⁻² with a very high S-number of 1.48 × 10⁸. Such impressive performances in PEMWE are not only attributable to the abundant and enduring Ir³⁺ species, but also stem from the enhanced mass transfer and optimized interfacial contact enabled by the porous and ultra-thin 2D nanosheet structure. This synergy underscores the formidable potential of the material for PEMWE under stringent operating conditions, as evidenced by the comparably low decay rate (1.24 mV per 1000 cycles at 2 A cm⁻²) in accelerated stress tests (ASTs).

Results and discussion

The heterointerface-rich Ir/MnO_x catalyst was synthesized by the use of an advanced in-situ reduction and phase-separation method with iridium-manganese bimetallic oxide (Ir-Mn BO) nanosheets as the precursors. Transmission electron microscopy (TEM, Supplementary Fig. 1) and atomic force microscopy (Supplementary Fig. 2) images of the as-formed nanosheets indicate that they show the spatially cross-linking morphology with an ultrathin thickness of mere 1.0 nm. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Supplementary Fig. 3) with the energy dispersive spectrometer (EDS) elemental mappings (Supplementary Fig. 4) confirms the homogeneous atomic-level dispersion of Ir throughout the Ir-Mn BO lattice even under a rather high Ir content up to 33 at.% (Supplementary Fig. 5). During the following annealing process under H₂/Ar atmosphere (Fig. 1a), the uniformly-distributed high-valence (near +4) Ir ions within the lattice of Ir-Mn BO (Supplementary Fig. 6) experience sufficient reduction to generate Ir atoms near the surface. Driven by spontaneous formation of oxygen vacancies, the as-formed Ir atoms generally diffuse outward and gather as Ir nanoclusters, thus creating abundant heterointerfaces between metal and oxide matrix. This hypothetical phase-separation process was verified by X-ray diffraction patterns (XRD, Fig. 1b; Supplementary Fig. 7) that the original characteristic peaks of Mn₂O₃ phase for Ir-Mn BO vanish after annealing while the typical signals of *fcc*-Ir (located at 40.7° and 69.1°, assigned to {111} and {220} planes, respectively) emerge for Ir/MnO_x. Moreover, an easily-overlooked widened diffraction peak around 60.0° attributed to the {224} facets of Mn₃O₄ suggests a phase transformation from the crude Mn₂O₃ matrix to near amorphous Mn₃O₄ phase induced by the H₂/Ar treatment, further confirmed by X-ray photoelectron spectroscopy (XPS) spectra with decreased Mn 2*p* binding energy and increased splitting degree of Mn 3*s* peaks (Supplementary Fig. 8) as well as the Raman spectra with dominant Mn-O stretching vibration peak exclusively indexing the Mn₃O₄ phase (Fig. 1c; Supplementary Fig. 9).

Because of the structural robustness of MnO_x matrix, the ultrathin two-dimensional morphology with reticular stereo configuration remains for Ir/MnO_x after 300 °C annealing (Fig. 1d) while its average thickness is measured to be around 1.67 nm (Supplementary Fig. 10), a little bit thicker than that of the precursor. High-resolution HAADF-STEM image (Fig. 1e) and corresponding EDS elemental mappings (Fig. 1f) further prove the formation of Ir nanoclusters with an average size of approximately 1.25 nm (Supplementary Fig. 11). The specific in-situ separation of Ir nanoclusters inevitably induces chaotic atomic arrangement, leading to abundant heterointerfaces and local pores within Ir/MnO_x (Fig. 1e). A *d*-spacing, measured as 0.191 nm, can be ascribed to {200} facets of *fcc* Ir, well consistent with the fast Fourier transform (FFT) pattern (Fig. 1g, obtained from the selected region in Supplementary Fig. 12) observed from [011] zone axis. In addition, an extra pair of reciprocal spots also show up, representative as {224} planes of Mn₃O₄, which is in accord with the XRD, XPS and Raman results discussed above. Further analysis on FFT pattern provides more specific facet information, reflecting an exposed (1–10) plane of Mn₃O₄ (Supplementary Fig. 13). To clarify the detailed structure of the

heterointerface, STEM-EDS mappings (Supplementary Fig. 14) as well as HAADF-STEM image (Fig. 1h) from the side view of the Ir/MnO_x were captured, mutually delineating the distribution of Ir clusters deeply embedded within the MnO_x substrate lattice, which implies intensive coupling with rather large interface areas. More advanced, clear lattice fringes can be seen for both Mn₃O₄ matrix and Ir clusters in Fig. 1h and Supplementary Fig. 15. Since the {220} plane of Mn₃O₄ share a similar *d*-spacing with that of {111} facets of Ir, one can explicitly observe the coherent grain boundary near the interfaces, speculating well-fitted epitaxial growth of Ir clusters derived from the phase-separation synthetic method, underscoring the uniform existence of strong interfacial couplings. Besides, the atomic ratio of Mn to Ir is determined to be 67.1 to 32.9 for Ir/MnO_x, revealing no obvious composition variation before and after annealing (Supplementary Figs. 16 and 17). As such, the well-designed Ir/MnO_x catalyst containing reticularly porous matrix and rich heterointerface-anchored Ir nanoclusters with high loading was successfully obtained.

To delve deeper into the support-metal interaction between in-situ formed Ir nanoclusters and Mn oxide substrate near the heterointerfaces, a reference sample, Ir+MnO_x, was prepared by synthesizing free-standing Ir nanoclusters with similar size, and then physically loading them onto Mn oxide nanosheets (Supplementary Figs. 18 and 19). XPS was subsequently employed to analyze the chemical state of Ir in both Ir+MnO_x and Ir/MnO_x. We find that Ir/MnO_x has a lower electron density of Ir (Supplementary Fig. 20), and also has the stronger electronic interaction between MnO_x and Ir due to the coupling heterointerfaces than that of Ir+MnO_x. Furthermore, control experiments with different annealing temperatures were carried out (Fig. 2a) to investigate the physicochemical nature of such intensified charge transfer wherein a linear negative relation was found between the Ir 4*f*_{7/2} binding energy and the as-applied temperature till 300 °C (Supplementary Fig. 21). Interestingly, when the annealing temperature continues to rise to 350 °C, the binding energy of Ir 4*f*_{7/2} for Ir/MnO_x keeps invariable and finally stabilizes at 61.38 eV, still higher than those of Ir+MnO_x (61.31 eV) and free-standing Ir clusters (61.29 eV). Given the fact that comparably high binding energy cannot be achieved through simply physical loading process (Supplementary Fig. 22), one can conceive that the stubbornly high Ir 4*f*_{7/2} binding energy stems from extra electronic donation of Ir except for conventional surface oxidation. Ultraviolet photoelectron spectroscopy (UPS) supports the same conclusion with obviously elevated working function for Ir/MnO_x (Fig. 2b)^{21,22}. A hypothetical Ir-O-Mn bond at the heterointerface was deduced as effective electron transfer channel (The inset of Fig. 2a), and insufficient reduction of Ir can be ascribed to unquenchable oxygen coordination derived from MnO_x matrix.

The elaborate fitting of extended X-ray absorption fine structures (EXAFS) was deployed in both *k* space and *R* space for precisely unveiling the local coordination mode of as-concepted Ir-O-Mn bonds (Supplementary Fig. 23). As demonstrated in Fig. 2c, in addition to metallic Ir-Ir bonds, Ir/MnO_x also presents a dominant Ir-O scattering path, the lengths of which follow the order of Ir/MnO_x > Ir+MnO_x > IrO₂ (Fig. 2d; Supplementary Table 1). Such prolonged Ir-O distance indicates asymmetrical coordination of oxygen atoms, implying extra connection of O with another transition metal, confirming the existence of Ir-O-Mn bonds. In addition, the identical scattering paths of Ir-O coordination to IrO₂ were applied to fit Ir/MnO_x, with a rather high coordination number (CN) of 1.8 in total, while an average equivalent path was adopted for Ir+MnO_x with lower CN of 0.4 (Supplementary Table 1). More delicate information about atom dispersion and bonding circumstance can be obtained by introducing additional *k*-space resolution. Compared to Ir foil, both Ir+MnO_x and Ir/MnO_x present more pronounced low-*k* oscillations (Supplementary Fig. 23), indicating abundant Ir-O coordination. In addition, the wavelet transformation (WT) patterns illustrate that although the second shell domain in Ir/MnO_x (marked by yellow dash

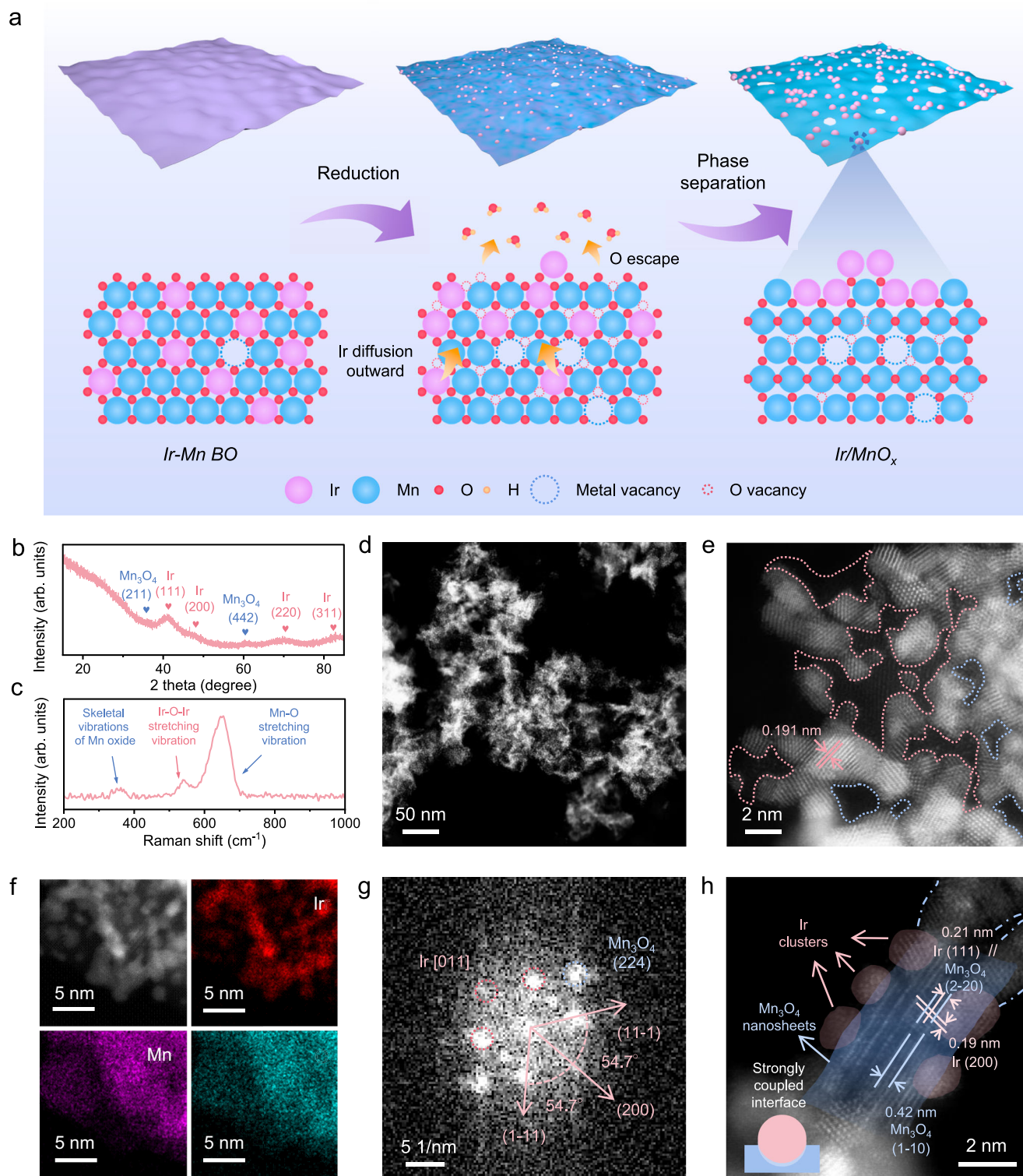


Fig. 1 | Synthesis and characterizations of Ir/MnO_x. **a** Schematic illustration of the synthetic approach for Ir/MnO_x. **b** XRD pattern of Ir/MnO_x. **c** Raman spectrum of Ir/MnO_x. **d** Dark-field STEM image of Ir/MnO_x. **e** HAADF-STEM image of the top view of Ir/MnO_x. **f** STEM-EDS elemental mappings of Ir/MnO_x. **g** Typical FFT pattern of Ir/MnO_x. **h** HAADF-STEM image of the side view of Ir/MnO_x.

line) has a similar R value to that of Ir-Ir scattering in Ir foil (marked by white dash line), their k values are quite different, which could be attributed to the weaker ability of Mn, as a low-atomic element, to scatter X-ray compared to Ir^{23–26} (Fig. 2e). Overall, the EXAFS analysis together with XPS and UPS data, collectively ensure the abundant existence of Ir-O-Mn bonds near the heterointerfaces.

The OER performances of Ir/MnO_x and other reference catalysts in acidic medium were evaluated in acidic media using a rotating disk electrode (RDE; Supplementary Fig. 24). The iR -corrected linear sweep voltammetry (LSV) curves reveal that Ir/MnO_x demonstrates a lower onset potential of 1.43 V versus RHE than Ir/C (1.47 V) and IrO₂ (1.54 V) (Fig. 3a). Furthermore, the Tafel slope of Ir/MnO_x was calculated to be

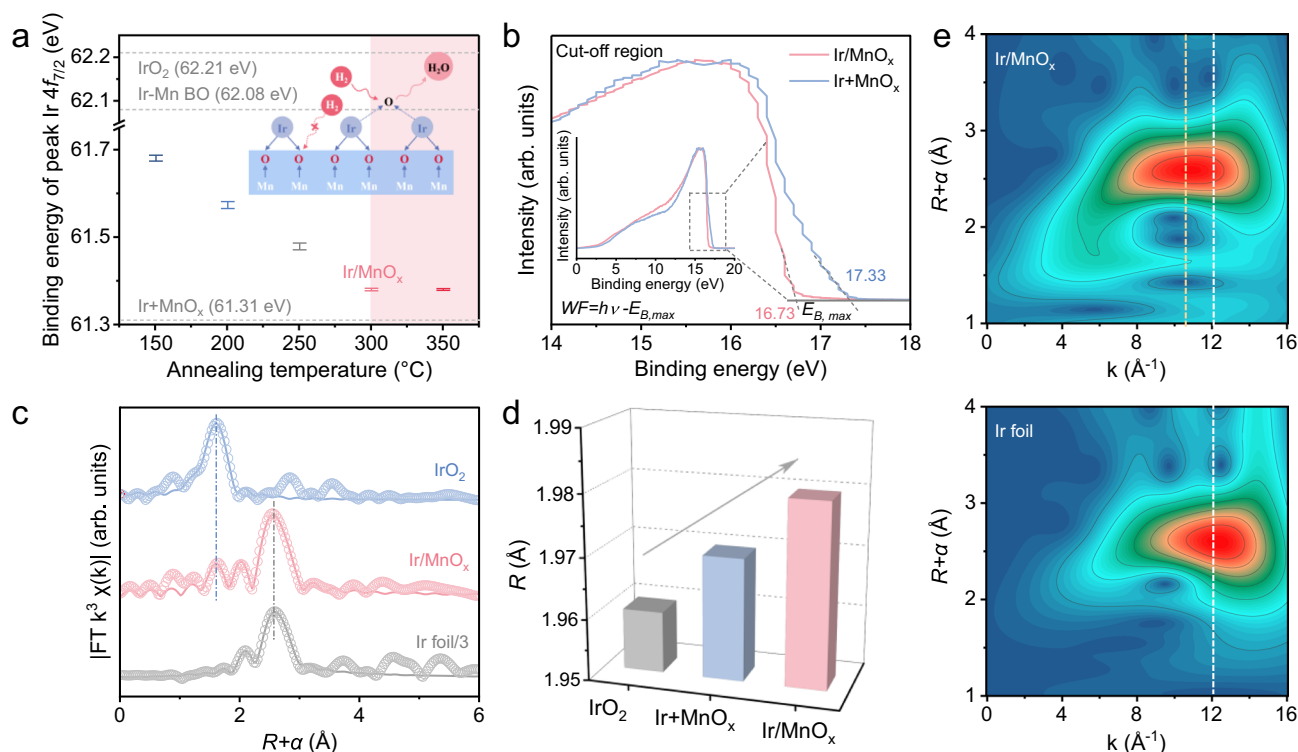


Fig. 2 | Verification of Ir-O-Mn bonds as electron transfer channels for Ir/MnO_x.

a Binding energy of XPS Ir 4f_{7/2} peak as a function of the annealing temperature of the precursor with a 95% confidence interval. The inset indicates robust Ir-O-Mn bonds generated near the heterointerfaces after annealing. **b** UPS spectra of Ir/MnO_x and Ir+MnO_x. **c** Comparison of *R*-space fitting results of Ir L₃-edge EXAFS spectra among different Ir-based samples. **d** Ir-O bond length comparison among different Ir-based samples. **e** The corresponding wavelet transform patterns of Ir/MnO_x and Ir foil.

42.5 mV dec⁻¹, lower than those of Ir/C (56.3 mV dec⁻¹) and IrO₂ (60.7 mV dec⁻¹), demonstrating a considerably accelerated OER kinetics (Fig. 3b). As such, Ir/MnO_x exhibits an overpotential of mere 238 mV at a current density of 10 mA cm⁻², roughly 49 mV and 121 mV smaller than that of commercial Ir/C and IrO₂, respectively (Fig. 3c). The mass activity (MA) of Ir/MnO_x even reaches 4 A mg_{Ir}⁻¹ at the overpotential of 300 mV, approximately 16.0 and 150.6 times higher than those of Ir/C (0.253 A mg_{Ir}⁻¹) and IrO₂ (0.027 A mg_{Ir}⁻¹). The Ir/MnO_x also delivers comparable OER activity in neutral electrolyte (Supplementary Fig. 25). In addition, the comprehensive electrochemical impedance spectroscopy (EIS) of Ir/MnO_x and commercial IrO₂ anode across the varying potential reveals that Ir/MnO_x has a notably lower interface charge transfer resistance (*R*_{ct}), facilitating a more expeditious electrocatalytic kinetics during the OER process (Supplementary Fig. 26).

Chronopotentiometry (CP) tests were implemented at a constant current density of 10 mA cm⁻² to evaluate the catalytic stability of Ir/MnO_x. As presented in Fig. 3d, the potential required for Ir/MnO_x to reach 10 mA cm⁻² shows negligible elevation during a 200-h test. On the contrary, Ir/C experiences a rapid increase of overpotential and collapses in just one day. The origin of the as-promoted OER stability was unraveled by quantitatively monitoring the leaching amount of Ir during CP test by the use of inductively coupled plasma mass spectrometer (ICP-MS, Fig. 3e). Ir/C shows severe Ir leaching while the dissolution rate of Ir in Ir/MnO_x is much slower with its stability number of 6.8 × 10⁵, 7.67 times higher than that of Ir/C (8.9 × 10⁴)²⁷. Moreover, TEM images and EDS mappings after CP test further reveal the morphological and compositional robustness of Ir/MnO_x with no obvious aggregation of either MnO_x nanosheets or Ir nanoclusters (Supplementary Fig. 27) and only slight changes of Mn/Ir elemental ratio (Supplementary Figs. 28 and 29), far surpassing the commercial Ir/C with terrible ripening (Supplementary Fig. 30). Taking the mass activity and S-number as two main indicators for OER activity and stability, respectively, Ir/MnO_x catalyst with strong coupling effects

induced by Ir-O-Mn bonds undoubtedly stands on the top among the state-of-the-art OER catalysts (Supplementary Table 2).

To delve into the mechanisms underlying the enhancement of OER activity and stability, XPS (Supplementary Fig. 31a, b)^{10,28,29} and X-ray absorption near-edge structure (XANES, Supplementary Fig. 31c, d)^{30–33} analysis were conducted to probe the chemical state changes of Ir/MnO_x after the high current density and long-term electrolysis.

Electrochemical oxidation of metallic Ir toward IrO_x occurs rapidly during OER, but it is worth noting that its valence state has been effectively controlled as low as +3.12. Meantime, the valence state of Mn rises from +2.75 to nearly +3.48. These phenomena imply that both Ir and Mn elements inevitably experience the oxidation under high OER potentials. Due to the effective electron buffer effect derived from the MnO_x substrate, the low-valence Ir³⁺ sites with higher intrinsic OER activity are generated and well maintained.

EXAFS analysis was also carried out to uncover the variation of local coordination configuration of the catalyst before and after reconstruction. The EXAFS fitting and wavelet transform patterns results show that, for Ir, the coordination configuration changes from *fcc*-Ir metallic bonds to IrO₂-type covalent bonds, implying in-situ electrochemical oxidation (Supplementary Figs. 32, 34a–c), while for Mn, its coordination environment does not change significantly, meaning that its phase remains unchanged during electrochemical reconstruction (Supplementary Figs. 33, 34e–g). Moreover, the Mn-O bond lengths, both prior to and subsequent to the reconstruction, are observed to be slightly shorter than those in Mn₃O₄ (Supplementary Table 3). This can be attributed to the compressive strain introduced into the ultrathin MnO_x nanosheets by the in-situ precipitation of Ir clusters at the interface, which aligns well with the rightward shift of the corresponding Mn oxide peaks observed in the XRD pattern (Fig. 1b). Furthermore, the left/right shifting of Ir-(O)-M/Mn-(O)-M scattering intensity maximum in wavelet transform patterns paralleling with the increase/decrease of Ir-O/Mn-O bond length persuasively

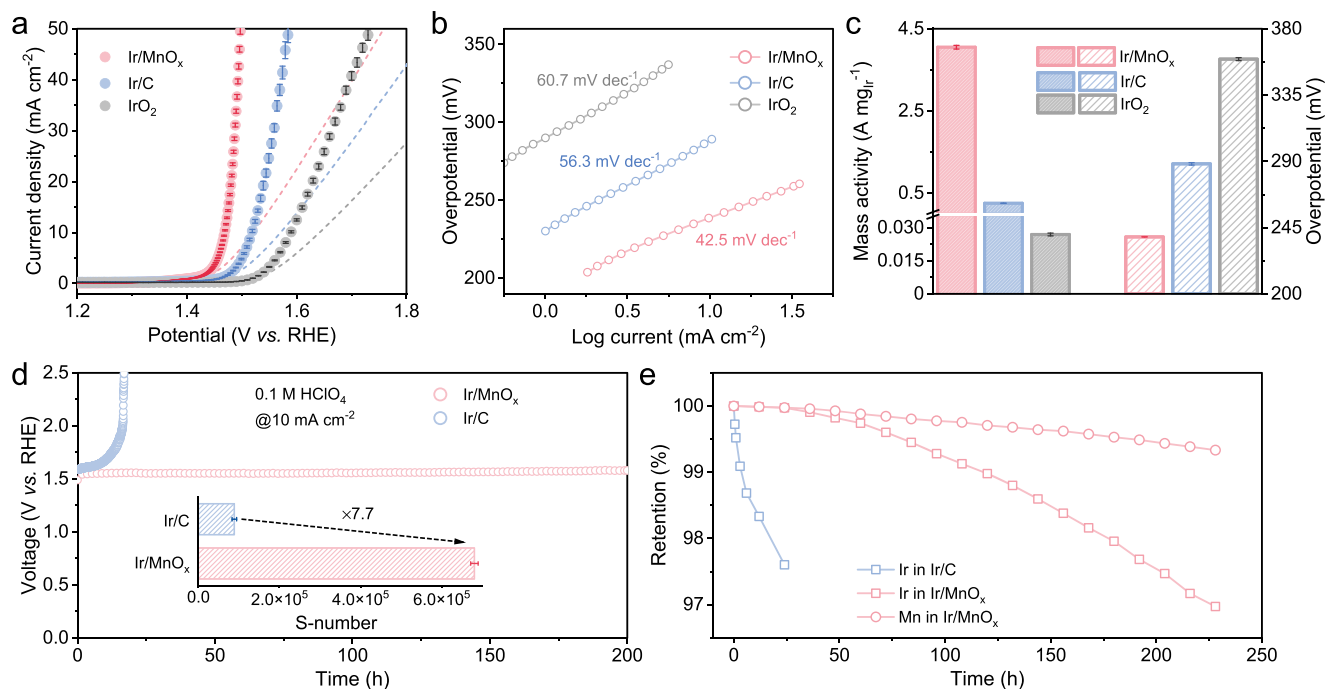


Fig. 3 | OER electrochemical performances of Ir/MnO_x at room temperature in 0.1 M HClO₄ (pH = 1 ± 0.1). **a** Polarization curves of Ir/MnO_x, Ir/C and IrO₂ with 90% *iR*-drop compensation, with dashed lines representing corresponding polarization curves without *iR*-drop compensation. **b** Tafel slopes of different catalysts. **c** Mass activity at the overpotential of 300 mV and the overpotential at 10 mA cm⁻² of Ir/

MnO_x, Ir/C and IrO₂. **d** Chronopotentiometry (CP) curves of Ir/MnO_x and Ir/C. The inset shows the calculated S-number. **e** Metal loading preservation percentage of Ir/MnO_x and Ir/C during CP test. All error bars in Fig. 3 represent the standard deviation.

proves the general existence of Ir-O-Mn, ensuring the strong interfacial coupling in IrO_x/MnO_x material (Supplementary Fig. 34c, d, g, h).

In addition, the reconstruction evolution of the material was also characterized using in-situ SERS (Fig. 4a and Supplementary Fig. 35a). The spectral bands at 360 cm⁻¹ and 650 cm⁻¹ are attributed to the skeletal vibration and Mn-O stretching vibration of Mn oxide, respectively. Notably, the positions of these two peaks remain unchanged with increasing voltage and prolonged electrolysis time, confirming that the Mn oxide matrix undergoes negligible phase transition before and after electrolysis^{34,35}. Additionally, the spectral bands at 548 cm⁻¹ and 790 cm⁻¹ correspond to Ir-O-Ir stretching and Ir-O out-of-plane vibration, respectively^{36,37}. By analyzing the intensity trend of the Ir-O-Ir stretching peak (Supplementary Fig. 35b, c), we demonstrate that Ir undergoes oxidative transformation during electrolysis and rapidly reconstructs to a stable state.

Furthermore, in-situ XAFS studies were also carried out to clarify the reconstruction process of Ir/MnO_x with varying voltage. An analysis of valence states using XANES spectra reveals that as the potential increases, both Ir and Mn undergo a limited degree of increase in valence state (Fig. 4b, c). Then, wavelet transformation of EXAFS provides a more intuitive view of real-time structural evolution, indicating that as the potential rises, Ir transforms from a metallic to an oxidized state, while the coordination structure of Mn remains almost unchanged (Supplementary Fig. 36). Moreover, the obvious lower second maximum intensity in *k* ($\approx 9 \text{ \AA}^{-1}$) of Ir L₃ edge over Ir/MnO_x compared to that of IrO₂ ($k \approx 13 \text{ \AA}^{-1}$) in the WT pattern verifies the general existence of Ir-O-Mn during the reconstruction process. Subsequently, the EXAFS of Ir with notable changes in coordination environment was fitted (Supplementary Fig. 37 and Supplementary Table 4), demonstrating that as potential increased, the average lengths of Ir-O and Ir-O-Ir bonds shortened significantly, accompanied by an increase in coordination number (CN). Conversely, Ir-Ir bonds were elongated, paralleling with a decrease of CN, confirming the in-situ transformation of Ir clusters into IrO_x clusters (Supplementary

Fig. 38). In summary, the active structure of the catalyst can be described as electrochemically in-situ oxidized IrO_x clusters embedded within MnO_x, with the active sites being the abundant and long-lasting Ir³⁺ species derived from the enduring electron transfer from the MnO_x matrix.

Based on the aforementioned reconstructed structure, density functional theory (DFT) calculation was further performed to evidence the electron-feeding effect toward the promoted OER activity and stability for IrO_x/MnO_x, the model of which was constructed derived from the experimental observation (Supplementary Fig. 39) by anchoring individual IrO_x clusters onto the surface of MnO_x (Supplementary Fig. 40, Supplementary Data 1 and 2). The charge density difference of IrO_x/MnO_x model indicates obvious electron cloud deviation from Mn to Ir near the heterointerfaces (Fig. 4d; Supplementary Fig. 41), proving the as-characterized electron feeding effect. The projected density of states clearly reveal that the Ir *d* orbit substantially overlaps with Mn *d* orbit, suggesting more prominent covalent nature and thus stronger electronic interaction between Ir and Mn atoms (Supplementary Fig. 42)²⁶. Bader charge of Ir in both individual IrO_x and IrO_x/MnO_x were further calculated to predict their adsorption behaviors toward multiple oxygenated intermediates during OER. As one can conclude from Supplementary Fig. 43, IrO_x/MnO_x showcases lower Bader charge of Ir under both bare and various adsorption states than individual IrO_x, well consistent with the experimental results that MnO_x matrix contributes to elevated electron density of Ir and thereby helps realize weaker adsorption of all the OER-involved intermediates. A step further, the charge-transfer energy defined by the energy gap between *d*-band center of Ir and *p*-band center of O was also calculated to evaluate the adsorption strengths (Supplementary Fig. 44), where the higher values of IrO_x/MnO_x indicate a less overlapping between its Ir 5*d* and O 2*p* orbitals, stressing its optimally modulated *d*-band structure with optimally weakened adsorptions¹².

The Gibbs free energy diagrams along OER reaction coordinate of the two IrO_x-based models were obtained under classic adsorption

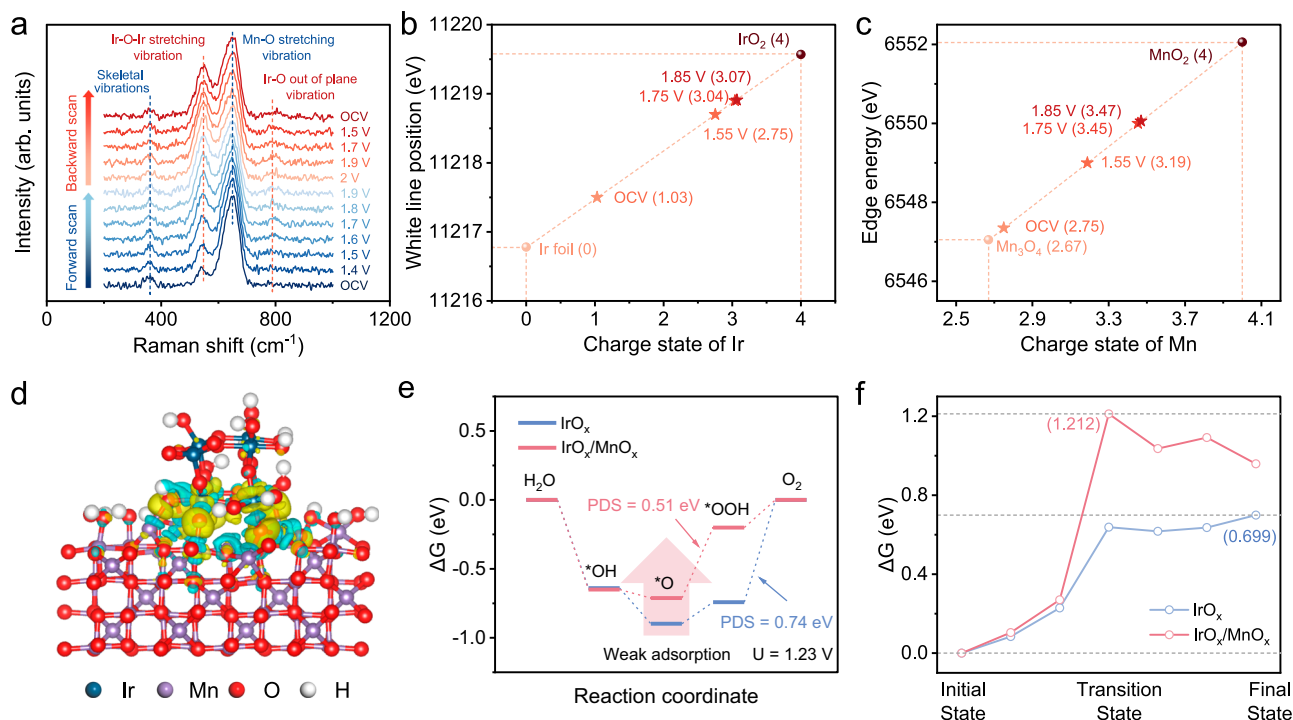


Fig. 4 | In-situ spectroscopic and theoretical study of IrO_x/MnO_x for its catalytic activity and stability enhancement. **a** In-situ SERS spectra of Ir/MnO_x (IrO_x/MnO_x) varying with potential. **b** Ir white-line peak position as a function of the oxidation states of Ir for Ir/MnO_x (IrO_x/MnO_x) in-situ operated at different potentials, with Ir foil (0) and IrO₂ (+4) as standards. **c** Mn K-edge energy as a function of the oxidation states of Mn for Ir/MnO_x (IrO_x/MnO_x) in-situ operated at different potentials, with

Mn₃O₄ (+2.67) and MnO₂ (+4) as standards. **d** Side panel of charge density difference on IrO_x/MnO_x. The yellow and cyan isosurfaces show the charge gain and lost regions, respectively. **e** The Gibbs free energy diagrams of the four-electron OER process on the Ir sites of IrO_x/MnO_x and individual IrO_x under the applied potential of 1.23 V vs. RHE. **f** The Gibbs free energy diagrams of the over-oxidation and leaching of Ir in IrO_x/MnO_x and IrO_x.

evolution mechanism (AEM) pathway (Supplementary Fig. 45). Subject to the over-strong binding of [•]OOH, individual IrO_x suffers from excessive energy barrier of potential determining step (PDS) ([•]OOH → [•] + H⁺ + e⁻ + O₂) under both U = 0 V vs. RHE (0.74 eV, Supplementary Fig. 46) and U = 1.23 V vs. RHE (1.97 eV, Fig. 4e)³⁸. However, due to the considerably weakened adsorption energies of multiple oxygenated intermediates, particularly the [•]O species, the deprotonation process of [•]OOH gets well accelerated on IrO_x/MnO_x, resulting in its PDS transposing to the conversion from [•]O to [•]OOH and its energy barrier decreasing to 0.51 eV (1.74 eV) under U = 1.23 V (0 V) vs. RHE. Both the alternation of PDS as well as the dramatically reduced energy barrier originate from the elevated surface reactivity of Ir through electron feeding effect and mutually account for the elevated OER activity of IrO_x/MnO_x. To explore the origins of promoted OER stability of IrO_x/MnO_x, the over-oxidation and leaching process of Ir in both IrO_x and IrO_x/MnO_x were investigated. In contrast with IrO_x (Supplementary Fig. 47), the strong-coupling of IrO_x and MnO_x in IrO_x/MnO_x introduces an extra kinetics-controlled transition state evolution (Supplementary Fig. 48), which increases the formation energy of Ir vacancy, effectively suppressing the over-oxidation and leaching of Ir and thus endowing IrO_x/MnO_x with excellent OER durability (Fig. 4f). To conclude, theoretical calculation ensures the indispensable role of Ir-O-Mn bond-derived electron feeding effect in generating and stabilizing highly active low-valence Ir species for acidic OER electrocatalysis¹².

A membrane electrode assembly was constructed (Supplementary Fig. 49) by employing Ir/MnO_x as the anodic catalyst for OER and Pt/C as the cathodic catalyst for HER, to evaluate its behaviors in practical PEMWE devices. As shown in Fig. 5a, even with mere one tenth of Ir loading, Ir/MnO_x exhibits better performance as its cell voltage demanded to deliver an industrial current density of 1 A cm⁻² reaches as low as 1.63 V, farther surpassing its commercial counterparts (IrO₂

with 2 mg_{Ir} cm⁻² and 0.2 mg_{Ir} cm⁻², donated as IrO₂-2 and IrO₂-0.2, respectively). It is worth noting that Ir/MnO_x remains the linear transcending mode even in the high-current-density region, indicative of its efficient mass transfer derived from the interlaced porous structure with densely distributed clusters³⁹. Besides, within the range of 1.5 V to 1.8 V vs. RHE, Ir/MnO_x exhibits much higher mass activity than IrO₂-0.2 and IrO₂-2, showing promising OER behaviors in practical devices with desirably low Ir loading (Fig. 5b; Supplementary Table 5), which makes it a most outstanding candidate among other reported OER catalysts for PEMWEs (Supplementary Table 6).

Unlike the RDE tests, which mainly reflect the kinetics, the PEMWE voltage is also influenced by the system's ohmic and mass-transfer resistance. Therefore, overpotential analysis was further carried out to discern the contributions of kinetic, ohmic, and mass-transport properties separately (Fig. 5c; Supplementary Figs. 50 and 51)^{19,20,40}. Substantial reduction of approximately 14.5% in kinetic overpotential at 2 A cm⁻² was observed for Ir/MnO_x relative to IrO₂-0.2, indicating the noteworthy enhanced OER kinetics over Ir/MnO_x. Moreover, Ir/MnO_x demonstrates a significantly decreased ohmic overpotential, roughly 29.6% lower than that of IrO₂-0.2 (Supplementary Fig. 52, Supplementary Table 7), implying the porous nanosheet structure effectively mitigates the interfacial contact between the catalyst layer and proton exchange membrane⁴⁰ (Supplementary Fig. 53). More importantly, Ir/MnO_x exhibits significant advantages in terms of mass-transport overpotential compared to IrO₂-0.2, particularly at high current densities, with mere 47.2-mV increase at current density of 2 A cm⁻², 73.0% lower than that of IrO₂-0.2. The prominently triggered mass transfer of Ir/MnO_x can be attributed to its reticular porous structure that enables smooth flow of reactants and products (Supplementary Fig. 55). Therefore, the PEMWE device based on Ir/MnO_x demonstrates comparable operation efficiency (Supplementary Fig. 54, Supplementary Table 8)

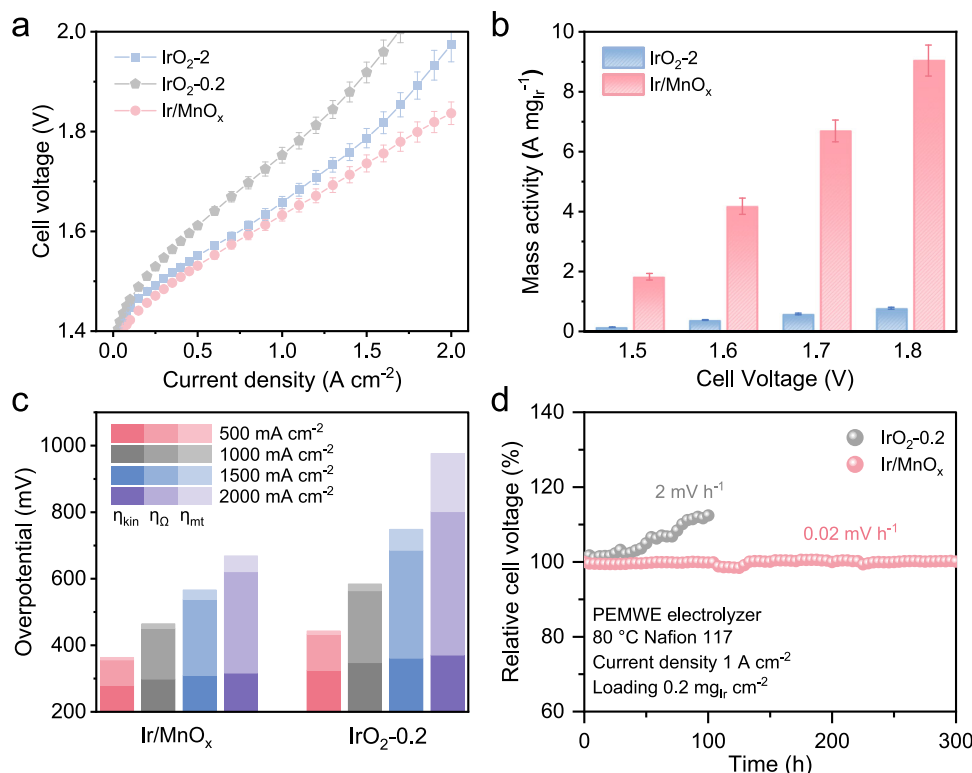


Fig. 5 | Electrochemical performances of Ir/MnO_x on PEMWE devices.

a Polarization curves for Ir/MnO_x (with 0.2 mg cm⁻² Ir loading), IrO₂-0.2 and IrO₂-2. "0.2" and "2" represents Ir loading. **b** Mass activities of Ir/MnO_x and IrO₂-2 at various cell voltage. **c** Various overpotential contributions to the polarization curves of Ir/MnO_x and IrO₂-0.2 at different current density. **d** Chronopotentiometry curves at current density of 1.0 A cm⁻² of Ir/MnO_x and IrO₂-0.2. All error bars in Fig. 5 represent the standard deviation.

and lower cost *per kilogram* of H₂ (Supplementary Fig. 56) compared to IrO₂-2 and IrO₂-0.2 (Supplementary Fig. 57).

The long-term stability is of utmost importance for practical application of OER catalysts. PEMWE based on Ir/MnO_x with an Ir loading of 0.2 mg cm⁻² exhibits stability over 300 h at 1 A cm⁻². In contrast, IrO₂-0.2 suffers from rapid decay after a mere 50-h operation (Fig. 5d). Over the 300-h operating period, the average energy consumption of Ir/MnO_x is quite low, calculated as 43.75 kWh kg⁻¹ H₂ (equated to 3.94 kWh m⁻³ H₂ at standard temperature and pressure, details in Supporting Information)⁴¹. ICP-MS was also employed to analyze the ion leaching during PEMWE stability test. The results indicate minor loss of only 1.81% Ir and 0.42% Mn leaching during 300-h test with a high S-number of Ir/MnO_x of 1.48×10^8 . In addition to better resistance against ion leaching, the comparable stability of Ir/MnO_x also stems from its notable structural stability, allowing the preservation of its advantageous architecture (Supplementary Fig. 58) to realize low ohmic and charge transfer resistance (Supplementary Fig. 59, Supplementary Table 7). The AST under various Ir loadings were also used to evaluate the stability of Ir/MnO_x-based PEMWE (Supplementary Fig. 60), showing that Ir/MnO_x-based PEMWE still exhibits excellent durability at lower Ir loading (0.1 mg_{Ir} cm⁻²) with an extremely low decay rate (1.275 mV increase *per* 1000 cycles at 2 A cm⁻²), much better than that of commercial IrO₂ with a higher loading of 2 mg_{Ir} cm⁻² (1.365 mV *per* 1000 cycles at 2 A cm⁻²).

In summary, we reported a highly efficient two-dimensional Ir/MnO_x catalyst with strong-coupling hetero-interfaces and high capacity of mass/charge transfer as an anode catalyst to achieve practical durable low-iridium PEMWE. Advanced characterizations and theoretical calculations reveal that abundant Ir-O-Mn near the hetero-interfaces of the reconstructed IrO_x/MnO_x catalyst can realize distinct charge transfer to effectively address the over-oxidation issue of Ir³⁺, resulting in a comparable mass activity (4 A mg_{Ir}⁻¹ at the overpotential

MnO_x and IrO₂-0.2 at different current density. **d** Chronopotentiometry curves at current density of 1.0 A cm⁻² of Ir/MnO_x and IrO₂-0.2. All error bars in Fig. 5 represent the standard deviation.

of 300 mV) and a significant S-number (6.8×10^5). Besides its excellent kinetic advantages, the unique spatially interlaced porous nanosheet structure of Ir/MnO_x as a catalyst layer confers notable electron and mass transfer with 29.6% and 73.0% of corresponding overpotential lower than that of commercial IrO₂ at a high working current of 2 A cm⁻² in practical PEMWEs. Notably, PEMWE utilizing Ir/MnO_x as anode catalysts with mere 0.2 mg_{Ir} cm⁻² loading achieves a high mass activity of 6.69 A mg_{Ir}⁻¹ at 1.7 V and can operate stably at an industrial current density of 1 A cm⁻² for 300 h, presenting the top level among the reported low-Ir-loading electrolyzers.

Methods

Chemicals

Hexachloroiridium acid hydrate (H₂IrCl₆·H₂O, Ir ≥ 35%) was obtained from Adamas-beta. Manganese chloride (MnCl₂) was obtained from Macklin. Potassium nitrate (KNO₃), potassium hydroxide (KOH, 95%) and perchloric acid (HClO₄, 70%) were obtained from Aladdin Reagent Co. Ltd. Nafion®D-521 dispersion (5 wt.%) was bought from Alfa Aesar. Isopropanol, ethanol, and cyclohexane were all supplied by Beijing Tongguang Fine Chemicals Company. Commercial Ir/C (20 wt% of 2–4 nm Ir nanoparticles on carbon black) and IrO₂ for RDE testing were purchased from Premetek Company. IrO₂ for PEMWE testing was purchased from Cotrun New Energy. Manganese acetate Hydrate (MnAc·4H₂O) was purchased from 3A Materials. Carbon paper (29 BC) was purchased from SIGRACET. Carbon cloth was purchased from Toray. All reagents were used as received without further purification. The water used in all experiments was ultrapure (18.2 MΩ cm).

Synthesis of Ir-Mn bimetallic oxide precursor

200 μL of 0.1 g mL⁻¹ solution of H₂IrCl₆·H₂O was added to 10 mL of 0.1 M KOH. The mixture was left undisturbed until the solution changed from brown to a nearly colorless state. Next, the resulting liquid

was transferred to a 40 mL glass vial and placed in an oil bath at 80 °C. The reactant's color turned light blue during this process. Once the solution was turned into the aforementioned light blue color, 1 mL of a 10 mg mL⁻¹ solution of MnCl₂ was added drop by drop into the mixture under stirring. The reaction mixture was then kept at 80 °C with continuous stirring for 2 h. The obtained black product was washed three times with deionized water and once with ethanol, and finally was dispersed in ethanol.

Synthesis of Ir/MnO_x catalyst

The total obtained precursor was mixed with 10 mg carbon black under ambient sonication for 1 h in ethanol. The resulting product was collected by centrifugation and dried at 60 °C in an oven for 3 h. Subsequently, it was calcined in H₂/Ar at 300 °C for 1 h to obtain the Ir/MnO_x. To obtain the Ir/MnO_x-T, the calcination step was performed at temperature of T with other conditions remaining unchanged.

Synthesis of Ir + MnO_x

Ir clusters and MnO_x were synthesized, respectively. As for Ir clusters of Ir+MnO_x, 250 mg CTAB was dissolved in 50 mL ethylene glycol (EG) and ultrasound for 1 h. Then, 600 μL of 0.1 g/mL solution of H₂IrCl₆·H₂O was dropwise added to above mixture under vigorous stirring. Then, the obtained mixture was heat up to 160 °C and refluxed for 3 h. Finally, the suspension was washed with a mixture of deionized water and ethanol. After that it was dispersed in ethanol. With regard to MnO_x, MnO_x was electrodeposited on carbon cloth. Before that, the carbon cloth was electrochemically treated in a three-electrode cell using 0.5 M KNO₃ electrolyte. A piece of graphite foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. A constant potential of 1.85 V vs. SCE was applied to the working electrode (carbon cloth) for 30 min to enhance the wettability of the electrode. The as-treated electrode was further scanned using cyclic voltammetry from -1.0 to 1.0 V vs. SCE for 50 cycles at a scan rate of 100 mV s⁻¹ to recover the conductivity of the carbon cloth. The electrodeposition of MnO_x on electrochemically treated carbon cloth was conducted in a three-electrode cell containing 0.3 M manganese acetate (MnAc·4H₂O), using a constant current density of 20 mA cm⁻² for 2 min. The prepared ethanol solution of Ir clusters was dropped onto MnO_x at room temperature.

Synthesis of Ir/MnO_x anode for the durability test

Appropriate amount of precursor without Nafion ionomer was sprayed onto carbon paper (1.0 × 1.5 cm²). Subsequently, it was calcined in H₂/Ar at 300 °C for 1 h to obtain Ir/MnO_x anode. The specific catalyst loading was calculated to be 0.056 mg_{Ir} cm⁻² (based on ICP-OES).

Electrochemical measurements in a three-electrode system

The electrochemical measurements of OER were conducted in a three-electrode system, utilizing a RDE apparatus (Pine Research Instrumentation, the United States) connected to CHI750e electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). In the three-electrode setup, a glassy carbon RDE (area: 0.196 cm²) coated with catalysts served as the working electrode, while a Pt foil (dimensions: 1.0 × 1.5 cm²) functioned as the counter electrode, and a SCE acted as the reference electrode. 2 mg of Ir/MnO_x was dispersed in 1 mL of a mixture of ultrapure water, isopropanol and Nafion[®] D-521 solution (volume ratio = 1:1: 0.04) by sonication for 1 h to get a catalyst ink. The same procedure was followed to prepare a catalyst ink of commercial Ir/C and IrO₂. Next, the ink was dropped onto the glassy carbon RDE, and the specific catalyst loading was calculated to be 0.056 mg_{Ir} cm⁻² for each catalyst (based on ICP-OES). For electrochemical assessments in acidic media, fast cyclic voltammograms (CVs, 500 mV/s, 0.05–1.4 V, in 0.1 M N₂-saturated HClO₄ solution (freshly prepared and promptly utilized (pH -

1)), at a rotating speed of 1600 rpm) were conducted to activate the catalysts until stable CVs were obtained, and then slow CVs at 50 mV/s from 0.05 V to 1.4 V (in 0.1 M N₂-saturated HClO₄ solution, without rotating) were recorded. OER polarization curves were recorded by LSV in 0.1 M O₂-saturated HClO₄ solution at the scan rate of 5 mV/s with 90% *i*R drop compensation at a rotating speed of 2000 rpm. The onset potential was defined as the intersection potential of the tangent line and the baseline⁴². EIS measurements were recorded across the varying potential and a frequency range from 100,000 to 0.01 Hz. Chronopotentiometry (CP) based on three-electrode system was utilized to assess the stability of electrocatalysts at a constant current density of 10 mA cm⁻² in 0.1 M HClO₄ solution. In the system, Ir/MnO_x anode was used as working electrode, Pt foil (1.0 × 1.5 cm²) was used as counter electrode and SCE was used as reference electrode. The dissolution of metal elements from the catalyst into the electrolyte solution during the durability test was quantified by collecting 2 mL electrolyte at regular intervals for the ICP-MS test. Subsequently, 2 mL of 0.1 M HClO₄ solution was added to the system. The final calculating results was based on the cumulative dissolution of metal elements.

Every time before using reference electrodes to conduct electrochemical tests, we calibrate the reference electrodes using the following method^{43,44}. The calibration process was carried out in an electrolyte saturated with high-purity hydrogen, using two Pt plates as the working electrode and counter electrode, respectively. Cyclic voltammetry (CV) scans were conducted at a rate of 1 mV/s, and the thermodynamic potential for the hydrogen electrode reactions was determined as the average of the two potentials at which the current crossed zero during these scans, which was used to scale the potential to reversible hydrogen electrode (RHE).

Synthesis of Ir/MnO_x anode for PEMWE

Appropriate amount of precursor without Nafion ionomer was sprayed onto Pt-plated titanium felt with a porosity of ~50% and a thickness of 0.25 mm. Subsequently, it was calcined in H₂/Ar at 300 °C for 1 h to obtain Ir/MnO_x anode.

Electrochemical measurements in PEM electrolyzer

Appropriate amount of Ir/MnO_x precursor or IrO₂ was sprayed onto Pt-plated titanium felt with a porosity of ~50% and a thickness of 0.25 mm, to prepare anodes using our designed automatic airbrush. Pt/C (70 wt.%) was used as the cathode catalyst. The ionomer to catalyst (I/C) ratio at cathode is controlled to be 0.25. The prepared cathode catalyst's ink was sprayed onto Nafion membrane (N117) using our designed automatic airbrush. X-ray fluorescence (XRF) was used to evaluate the loading of catalyst and uniformity of the catalyst layer. The Nafion perfluorosulfonic acid membrane was treated by 5 wt% H₂O₂, 0.5 M H₂SO₄ at 80 °C for 1 h each step to remove impurities and protonate the sulfonic-acid groups before usage. Pt-plated sintered titanium with a porosity of ~50% and a thickness of 0.25 mm was used as porous transport layers (PTL) at cathode. Anode and cathodic catalyst coated membrane were assembled in homemade single cell hardware with titanium parallel flow field on cathode and platinized titanium parallel flow field on anode. The PEM electrolyzer was operated at the temperature of 80 °C using distilled water as the electrolyte solution under the flowing rate of 40 mL min⁻¹ cm⁻². The EIS was carried out at 1 A cm⁻² by applying an alternated signal of 50 mA over the frequency range from 10 kHz to 1 Hz. The stability of the PEM electrolyzer was evaluated by measuring chronopotentiometry at 1 A cm⁻². The dissolution of metal elements in the anode solution during the 300 h test was quantified by ICP-MS.

Characterizations

TEM was performed using a HITACHI HT7700 instrument, operated at an accelerating voltage of 100 kV. XRD patterns were acquired using a

Rigaku D/max-2500 powder diffractometer, employing Cu-K α radiation with a wavelength of 0.154 nm. HAADF-STEM and energy-dispersive X-ray spectroscopy (EDS) element mappings were carried out on an aberration-corrected JEOL 2200FS STEM/TEM microscope, which was operated at 300 kV and equipped with a Bruker-AXS SDD detector. The composition and concentration of the catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES), specifically the Agilent 5110 model. The mass loading on CCM is determined by X-ray Fluorescence Spectrometer. The dissolution of metal elements from the anode catalyst into the electrolyte solution during the test was quantified by ICP-MS. UPS and XPS measurements were conducted on an XPS AXIS Ultra DLD (Kratos Analytical).

Raman spectra were obtained using a HORIBA-Xplora Plus confocal microprobe Raman system. A 50 $\times$ objective with an 8 mm working distance was utilized for the measurements. The excitation source was a 532 nm He-Ne laser with an approximately 6 mW of power. Calibration of the Raman frequencies was performed with a Si wafer spectrum. Each displayed spectrum was collected over a 120 s acquisition time and represents the average of two measurements. In-situ Raman experiments were performed in a membrane separation flow cell using a CHI760E electrochemical workstation, using a counter electrode and a reference electrode, in an electrolyte solution with a volume of approximately 20 mL. The in-situ XAS experiments were conducted under the same conditions as those used for the electrocatalytic characterization, employing a single cell that had its opening securely sealed with Kapton tape⁴⁵.

S-number calculation

The S-number was calculated based on the following equation:

$$S - \text{number} = \frac{n_{O_2}}{n_{Ir}} \quad (1)$$

where n_{O_2} is the amount of oxygen molecules produced during the durability test (mol), according to the Faraday's laws of electrolysis:

$$n_{O_2} = \frac{j \times s \times t}{z \times F} \quad (2)$$

where j is the current density (A cm⁻²), s is the geometry area of the electrode (cm²), t is the electrolysis time (s), z is the number of electrons transferred to produce an oxygen molecule (=4), F is the Faraday constant (96484 C mol⁻¹). n_{Ir} is the total amount of Ir dissolved in the electrolyte (mol).

Theoretical computation

We utilized the Vienna Ab initio Simulation Package (VASP) for conducting all DFT computations, adopting the generalized gradient approximation (GGA) framework with the Perdew-Burke-Ernzerhof (PBE) functional. In our approach, we selected the projected augmented wave (PAW) potentials to represent the ionic cores, while accounting for the valence electrons through a plane wave basis set, imposing a kinetic energy cutoff of 450 eV. To address the highly localized 3d states in Mn, the DFT + U method was employed with specific parameters of $U \cdot J = 3.9$ eV. Additionally, the spin-polarization effect was taken into account. The transition states were identified using the climbing image nudged elastic band (CI-NEB) method, adhering to a consistent convergence criterion. The free energy changes (ΔG) for each fundamental step in the OER were estimated using the computational hydrogen electrode (CHE) model. Here, the chemical potential aligns with half the energy of gaseous H₂ at 0 V relative to the reversible hydrogen electrode (RHE). During an electron transfer step, the electrode potential (U relative to RHE) is accounted for by subtracting eU from the free energy. This can be expressed as

$G(U) = G(0 \text{ V}) - neU$, where e represents the elementary charge of an electron, n is the number of proton-electron pairs transferred, and U is the applied potential. The Gibbs free energy (ΔG) was determined using the equation provided below:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad (3)$$

where the value of ΔE , ΔE_{ZPE} and ΔS represents the variations in DFT energy, zero-point energy and entropy at a temperature of 298.15 K, respectively^{46,47}.

Overpotential analysis

The cell voltage, E_{cell} , consists of the reversible cell potential E_{rev}^0 and three primary overpotentials: kinetic overpotential (η_{kin}), ohmic overpotential (η_{Ω}), and mass transport overpotential (η_{mt}). Given that the hydrogen evolution reaction (HER) exhibits more preferable kinetics and mass transport under current testing conditions compared to the OER, the overpotential analysis focuses solely on the OER side.

$$E_{cell} = E_{rev}^0 + \eta_{kin} + \eta_{\Omega} + \eta_{mt} \quad (4)$$

The temperature-dependent, standard reversible potential for the water splitting reaction is computed using the following formula:

$$E_{rev}^0 = 1.2291 - 0.0008456 \times (T - 298.15) \quad (5)$$

Under the current electrolyzer testing conditions, the voltage is calculated to be 1.168 V, with a thermoneutral voltage of 1.42 V.

EIS was utilized to assess the high-frequency resistance (HFR), which signifies the overall electronic resistance of the cell. Consequently, the ohmic overpotential (η_{Ω}) can be determined as follows:

$$\eta_{\Omega} = i \times R_{tot} = i \times HFR \quad (6)$$

The kinetic overpotential is derived using the Tafel model, where the Tafel slope b and exchange current density i_0 are the key kinetic parameters. Under the assumption of a non-polarizable HER, the entire kinetic overpotential of the cell is determined by OER. The Tafel slope b for OER is given as $2.303 \times RT / 4F$, where R is the ideal gas constant, T is the temperature, F is Faraday's constant.

$$\eta_{kin} = b \times \log \left(\frac{i}{i_0} \right) \quad (7)$$

The mass transport encompasses the transfer of gases and liquids within the porous transport layer (PTL) and catalytic layer (CL), as well as the ionic transport within the CLs. In this research, it is determined by deducting the reversible cell potential, along with kinetic and ohmic overpotentials, from the observed cell potential⁴⁰.

Operation efficiency to produce H₂

The operation efficiency to produce H₂ was calculated based on the following equation:

$$\text{Operation efficiency} = \frac{H_2 \text{ power out}}{\text{Electrolyzer power}} \quad (8)$$

In the equation above, electrolyzer power was calculated based on the following equation:

$$\text{Electrolyzer power} = U \times j \quad (9)$$

where U is the voltage of PEMWE electrolyzer (V), j is the current density (A cm⁻²).

H₂ power out was calculated based on the following equation:

$$\text{H}_2 \text{ power out} = \frac{j \times M_{\text{H}_2} \times q}{n \times F} \quad (10)$$

where j is the current density (A cm⁻²), M_{H_2} is molar mass of H₂ (2 g mol⁻¹), F is the Faraday constant (96484 C mol⁻¹), n is the number of electrons transferred to produce a hydrogen molecule (=2), q is the heating value of H₂ where the lower heating value (LHV = 1.185 × 10⁵ J g⁻¹) and the higher heating value (HHV = 1.43 × 10⁵ J g⁻¹) are applied to calculate operation efficiency, respectively.

Energy consumption per kilogram of H₂ calculation

The Energy consumption per kilogram of H₂ (kWh kg⁻¹ H₂) was calculated based on the following equation:

$$\text{Energy consumption per kilogram of H}_2 = \frac{U \times j \times A \times t}{1000 \times m_{\text{H}_2}} \quad (11)$$

where U is the voltage of PEMWE electrolyzer (V), j is the current density (A cm⁻²), A is the effective working area of electrolyzer (cm²), t is the electrolysis time (h). The average energy consumption per kilogram of H₂ is calculated by integrating U with respect to t . m_{H_2} is mass of H₂ (kg) based on the following equation:

$$m_{\text{H}_2} = \frac{j \times A \times t \times M_{\text{H}_2}}{1000 \times n \times F} \quad (12)$$

where j is the current density (A cm⁻²), A is the effective working area of electrolyzer (cm²), t is the electrolysis time (s), M_{H_2} is molar mass of H₂ (2 g mol⁻¹), n is the the number of electrons transferred to produce a hydrogen molecule (=2), F is the Faraday constant (96484 C mol⁻¹).

Energy consumption per cubic meter of H₂ calculation

The Energy consumption per kilogram of H₂ (kWh m⁻³ H₂) was calculated based on the following equation:

$$\frac{\text{Energy consumption per cubic meter of H}_2}{\text{Energy consumption per kilogram of H}_2 \times \rho} \quad (13)$$

where ρ is the density of H₂ (0.09 kg m⁻³) at standard temperature and pressure.

Energy cost per kilogram of H₂ calculation

Energy cost per kilogram of H₂ (USD kg⁻¹ H₂) was calculated based on the following equation:

$$\frac{\text{Cost per kilogram of H}_2}{\text{energy consumption per kilogram of H}_2 \times \text{electricity bill}} \quad (14)$$

where electricity bill obtained from the previous reports is USD 0.02 kWh⁻¹.

Data availability

The data that support the findings of this study are available in the supplementary material of this article. Source data are provided with this paper.

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Author contributions

D.W. and F.Lv. designed research; D.W. performed research; H.L., J.Z., W.Z., and Y.Wang. offered assistance in experimental operation; Y.Wei, Q.Z., and L.G. contributed analytic tools; L.L. performed computation; D.W. wrote the first draft of the paper; F.Lin, F.Lv., M.L., and S.G. revised the paper.

Competing interests

The authors declare no competing interests.

Additional information

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