

Dynamic amorphous confinement stabilizes crystalline IrO₂ for ultra-durable proton exchange membrane water electrolysis

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Abstract

Crystalline IrO₂ exhibits high conductivity and structural robustness but suffers from limited active-site exposure, whereas amorphous IrO_x provides abundant active motifs yet rapidly degrades during operation. Here we report a crystalline–amorphous hybrid IrO₂ catalyst in which conductive crystalline IrO₂ nanodomains are confined within a porous amorphous iridium oxide matrix. The catalyst achieves 6.4 A cm⁻² at 2.0 V in a proton exchange membrane water electrolysis cell with an ultralow Ir loading of 0.2 mg_{Ir} cm⁻² and exhibits negligible degradation over 3400 hours at 3 A cm⁻². Operando spectroscopy reveals that the amorphous framework enables reversible surface reconstruction of crystalline IrO₂ into active oxyhydroxide species while suppressing irreversible coarsening and dissolution. Density functional theory calculations suggest that the crystalline–amorphous architecture strengthens Ir–O electronic coupling and facilitates *OOH formation. This work demonstrates that dynamically stabilized crystalline–amorphous interfaces can overcome the conventional activity–stability limitation of acidic oxygen evolution catalysts.

Main

The transition toward a carbon-neutral energy infrastructure critically depends on scalable technologies for converting intermittent renewable electricity into chemical fuels^{1–4}. Among the available approaches, proton exchange membrane water electrolysis (PEMWE) is regarded as a promising route for green hydrogen production because of its rapid dynamic response, compact system design, and compatibility with fluctuating renewable power sources^{5–7}. However, the practical deployment of PEMWE at the terawatt scale remains hindered by the sluggish anodic oxygen evolution reaction (OER), which proceeds under highly acidic and oxidative conditions and therefore requires catalysts with simultaneously high activity and long-term durability^{8–10}.

Iridium-based oxides are currently the only practical OER catalysts capable of sustained long-term operation in PEMWE⁹. Yet the scarcity and high cost of iridium impose stringent constraints on catalyst loading and utilization efficiency^{11, 12}. Reducing the iridium loading of PEMWE anodes from conventional milligram-level values to below 0.1–0.2 mg_{Ir} cm⁻² requires catalysts that can maintain rapid oxygen evolution kinetics under industrial current densities while resisting dissolution, agglomeration, and structural degradation during prolonged operation¹³. A central challenge in the design of Ir-based catalysts lies in the intrinsic trade-off between catalytic activity and stability (Fig. 1a). Highly crystalline IrO₂ possesses excellent conductivity and structural robustness but exposes limited catalytically active sites because of its low defect density and rigid lattice structure¹⁴. In contrast, amorphous IrO_x generally exhibits higher intrinsic activity owing to its abundant coordinatively unsaturated motifs and structural flexibility^{15, 16}. However, this disordered structure readily undergoes irreversible oxidative reconstruction and dissolution under harsh anodic potentials, leading to rapid degradation during PEMWE operation^{17, 18}. Previous efforts to balance these competing properties have focused on defect engineering,

heterostructure design, and support stabilization, yet achieving simultaneously high current density, low Ir loading, and industrial durability remains a major challenge^{19, 20}.

Hybrid structures combining crystalline and amorphous domains have emerged as a promising approach. The crystalline regions provide long-range order, electronic conductivity, and structural robustness, while the amorphous network offers high-density active sites and efficient mass transport pathways^{14, 21, 22}. However, the synthesis of such architectures is challenging, demanding precise control over nucleation, growth, and spatial confinement to avoid aggregation or phase separation^{23, 24}. Furthermore, the interfacial electronic structure at the crystalline–amorphous boundary is expected to modulate adsorption energies of oxygen intermediates, accelerating reaction kinetics, yet direct experimental validation and mechanistic understanding remain limited²⁵.

Here, we present a simple carbon-templated approach to synthesize a dynamically amorphous-confined IrO₂ catalyst (DAC-IrO₂), in which rutile IrO₂ nanocrystals are uniformly embedded in an amorphous cotton-like matrix. The method employs polycyclic aromatic hydrocarbons as transient templates, which, under thermal treatment, confine IrO₂ nucleation and growth, producing a porous interconnected composite upon template removal. Structural characterization confirms well-dispersed crystalline domains within an amorphous matrix, with abundant interfaces and defects. X-ray absorption and photoelectron spectroscopies reveal electronic reconstruction at the interface, consistent with enhanced oxygen intermediate adsorption. The hybrid catalyst exhibits high PEMWE performance at ultralow Ir loading (0.2 mg cm⁻²), achieving high current densities (6.4 A cm⁻² at 2.0 V) and long-term stability exceeding 3400 h under the stated conditions. Integrating crystalline and amorphous motifs enhances activity, durability, and Ir utilization in acidic water electrolysis, providing a pathway for high-performance PEMWE catalysts and mechanistic insight into interfacial electronic effects.

Synthesis and characterization of catalysts

The design principle of DAC-IrO₂ is summarized in Fig. 1a. Fully crystalline IrO₂ provides high electronic conductivity and structural robustness but exposes relatively few active sites and is susceptible to particle sintering and loss of accessible surface area. Conversely, amorphous IrO_x offers a high density of coordinatively unsaturated sites and open transport pathways, but its disordered framework is vulnerable to oxidative dissolution. DAC-IrO₂ combines these complementary attributes by embedding rutile IrO₂ nanocrystals within a continuous amorphous, cotton-like iridium oxide matrix. The synthesis begins by dissolving iridium trichloride (IrCl₃), sodium nitrate (NaNO₃), and polycyclic aromatic hydrocarbons (PAHs, such as pyrene or anthracene) in water (**Fig. S1**). Upon heating at 80°C, the PAHs become uniformly distributed around the precursor salts, forming a homogeneous organic–inorganic intermediate²⁶. After drying, the solid is calcined in air, during which the PAHs undergo carbonization and oxidative decomposition, transiently providing a carbonaceous confinement environment that confines the iridium species, while the decomposition of NaNO₃ generates a highly oxidative local environment

that facilitates conversion of IrCl_3 to IrO_2 ²⁷. Under this spatial confinement, a fraction of IrO_2 crystallizes into fine nanoparticles, while the remainder forms a continuous amorphous cotton-like matrix. Oxidative removal of the carbon template yields a porous DAC- IrO_2 composite. This hierarchical structure synergistically combines the high conductivity of crystalline domains with the high surface area and defect richness of the amorphous matrix, offering significant advantages for electrocatalytic applications. By varying the IrCl_3 -to-PAHs feed ratio, we obtained crystalline–amorphous composites with distinct micro-/nanomorphologies, highlighting the versatility of this approach for morphological control (**Fig. S2**). In the absence of PAHs, the reaction produces predominantly crystalline IrO_2 nanoparticles. Incorporation of PAHs leads to formation of the amorphous cotton-like matrix (**Fig. S3**), and excess PAHs drive the evolution of ultra-long amorphous IrO_2 nanowires supporting crystalline nanoparticles (**Fig. S4**). The microstructure of DAC- IrO_2 was characterized by transmission electron microscopy (TEM), revealing a continuous amorphous iridium oxide matrix (Fig. 1b–c). Atomic-resolution high-angle annular dark-field scanning TEM (HAADF-STEM) clearly resolved lattice fringes of the embedded nanoparticles (Fig. 1d). High-resolution TEM (HRTEM) images confirmed that the crystalline nanoparticles are uniformly distributed within the amorphous matrix, while selected-area electron diffraction (SAED) patterns show bright spots alongside diffuse rings, verifying the coexistence of long-range ordered crystalline and short-range ordered amorphous phases (**Fig. S5**). The observed interplanar spacing of 0.26 nm corresponds to the (101) plane of IrO_2 , confirming the crystalline nature of the nanoparticles (Fig. 1e). Energy-dispersive X-ray spectroscopy (EDS) line scans indicated a homogeneous distribution of Ir and O throughout the cotton-like matrix (Fig. 1f, **Fig. S8**), while inductively coupled plasma (ICP) analysis determined an Ir content of 33%, further defining the chemical composition of the composite.

The surface chemical states of DAC- IrO_2 were examined using X-ray photoelectron spectroscopy (XPS). Compared to synthesized IrO_2 and commercial IrO_2 (Com- IrO_2), the Ir 4f peaks of DAC- IrO_2 shift to lower binding energy (Fig. 1g), while the O 1s spectrum revealed a higher proportion of surface oxygen species commonly assigned to adsorbed or defect-associated oxygen, which are commonly associated with enhanced catalytic activity (**Fig. S10**). N_2 physisorption measurements further revealed that DAC- IrO_2 possesses a Brunauer–Emmett–Teller (BET) specific surface area of $212.9 \text{ m}^2 \text{ g}^{-1}$, substantially higher than that of Com- IrO_2 ($49.0 \text{ m}^2 \text{ g}^{-1}$) and synthesized IrO_2 ($41.1 \text{ m}^2 \text{ g}^{-1}$) (**Fig. S11**). These results indicate a highly porous structure with a well-developed mesoporous network and open three-dimensional pore architecture (Fig. 1a), facilitating rapid mass transport and efficient oxygen release under high current density conditions.

To probe the local atomic structure and electronic properties, X-ray absorption fine structure (XAFS) spectroscopy was employed (Fig. 1h–i). The XANES spectra show that the L_3 absorption edge of Ir in DAC- IrO_2 shifts to lower energy relative to IrO_2 , consistent with a lower average oxidation state and a modified local coordination and covalency²⁸. Fourier-transform EXAFS analysis reveals increased disorder in the Ir–O shell ($\sim 1.6 \text{ \AA}$) and attenuated intensity in the Ir–Ir/Ir–O–Ir shell ($\sim 2.2 \text{ \AA}$), confirming

the coexistence of a short-range ordered amorphous matrix with embedded crystalline nanoparticles (**Fig. S13**). These structural features generate abundant interfacial defects and strain, providing numerous active sites for the adsorption and conversion of OER intermediates. The k-space EXAFS oscillations of DAC-IrO₂ are significantly damped relative to crystalline IrO₂ and metallic Ir foil, highlighting the high degree of local structural disorder.

Understanding the mechanism

Electrochemical measurements in a conventional three-electrode configuration (**Fig. S14–S16**) confirm the superior acidic OER performance of DAC-IrO₂ relative to commercial IrO₂. DAC-IrO₂ requires an overpotential of only 289 mV to reach 10 mA cm⁻² and exhibits a reduced Tafel slope of 52.4 mV dec⁻¹, indicating enhanced reaction kinetics. The larger C_{dl} value and lower charge-transfer resistance further suggest an increased number of accessible active sites and accelerated interfacial electron transfer. Moreover, the near-Nernstian pH-dependent potential shift suggests a proton-coupled electron-transfer process following an Ir-site adsorbate evolution pathway. The catalyst also shows remarkable operational stability for over 1700 h at 50 mA cm⁻², demonstrating its robustness under acidic OER conditions.

To gain insight into the reaction mechanisms underlying its high performance, *in-situ* ATR-IR and Raman spectroscopy were conducted. ATR-IR measurements revealed the progressive formation of oxyhydroxide-related oxygenated intermediates under OER conditions, indicating that the reaction proceeds via the adsorbate evolution mechanism (AEM)²³ (Fig. 2a). In situ Raman spectra collected under actual PEMWE operation show that the B_{2g} and A_{1g} modes of crystalline IrO₂ evolve differently for IrO₂ and DAC-IrO₂ (Fig. 2b, c). In DAC-IrO₂, the A_{1g} feature reversibly attenuates as the cell voltage increases and recovers when the potential is released, indicating reversible formation of a thin, disordered IrO_x(OH)_y working-state layer rather than permanent bulk amorphization. The amorphous matrix therefore acts as a dynamic confinement framework: it permits surface activation of the crystalline domains while suppressing irreversible coarsening and dissolution^{24, 29, 30}. This interpretation is consistent with recent operando studies showing that potential-dependent Ir and O redox states must be correlated to distinguish reactive oxygen species from persistent high-valence metal states.

To further elucidate the origin of the superior OER performance of DAC-IrO₂, density functional theory (DFT) calculations were carried out. As shown in Fig. 2d, the OER on DAC-IrO₂ proceeds through the adsorbate evolution mechanism (AEM), which is consistent with the *in-situ* ATR-IR results discussed above, where oxygenated surface intermediates were detected under operating conditions. The corresponding free-energy diagram in Fig. 2e identifies the *O to *OOH conversion as the potential-determining step for both catalysts. Notably, the free-energy requirement for this step is reduced from 1.83 eV on IrO₂ to 1.72 eV on DAC-IrO₂, indicating that the formation of the *OOH intermediate is energetically more favorable on DAC-IrO₂. This result agrees well with the experimentally observed lower anode overpotential and faster reaction kinetics of DAC-IrO₂ in the PEMWE device.

To gain further insight into the electronic origin of this enhancement, the projected density of states (PDOS) of Ir 5d and O 2p orbitals was analyzed. As shown in Fig. 2f-g, the Ir 5d band center of DAC-IrO₂ is slightly shifted to a lower energy relative to that of IrO₂ (− 2.464 vs. −2.361 eV), while the O 2p band center shifts upward toward the Fermi level (− 4.091 vs. −4.391 eV). As a consequence, the energy separation between the Ir 5d and O 2p band centers is decreased from 2.030 eV for IrO₂ to 1.628 eV for DAC-IrO₂, as summarized in Fig. 2h. The reduced d–p band-center gap indicates strengthened Ir–O electronic coupling in DAC-IrO₂, which is beneficial for interfacial charge redistribution and for optimizing the adsorption and conversion of oxygenated intermediates during OER¹⁵(Fig. 2i). This electronic-structure modulation is in good agreement with the experimentally observed lower Ir 4f binding energy, the negatively shifted Ir L₃-edge, and the reduced charge-transfer resistance of DAC-IrO₂, collectively confirming that the crystalline–amorphous hybrid structure promotes OER kinetics by facilitating the key *OOH formation step and enhancing Ir–O orbital interaction⁸.

PEMWE device performance

The integrated performance evaluation, conducted in a practical PEMWE configuration equipped with a Nafion 212 membrane, demonstrates the outstanding activity and durability of the DAC-IrO₂ catalyst (Fig. 3a). Membrane cross-section images showed uniform distribution of the anode catalyst on the Nafion membrane surface, with no noticeable cracks or pores, ensuring good contact between the porous transport layer (PTL) and anode catalyst layer (CL), preventing electrochemical ‘dead zones’^{31–33}(Fig. 3b). To achieve optimal electrocatalytic performance in the PEMWE, a systematic optimization study was conducted on the anode catalyst layer, focusing on the ionomer content and catalyst loading. As summarized in **Fig. S19**, both parameters were carefully evaluated to maximize cell efficiency. The optimal configuration was identified as an ionomer content of 13.0 wt% and an Ir loading of 0.2 mg_{Ir} cm^{−2}, under which the PEMWE exhibited the highest overall performance. To optimize the synthesis and explore the structure-activity relationship, a series of catalysts were prepared by systematically varying the molar feed ratio of IrCl₃ to PAHs. The corresponding PEMWE polarization curves are presented in **Fig. S21**, revealing a pronounced dependence of the electrochemical performance on the precursor stoichiometry.

When applied as an anodic catalyst in a membrane electrode assembly (MEA), the DAC-IrO₂-based MEA achieves a high current density of 6.4 A cm^{−2} at 2 V with only 0.2 mg_{Ir} cm^{−2} of iridium loading, significantly outperforming a Com-IrO₂-based catalyst with the same noble metal loading (4.0 A cm^{−2}) (Fig. 3c). Consequently, this low-loading DAC-IrO₂ anode surpasses the U.S. Department of Energy (DOE) 2026 technology target (PGM loading target of 0.5 mg cm^{−2}) in iridium dosage, electrical efficiency, and overall, MEA performance. To evaluate the noble metal utilization efficiency of the catalysts, we further compared the mass activity normalized to the iridium loading (**Fig. S22**). DAC-IrO₂ exhibits exceptional mass activity, reaching 32.4 A mg_{Ir}^{−1} at 2.0 V, which is significantly higher than that of the IrO₂ (20.0 A

$\text{cm}_{\text{Ir}}^{-1}$) and Com-IrO₂. This superior mass activity indicates that a much lower Ir loading is required for DAC-IrO₂ to achieve the same current density compared to Com-IrO₂ catalysts. This not only reduces the manufacturing cost of the membrane electrode assembly but also provides a critical material foundation for developing high-performance, low-iridium-loading PEMWE electrolyzers.

Electrochemical Impedance Spectroscopy (EIS) tests in PEMWE showed that DAC-IrO₂ exhibits extremely low charge transfer resistance (R_{ct}) at industrial current densities ($0.1\text{--}1.0\text{ A cm}^{-2}$), especially at high current densities (0.5 and 1.0 A cm^{-2}), while maintaining excellent reaction kinetics (**Fig. S23**). This property is primarily attributed to the unique composite structure of DAC-IrO₂, which forms a high density of active sites and optimized interfacial properties, significantly facilitating charge transfer during the oxygen evolution reaction. Additionally, analysis of the EIS high-frequency region showed that the ohmic resistance of DAC-IrO₂-based MEAs ($R_{\text{s}} = 88.7\text{ m}\Omega\text{ cm}^2$) was significantly lower than that of Com-IrO₂ ($R_{\text{s}} = 99.5\text{ m}\Omega\text{ cm}^2$), due to its three-dimensional porous structure and high specific surface area, which enhance proton and electron conduction, and improve interfacial contact³. Thus, the performance advantage of DAC-IrO₂ arises from the synergistic effect of reduced ohmic loss and enhanced reaction kinetics (**Fig. S23**).

To identify the origin of the cell-level performance advantage, the measured voltage was decomposed into kinetic, transport-associated, and ohmic contributions (Fig. 3d, e). The DAC-IrO₂ cell exhibits a consistently lower kinetic contribution throughout the polarization range, in agreement with the facilitated *OOH formation and reduced interfacial charge-transfer resistance. Its transport-associated contribution increases gradually with current density and is slightly larger than that of the IrO₂ cell at comparable current densities. This behavior does not necessarily indicate inferior mass transport; rather, the substantially accelerated OER kinetics of DAC-IrO₂ generate higher local oxygen fluxes and water-transport demands, shifting the dominant limitation from interfacial reaction kinetics towards gas–liquid transport at high current densities. The porous cotton-like network nevertheless prevents a sharp increase in transport polarization and enables stable operation up to 6.4 A cm^{-2} . Meanwhile, the ohmic contribution of the DAC-IrO₂ cell increases approximately linearly with current density but remains lower than that of the IrO₂ cell, indicating improved electronic and ionic continuity and reduced interfacial contact losses within the low-Ir catalyst layer. Consequently, the overall cell-voltage advantage of DAC-IrO₂ arises predominantly from the marked suppression of kinetic and ohmic losses, while the modest transport-associated penalty reflects a shift in the performance bottleneck under accelerated oxygen evolution rather than a deterioration of the porous electrode architecture. This multicomponent loss analysis highlights the importance of simultaneously maintaining rapid reaction kinetics, continuous conductive networks, and effective water and oxygen transport in low-Ir PEMWE anodes^{32, 34}.

Stability evaluation of PEMWE devices using DAC-IrO₂ catalysts at ampere-level current densities showed remarkable performance. At 80°C and 3 A cm^{-2} , the PEMWE operated stably for over 3400 hours with negligible decay (Fig. 3f). The catalytic performance and long-term stability of the DAC-IrO₂

MEA compare favorably with reported Ir-based catalysts under comparable conditions. Overall, the exceptional MEA performance and long-term durability position the DAC-IrO₂ anode as a competitive low-Ir anode candidate for PEMWE. To evaluate the structural stability of the MEA during electrolysis, cross-sectional and surface morphological analyses of the catalyst-coated membrane (CCM) were conducted before and after testing. As shown in the cross-sectional SEM images (**Fig. S24-25**), the thickness of the anode catalyst layer (DAC-IrO₂) experienced only a minor reduction from approximately 3.7 μm to 3.2 μm after 3400 hours of operation, indicating that the structural integrity of the catalyst layer was largely maintained without significant detachment or severe corrosion. Furthermore, a comparison of the surface SEM images of the catalyst layer (**Fig. S25a-b**) reveals that the macroscopic morphology and particle distribution remained largely unchanged after the stability test. The characteristic structure of DAC-IrO₂ was well-preserved, and no obvious delamination or damage was observed at the interface between the catalyst layer and the Nafion 115 membrane. These morphological results demonstrate that the DAC-IrO₂ catalyst and the resulting catalyst layer possess excellent physical and chemical stability under the harsh anode conditions of strong acidity and high potential. This remarkable structural robustness is a key factor contributing to the long-term durability observed in the PEMWE tests. Moreover, the structural stability of the catalyst is essential for its practical application. TEM characterization of the samples after the stability test revealed that the DAC-IrO₂ catalyst retained its original morphology after the rigorous electrochemical test, further demonstrating its excellent structural stability and durability (Fig. 3g). Figure 3g presents the HAADF-STEM image and the corresponding Ir elemental mapping of the sample after the reaction. The results indicate that Ir is uniformly distributed on cotton-like matrix without obvious aggregation or spatial redistribution, demonstrating its high dispersion and stability during the reaction process.

An internal voltage-sensing method was used for accurate, *in-situ* measurement of the internal potential of PEMWE under operating conditions. This is achieved by integrating ultra-thin gold ribbon sensing wires at key interfaces within the MEA (Fig. 4a). This unique hierarchical configuration allows the breakdown of total voltage drop into specific components, such as anode overpotential, cathode overpotential, and membrane resistance, enabling independent, quantitative analysis of electrode kinetics and ohmic losses. Test results consistently showed that the DAC-IrO₂ catalyst significantly outperformed Com-IrO₂ across all tested current densities (Fig. 4b). At 0.2 A cm⁻², the overpotential of DAC-IrO₂ was approximately 30 mV lower than that of Com-IrO₂. As the current density increased to 1.0 A cm⁻², the gap between the two widened, with the advantage expanding to over 70 mV, directly reflecting the much faster OER kinetics. For anode electrode resistance ($R_{a,el}$) at low current densities (0.1 A cm⁻²), the resistance of DAC-IrO₂ is about 450 m Ω cm² lower than that of Com-IrO₂ (Fig. 4c). As current density increases, the resistance of DAC-IrO₂ rapidly decreases to about 700 m Ω cm² at 1.0 A cm⁻², while Com-IrO₂'s resistance decreases more slowly, remaining as high as 1000 m Ω cm² at the same current density. This suggests that DAC-IrO₂ exhibits lower electrode-related resistance and a more favorable current-density response.

To test the stability of DAC-IrO₂ in PEMWE under fluctuating conditions, we performed both accelerated stress tests (AST) and stage current tests. Cyclic mechanical stress and transient potential shifts accelerate catalyst dissolution, causing dynamic degradation to occur faster than steady-state degradation. In the AST tests at 0.1, 2.0, and 6.0 A cm⁻², after 8000 cycles (90 s per cycle) (Fig. 4d, **Fig. S26a**), the catalytic performance of the DAC-IrO₂ MEA remained largely unaffected, while the Com-IrO₂ catalyst experienced significant performance decay (Fig. 4e, **Fig. S26b**). The increasing diameter of the Com-IrO₂ Nyquist semicircle indicates a rise in R_{ct} , likely associated with Ir dissolution, particle agglomeration and progressive loss of interfacial contact with the porous transport layer. (Fig. 4f, **Fig. S26c**). In contrast, the DAC-IrO₂ catalyst exhibits excellent durability, with its EIS spectrum nearly coinciding with the initial state after 8000 cycles, demonstrating that its charge transfer impedance and electrochemically active surface area are well maintained. This phenomenon is attributed to the unique 'crystalline nanoparticles embedded in an amorphous cotton-like matrix' composite structure of DAC-IrO₂. The amorphous phase serves as a solid anchor, effectively preventing migration and coarsening of the crystalline phase during cycling, while buffering the volumetric strain caused by electrochemical cycling. This maintains the structural integrity of the electrodes and the stability of the catalytic interface. The stability of the catalytic interface and the integrity of the electrode structure are thus preserved, providing great potential for use in high-performance, long-life PEMWE.

By applying different constant current densities (1.0, 3.0, 5.0, 6.0 A cm⁻²) at each stage, the stability of the catalyst in PEMWE can be investigated under staged current profiles that emulate fluctuations in renewable-power input (e.g., wind and solar power) (Fig. 4g). The PEMWE voltage remained stable at each constant current stage, with minimal fluctuations. This suggests that the DAC-IrO₂ catalyst maintained its activity throughout the test, with core components of the electrolysis cell (membrane, catalyst layer, transport layer) remaining intact. The catalyst remained stable at a high current density of 6.0 A cm⁻². This demonstrates its excellent mass transfer capability (efficient transport of water and oxygen) and electron/proton conductivity, preventing voltage spikes at high loads caused by reactant shortages or product blockage. When the current density is switched from a high (6.0 A cm⁻²) to a low point (1.0 A cm⁻²), the voltage rapidly returns to approximately its previous level. This indicates that all performance changes are fully reversible, with no irreversible damage or aging caused by high-load operation. Over 2400 hours of testing, the voltage profile remained stable, providing strong evidence of the DAC-IrO₂ catalyst's long-term operational stability under dynamic current loading. It can operate efficiently at high current densities (> 3.0 A cm⁻²), while withstanding frequent current fluctuations and exhibiting extremely low performance degradation over 2400 hours of testing. This is attributed to its unique crystalline-amorphous composite structure, which effectively inhibits active site deactivation under long-term high-potential operation, providing a solid foundation for the development of the next generation of high-performance, long-life PEMWE.

Conclusions

In summary, we have developed a crystalline–amorphous hybrid IrO₂ catalyst that overcomes the conventional activity–stability trade-off in acidic oxygen evolution catalysis. By embedding conductive crystalline IrO₂ nanodomains within a porous amorphous iridium oxide framework, the catalyst simultaneously achieves rapid charge transport, abundant active-site exposure, and exceptional structural robustness under PEMWE operating conditions. The hybrid catalyst delivers industrial-level activity at ultralow Ir loading while maintaining outstanding long-term stability under both steady-state and dynamic operating conditions. Operando spectroscopy and theoretical calculations reveal that the crystalline–amorphous interface promotes reversible surface reconstruction, strengthens Ir–O electronic coupling, and stabilizes catalytically active oxyhydroxide species during oxygen evolution. This work establishes dynamically stabilized crystalline–amorphous interfaces as an effective strategy for designing next-generation electrocatalysts for sustainable hydrogen production.

Declarations

Conflict of Interest

The authors declare no competing financial interest.

Author contributions

B.P., Y.L., and Y.H. contributed equally to this work. X.T., W.S., and Z.K. supervised the project. B.P., Y.L., Y.H., and X.T. conceived the idea and designed the experiments. B.P., Y.L., and Y.H. performed the experiments and analyzed the data. H.C., S.Z., J.L., Y.Y., P.R., and X.S. participated in the material characterization, electrochemical measurements, and data analysis. B.P., Y.L., and Y.H. prepared the figures and organized the experimental results. B.P. and X.T. wrote the manuscript with input from W.S. and Z.K. All authors discussed the results and commented on the manuscript.

Acknowledgments

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Data availability

All data supporting the findings of this study are available within the paper and its supplementary information files or from the corresponding authors upon request.

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Figures

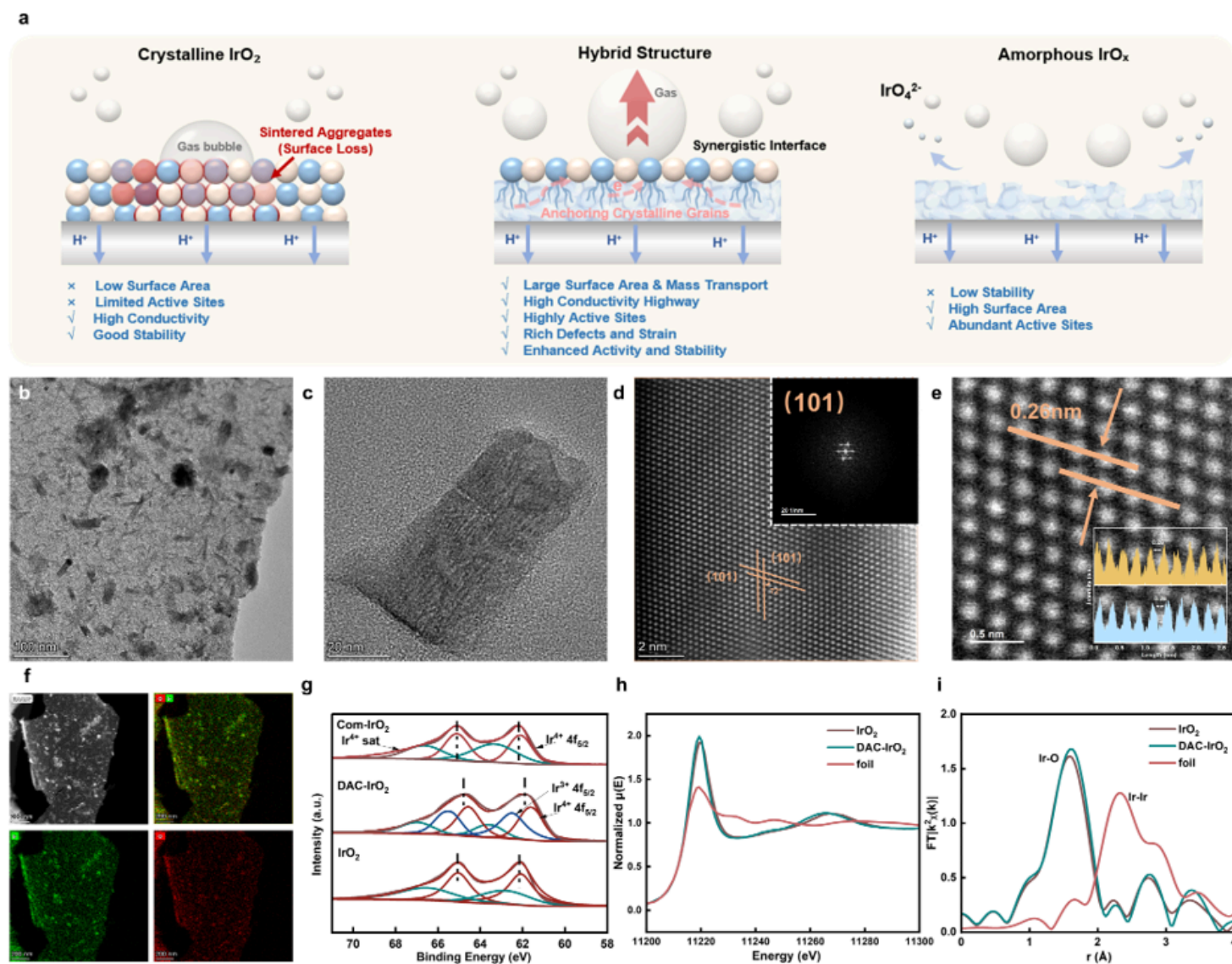


Figure 1

Dynamic amorphous confinement and interfacial electronic reconstruction in DAC-IrO₂ (a) Schematic comparison of crystalline IrO₂, DAC-IrO₂ and amorphous IrO_x. (b-c) TEM images of DAC-IrO₂. (d) Atomic-resolution HAADF-STEM image of DAC-IrO₂. (e) HRTEM image with the measured spacing of DAC-IrO₂. (f) HAADF-STEM images and corresponding EDX mapping. (g) The high-resolution Ir 4f spectra. (h) Ir L₃-edge XANES spectra of Ir foil and DAC-IrO₂, IrO₂. (i) Fourier transform of K³-weighted Ir L₃ edge EXAFS spectra of Ir foil and DAC-IrO₂, IrO₂.

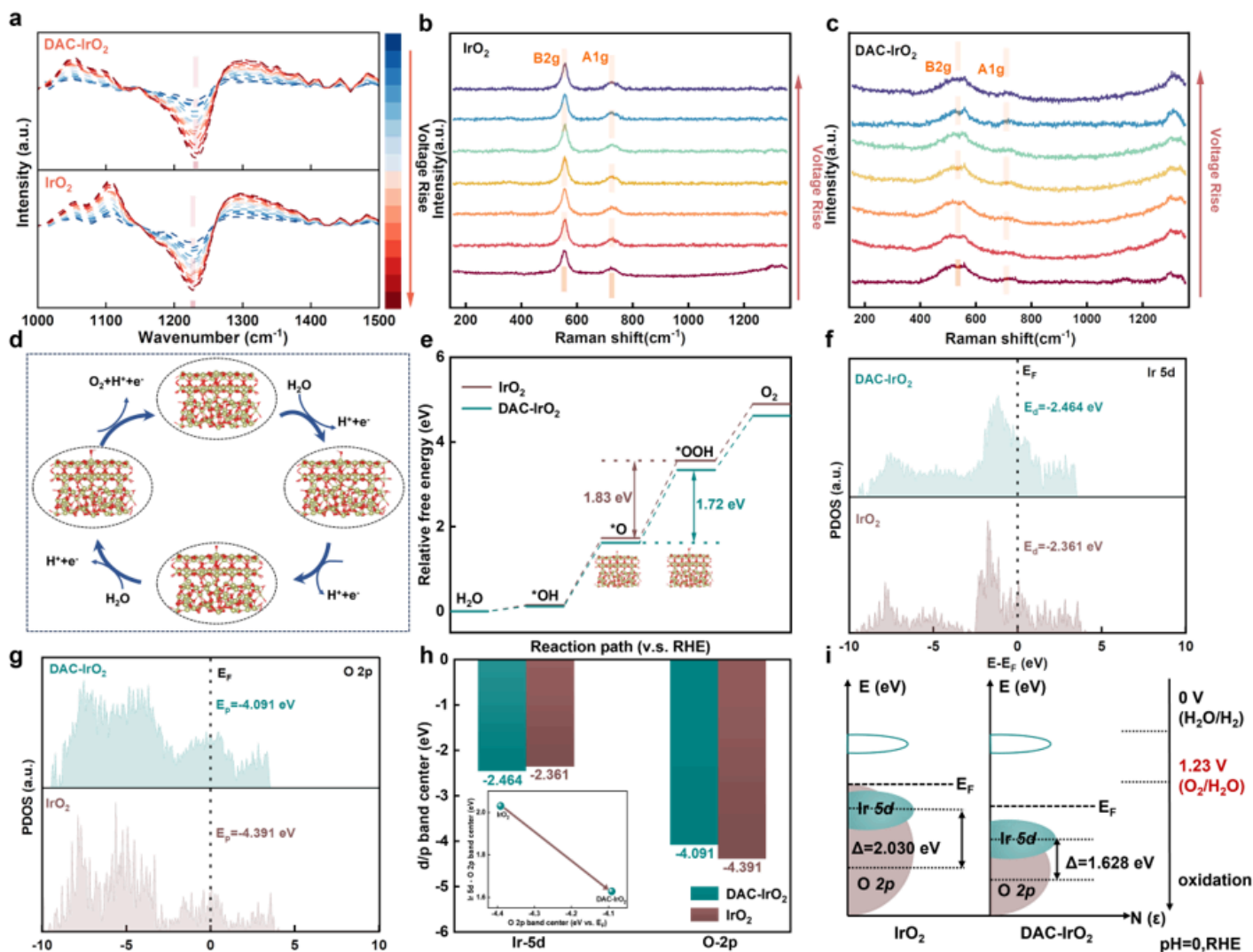


Figure 2

Reversible working-state reconstruction and electronic origin of enhanced OER on DAC-IrO₂. (a) In situ ATR-IR spectra recorded during the multi-potential steps of DAC-IrO₂ and IrO₂. In situ Raman spectra of (b) IrO₂ and (c) DAC-IrO₂ at different polarization potentials under actual PEMWE operating conditions. DFT investigation of the OER mechanism and electronic structure of DAC-IrO₂ and IrO₂. (d) Schematic illustration of the AEM on DAC-IrO₂ during OER. (e) Calculated free-energy diagrams of the OER pathway on IrO₂ and DAC-IrO₂, showing that the *O to *OOH conversion is the potential-determining step. (f,g) Projected density of states (PDOS) of Ir 5d and O 2p orbitals for DAC-IrO₂ and IrO₂, respectively. (h) Comparison of the Ir 5d and O 2p band centers. (i) Schematic illustration of the reduced Ir 5d-O 2p band-center separation in DAC-IrO₂ relative to IrO₂.

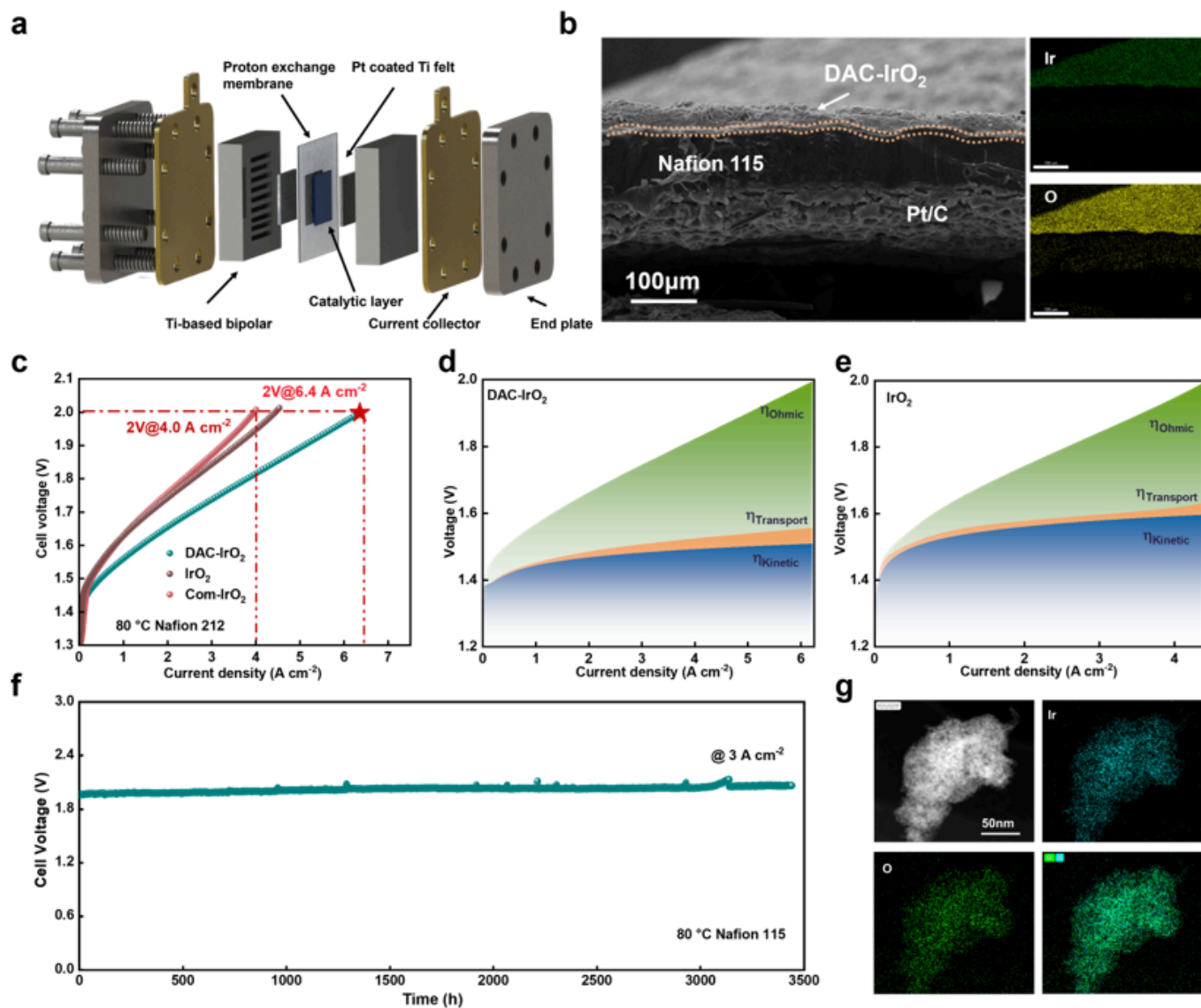


Figure 3

High-current-density PEMWE and resolved voltage losses at ultralow Ir loading. (a) Schematic diagram of PEMWE. (b) SEM image of a cross section of CCM. (c) Polarization curves of PEMWE at 80 °C. Breakdown of ohmic, transport, and kinetic losses for (d) DAC-IrO₂ and (e) IrO₂ cell. (f) Long-term stability of the PEMWE using DAC-IrO₂ operated at 3 A cm⁻². (g) HAADF-STEM image and corresponding elemental maps of the post-test anode catalyst.

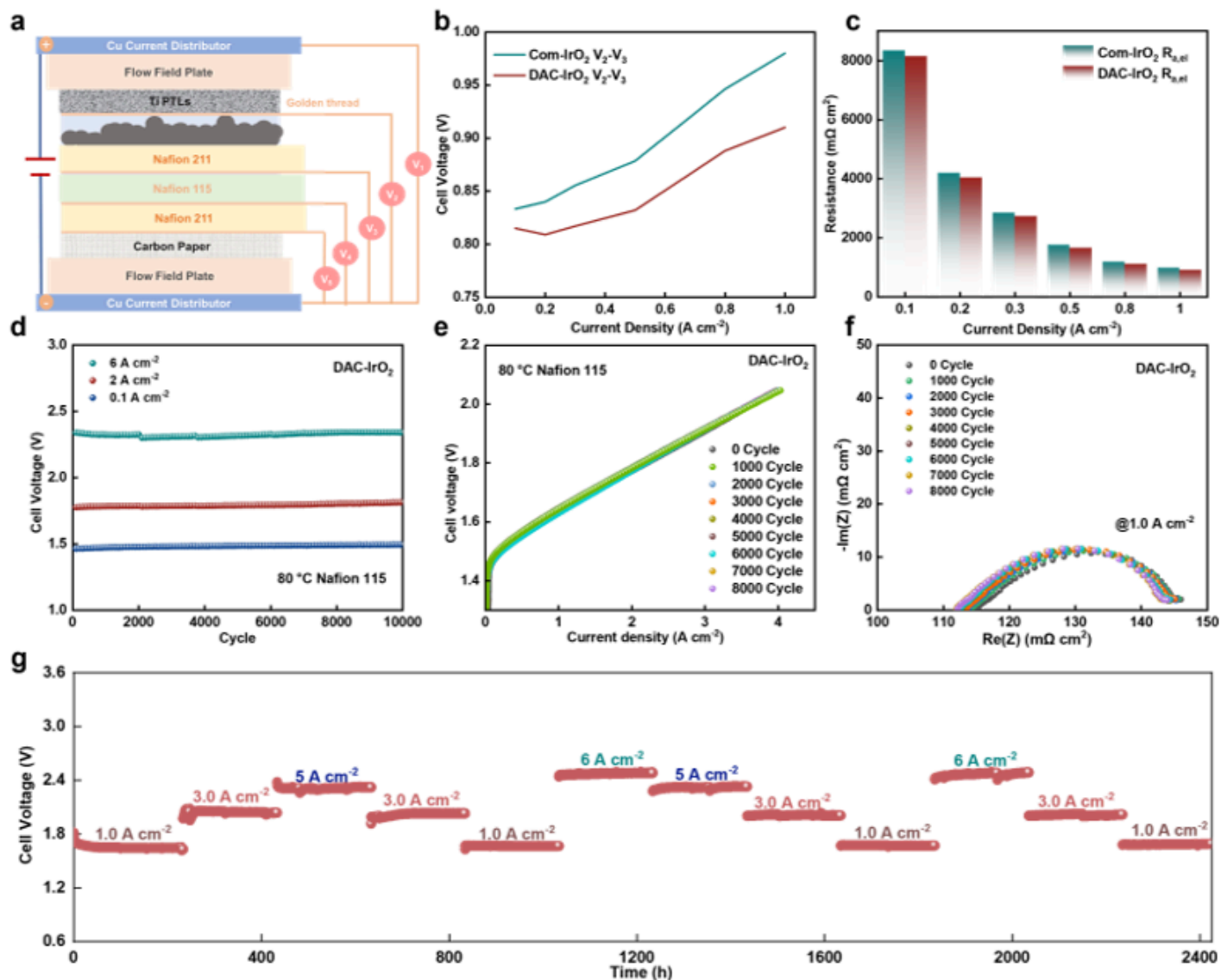


Figure 4

Electrode-resolved voltage diagnosis and dynamic-load durability of DAC-IrO₂ PEMWE. (a) Schematic of the hierarchy configuration for the internal sensing technique. (b) Total overpotential of anode electrode. (c) Anode-related resistance ($R_{a,el}$) of Com-IrO₂ and DAC-IrO₂ as a function of current density. (d) Cell-voltage response of DAC-IrO₂ during accelerated stress testing at different current densities. Polarization curves of (e) DAC-IrO₂. Nyquist plots of (f) DAC-IrO₂. (g) Stage current test plot of DAC-IrO₂ catalyst in PEMWE for long term operation.

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