

Surface topology engineering of cathode catalyst layers for bubble management in cathode-fed PEM water electrolysis

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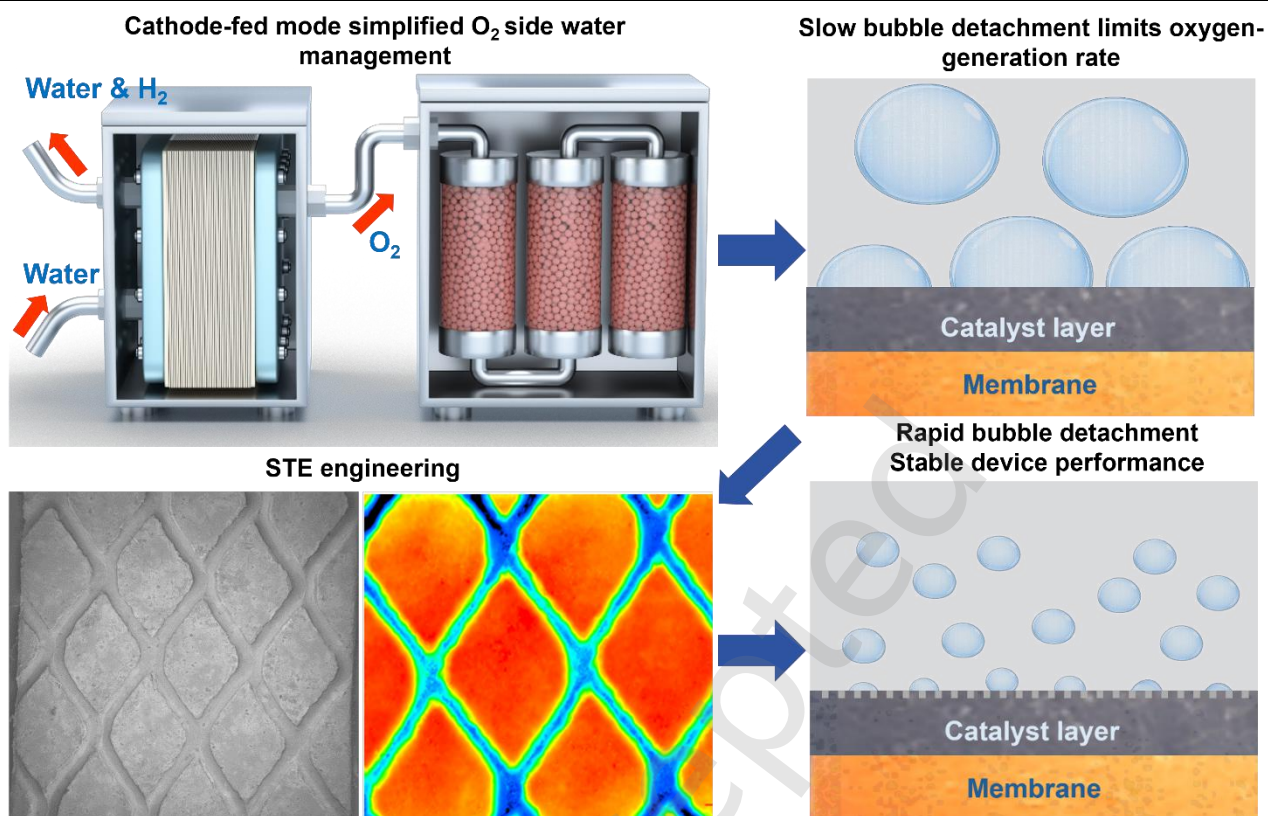
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Surface topology engineering (STE) patterns the cathode catalyst layer to regulate the gas-liquid-solid interface in cathode-fed PEM water electrolysis, promoting earlier H_2 bubble departure while preserving water-access pathways. This manufacturable MEA-level strategy mitigates cathode-side water limitation and enables stable, lightweight oxygen generation without additional gas-liquid management hardware.

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ABSTRACT: Proton exchange membrane water electrolysis (PEMWE) is a promising technology for regenerative oxygen generation in long-duration space missions and lunar-resource-utilization systems, where mass, volume, reliability, and auxiliary fluid-management requirements are severely constrained. Cathode-fed PEMWE offers a simplified architecture for such oxygen generation systems by supplying water from the hydrogen side and transporting it across the membrane to the oxygen-evolving anode, thereby reducing liquid-water discharge and downstream separation on the oxygen side. However, this configuration shifts the key water-management bottleneck to the cathode-membrane electrode assembly (MEA) interface, where retained H₂ bubbles can block water access, disrupt liquid continuity, and restrict transmembrane water supply. Here, we develop a cathode surface topology engineering (STE) strategy to regulate gas-liquid-solid contact within the MEA interface. The patterned cathode topology weakens bubble contact-line pinning, limits lateral bubble spreading, and promotes earlier H₂ bubble departure while preserving water-access pathways. Bubble-release analysis, transparent-cell visualization, electrochemical stability testing, and impedance measurements reveal that effective STE requires an appropriate morphology window rather than maximized roughness or deformation. Experimental validation under terrestrial gravity conditions (1g) shows that a moderately developed topology enables stable cathode-fed operation, reaching 1.813 V at 1.0 A cm⁻² after 250 min and an average degradation rate of 0.21 mV h⁻¹ during 200 h operation at 0.5 A cm⁻². This work establishes cathode-interface topology as a template-assisted MEA-level strategy for passive two-phase management in lightweight PEMWE oxygen generation systems.

KEYWORDS: cathode-fed proton exchange membrane water electrolysis; membrane electrode assembly; surface topology engineering; water starvation; two-phase transport

Introduction

Proton exchange membrane water electrolysis (PEMWE) is an attractive electrochemical technology for compact hydrogen and oxygen generation because it enables high-current-density operation using pure water and a solid polymer electrolyte.[1-19] For closed-loop life-support systems in spacecraft, lunar bases, and in-situ resource utilization scenarios, water electrolysis is more than a gas-generation process; it provides a route to couple water resources, solar electricity, breathable oxygen, and storable chemical energy within a single regenerative architecture.[20-32] Compared with terrestrial hydrogen-production systems, however, space-oriented oxygen generation systems are subject to much stricter constraints on mass, volume, reliability, power consumption, and auxiliary fluid-management complexity. Therefore, reducing

balance-of-plant burden while maintaining stable electrolysis operation is a central challenge for the development of lightweight PEMWE-based oxygen generation systems.[20-32]

As shown in Fig. 1a, conventional PEMWE is typically operated in an anode-fed configuration, in which liquid water is supplied to the oxygen-evolving electrode and the outlet stream contains O₂ together with liquid water and water vapor. In terrestrial systems, this outlet stream can be managed using gas-liquid separators, dryers, and water-recirculation loops; however, for space-constrained platforms, these auxiliary components introduce substantial penalties in mass, volume, and failure risk.[23, 26, 33, 34] Cathode-fed PEMWE offers an appealing alternative system architecture: water is supplied from the hydrogen-evolving side and transported through the proton exchange

membrane to the anode for oxygen evolution. By decoupling oxygen production from bulk liquid-water discharge, cathode-fed operation can potentially simplify the oxygen-side balance of plant and reduce the demand for downstream drying, separation, and water recovery.[35-38] Nevertheless, this system-level simplification shifts the dominant water-management challenge to the cathode-membrane electrode assembly (MEA) interface. Because the anode relies on water transported across the membrane from the cathode side, the cathode interface becomes the critical gateway for sustaining water delivery to the oxygen-evolving electrode. During operation, H₂ bubbles generated at the cathode continuously alter the local gas-liquid-solid

contact state. Previous studies have shown that retained or coalesced bubbles can shield electrochemically active surfaces, hinder the access of reactant water, increase gas-phase blockage, and aggravate two-phase transport limitations in membrane water electrolyzers. [39-47] In cathode-fed PEMWE, persistent bubble coverage at the cathode-MEA interface is therefore expected to reduce the spatial and temporal continuity of liquid-water contact. Once cathode-side water contact becomes insufficient, transmembrane water delivery to the anode may become restricted, increasing the likelihood of anode-side water starvation, transport losses, and progressive voltage rise.

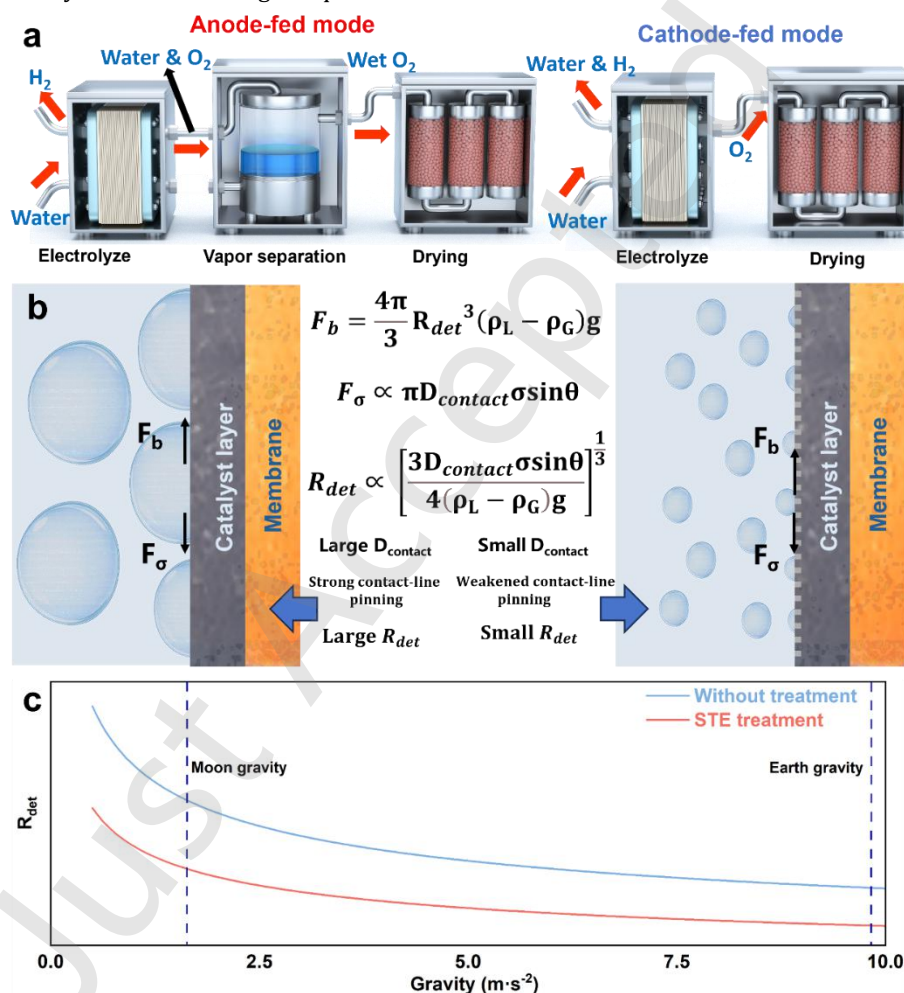


Figure 1. Advantages and challenges of cathode-fed operation for space exploration. (a) Differences in system complexity between anode-fed and cathode-fed PEMWE under low-gravity conditions (e.g., on the Moon). (b) Schematic force-balance rationale for bubble detachment. (c) General force-balance-based dependence of the critical detachment radius, R_{det} , on gravity and interfacial retention. All experimental validation in this work was conducted under terrestrial gravity conditions (1g); the reduced-gravity description is used as the application background and mechanistic motivation.

This issue is expected to become more pronounced in reduced-gravity environments. Under terrestrial conditions, buoyancy assists bubble detachment from electrode surfaces, whereas in reduced-gravity or low-buoyancy scenarios, the weakened detachment force can allow bubbles to remain attached for longer periods and cover larger portions of the reactive interface. Therefore, cathode-fed PEMWE for space-

oriented oxygen generation requires more than highly active catalysts or low-resistance MEAs; it requires an interfacial strategy that can passively promote bubble departure, preserve liquid-phase connectivity, and sustain transmembrane water supply without introducing additional gas-liquid-management hardware. Existing two-phase management approaches commonly rely on flow-field

optimization, porous transport layer design, external circulation, gas-liquid separation, or additional wettability-control layers. Although these strategies can improve water and gas transport, they often increase system complexity, introduce additional fabrication steps, or compromise compatibility with compact MEA-based devices. In contrast, directly encoding bubble-management functionality into the MEA interface represents a more integrated design concept. From this perspective, the cathode catalyst layer should not be regarded only as an electrochemical reaction site, but also as a structured two-phase transport interface where surface geometry, contact-line dynamics, and gas-liquid-solid interactions can be engineered to regulate bubble residence and water access.

Here, we propose a cathode surface topology engineering (STE) strategy for cathode-fed PEMWE, aiming to integrate bubble management and water-contact regulation directly into the cathode-side MEA interface. Unlike conventional approaches that rely on external gas-liquid separation, circulation, or additional water-management components, STE reshapes the local gas-liquid-solid contact state through a patterned cathode interface, thereby enabling the growth, spreading, and departure of H_2 bubbles to be actively regulated by interfacial geometry. The patterned topology can disrupt continuous bubble-coverage domains, shorten the effective bubble-solid contact length scale, weaken contact-line pinning, and provide more stable interfacial pathways for liquid access and transmembrane water replenishment. As a result, cathodic H_2 bubbles can detach from the catalyst-layer surface at smaller sizes, reducing local dehydration and interfacial blockage caused by long-lived bubble retention and thereby mitigating voltage growth associated with anode-side water starvation in cathode-fed PEMWE. In this work, wettability and bubble-release measurements, transparent-cell visualization, bubble-size statistics, quasi-static detachment simulations, electrochemical stability tests, electrochemical impedance spectroscopy, and surface topography characterization are combined to reveal the relationship among patterned cathode topology, bubble-removal behavior, water-contact stability, and voltage evolution. By regulating the topological length scale and surface morphology window, we show that a moderately patterned cathode interface can balance bubble detachment, liquid contact, and MEA structural integrity, and that the performance improvement does not simply originate from increased surface roughness. This study establishes cathode-interface topology as an effective MEA-level passive bubble-management strategy for cathode-fed PEMWE and provides a new interfacial design principle for two-phase transport regulation in simplified and lightweight oxygen generation systems.

Design Rationale for Cathode Surface Patterning

Following the interfacial design concept introduced above, the central challenge in cathode-fed PEMWE can be further described as a two-phase transport problem at the cathode interface: while H_2 is continuously generated, liquid water must remain in stable contact with the membrane electrode assembly (MEA) and be transported through the proton exchange membrane to the anode. In this configuration, the cathode interface functions simultaneously as a gas-evolution surface and as the water-supply gateway for the oxygen-evolving electrode. On a flat or weakly structured cathode catalyst layer, newly generated H_2 bubbles tend to spread over the local surface, grow, and coalesce, forming large gas-covered domains. These retained bubbles occupy regions where liquid water should contact the MEA, reduce the effective water-MEA contact area, and locally interrupt liquid-phase pathways. Once such gas coverage persists, cathode-side water delivery becomes neither continuous nor uniform, which restricts transmembrane water supply and ultimately contributes to anode-side water starvation and voltage rise. Therefore, stable operation of cathode-fed PEMWE depends not only on electrochemical reaction kinetics, but also on whether the cathode interface can preserve water access during continuous gas evolution.

From this perspective, cathode surface patterning is designed not to simply increase surface roughness, but to reconstruct the interfacial geometry and thereby alter how bubbles attach to and depart from the electrode surface. Bubble departure is governed by the competition between forces that promote detachment and interfacial adhesion that resists detachment. On an unpatterned surface, the bubble base can form a relatively large continuous contact domain, and the three-phase contact line can be pinned by microscopic heterogeneities, defects, or pores in the catalyst layer. As the bubble grows, this extended contact line remains anchored, so the bubble must reach a larger size before the detachment force becomes sufficient to overcome interfacial adhesion. In contrast, a patterned cathode interface can divide the originally continuous bubble-solid contact region into smaller local contact domains, shorten the effective contact length, disrupt long-range contact-line pinning, and limit lateral bubble spreading along the surface. As a result, bubbles can become unstable and detach at smaller sizes, reducing long residence times and suppressing the formation of large coalesced bubbles.

Surface patterning can also help preserve more stable pathways for liquid water. On a flat surface, spreading and coalescence of bubbles can form a continuous gas-blocked region, forcing water to rewet the interface mainly from the bubble perimeter. On a patterned surface, the geometric relief and periodic interfacial heterogeneity can interrupt

the continuity of gas coverage, making it more difficult for bubbles to establish large-area stable attachment while retaining local liquid passages between neighboring bubbles. In this way, the cathode interface can maintain a higher fraction of water-contacting area during H_2 evolution, providing more continuous entry points for transmembrane water replenishment. This is the basic rationale for using surface topology engineering (STE) in cathode-fed PEMWE: interfacial geometry, rather than additional external gas-liquid-management components, is used to couple bubble removal with water-contact maintenance within the MEA.

Fig. 1a summarizes the system-level rationale, while Fig. 1b,c illustrate the bubble-detachment design rationale. Compared with anode-fed PEMWE, cathode-fed operation can reduce the need for oxygen-side gas-liquid separation, water recirculation, and oxygen drying, thereby simplifying the oxygen generation system. [23, 26, 33, 34] However, this simplification requires the cathode interface to continuously serve as the water-supply entrance while H_2 is being generated. [35-38] Consequently, the growth, coalescence, and detachment of cathodic H_2 bubbles become key interfacial events that determine the stability of transmembrane water supply. [39-42] To qualitatively describe how bubble detachment is jointly controlled by interfacial geometry and gravity, a simplified force-balance analysis can be used (Fig. 1b). [48-50] For a bubble attached to a solid surface, buoyancy can be approximated as Eq. (1):

$$F_b = \frac{4\pi}{3} R^3 (\rho_L - \rho_G) g \quad (1)$$

where R is the equivalent bubble radius, ρ_L and ρ_G are the densities of the liquid and gas phases, respectively, and g is the gravitational acceleration. The force-balance treatments reported by Demirkır et al., Wang et al., and Zeng et al. indicate that the surface-tension-related retention force is jointly governed by the characteristic size of the bubble-solid contact region, the gas-liquid surface tension, and the bubble-side contact angle. [48-50] These treatments can be summarized by the following scaling relationship as Eq. (2):

$$F_\sigma \propto \pi D_{\text{contact}} \sigma \sin \theta \quad (2)$$

where D_{contact} is the effective contact diameter of the bubble on the solid surface, σ is the surface tension, and θ is the effective bubble-side contact angle at the gas-liquid-solid contact line at or near the detachment condition. This angle is physically different from the water contact angle measured using a sessile water droplet. The water contact angle characterizes liquid-water wetting and accessibility to the cathode surface, whereas θ , together with D_{contact} and contact-line hysteresis, governs the capillary retention of the bubble. When the detachment force balances the retention force, the critical detachment radius can be approximated as Eq. (3):

$$R_{\text{det}} \propto \left[\frac{3D_{\text{contact}} \sigma \sin \theta}{4(\rho_L - \rho_G) g} \right]^{\frac{1}{3}} \quad (3)$$

This relationship indicates that the critical bubble-detachment size is jointly controlled by gravity, the effective bubble-solid contact diameter, and the bubble-side contact-line state. In reduced-gravity or low-buoyancy environments, bubbles must generally grow to larger sizes before detaching, thereby intensifying gas coverage and local water-access loss at the cathode interface (Fig. 1c). Under a given gravity condition, however, decreasing D_{contact} directly reduces the capillary retention force and lowers the characteristic bubble size required for detachment. Therefore, the principal geometric role of STE is to divide the originally continuous bubble-solid contact domain into smaller localized regions, thereby reducing the effective D_{contact} and weakening long-range contact-line pinning, rather than relying on a change in contact angle alone.

It should be noted that all experimental validation in this work was conducted under terrestrial gravity conditions (1g) and cathode-fed operation. Therefore, the reduced-gravity discussion should be understood as the application background and mechanistic extrapolation for cathode-interface design, rather than as direct validation under a space environment. The central question addressed in this study is whether an appropriately patterned cathode topology can reduce the retained size and residence time of H_2 bubbles, improve cathode-side water contact, and thereby suppress voltage growth associated with insufficient water supply in cathode-fed PEMWE. The following wettability measurements, bubble-release tests, transparent-cell visualization, and electrochemical stability results are organized around this design rationale.

Formation of Cathode-Side STE Topology and Bubble-Detachment Mechanism

To verify whether cathode surface patterning can effectively regulate bubble behavior, a 0.8×1.6 mm diamond-shaped topology was first selected as a model STE structure to construct a cathode interface with a defined characteristic length scale. Fig. S1a,b show the STE process and the diamond-patterned template, while the Scanning Electron Microscope (SEM) images in Fig. S1c, 1d confirm that the pattern was clearly transferred onto the cathode side of the MEA, forming periodic diamond-shaped topological units on the catalyst layer. It should be emphasized that STE does not introduce random surface roughening, but rather a spatially continuous surface pattern with well-defined geometric boundaries. For cathode-fed PEMWE, the significance of this structure lies in its ability to divide the originally continuous bubble-solid contact interface into multiple localized contact domains, thereby altering the spreading, pinning, and detachment behavior of bubbles on the catalyst-layer surface. In other words, the patterned topology imposes geometric constraints on bubble growth while preserving potential pathways for liquid water to re-enter the cathode

interface, which provides the structural basis for accelerated bubble release and sustained water contact. To distinguish the effect of the patterned topology from that of the thermal-mechanical treatment alone, an additional control MEA was hot-pressed under the same temperature, pressure, and duration as the STE-treated MEA but without the Ti-mesh template. The hot-pressing control retained a relatively smooth surface and exhibited water wettability and static bubble-release behavior comparable to those of the untreated MEA (Fig. S2). Moreover, the two samples showed similar voltage evolution under cathode-fed operation at 0.5 and 1.0 A cm⁻² (Fig. S3), indicating that hot pressing alone did not produce an appreciable performance improvement.

Fig. 2a, 2b first show that STE modifies the liquid-water wetting state of the cathode surface. The water contact angle decreases from approximately 150° for the untreated MEA to approximately 122° after STE treatment, indicating improved liquid-water accessibility to the cathode catalyst layer. This water contact angle characterizes liquid wetting and is not the interfacial angle used directly in the bubble force-balance relationship. Fig. 2c, 2d provide complementary information on the static bubble-surface contact state. On the untreated MEA, the static apparent bubble release angle is approximately 44°, and the bubble spreads extensively along the surface, indicating a relatively large bubble-solid contact region and strong contact-line pinning. After STE treatment, the apparent bubble release angle increases to approximately 167.5°, while the bubble adopts a more spherical shape with a much smaller contact region. The opposite changes in the water contact angle and the bubble release angle are therefore not contradictory, because the two measurements describe different interfacial configurations. The water contact angle reflects liquid-water access, whereas the static bubble release angle serves only as a comparative indicator of bubble spreading, contact-line pinning, and relative detachment tendency. Because it was measured under static conditions, the bubble release angle is not used as a quantitative predictor of the dynamic bubble-detachment size during electrolysis.

To further confirm whether these interfacial effects translate into differences in bubble behavior during operation, the cathodic hydrogen-evolution process was visualized using a transparent single cell. Fig. 2e, 2f present bubble evolution on the untreated and STE-treated MEAs within a 1 s time window at 0.5 A cm⁻². The corresponding bubble-evolution videos are provided as Videos S1 and S2. Because both MEAs were operated at the same current density, the H₂ generation rate was mainly determined by the applied current; therefore, the observed differences in bubble size and residence state primarily reflect changes in interfacial detachment ability rather than differences in gas-generation rate. On the untreated MEA, numerous large

bubbles highlighted by red circles can be observed. These bubbles remain attached over the short observation period, continue to grow, and frequently coalesce, indicating that bubbles must reach relatively large sizes before overcoming interfacial adhesion and detaching from the surface. In contrast, large bubbles are markedly reduced on the STE-treated MEA; the bubbles are more discrete and show more frequent renewal and release. The bubble-size statistics in Fig. 2g and Table S1 further quantify this change. The distributions were obtained from time-resolved analysis of one 33.3 s video comprising 500 consecutive frames and one fixed field of view for each MEA. Detected bubbles were linked across consecutive frames according to their center positions and size similarity; tracks lasting fewer than five frames were excluded, and each retained trajectory was counted once using its maximum diameter for size classification. After tracking and cross-frame deduplication, 415 and 303 bubble trajectories were retained for the untreated and STE-treated MEAs, respectively. The complete image-preprocessing and tracking procedure is provided in the Supporting Information. Among the tracked bubbles with diameters over 1.0 mm, 39.0% had diameters ≥1.50 mm for the untreated MEA, whereas only 6.3% fell within this range for the STE-treated MEA. This demonstrates that STE does not merely change the number of bubbles, but markedly reduces the retained bubble size on the cathode surface, allowing bubbles to detach before forming extensive coverage and severe coalescence. For cathode-fed PEMWE, such small-size and short-residence bubble behavior is beneficial for reducing gas shielding, maintaining more continuous water contact with the MEA, and lowering the likelihood of restricted transmembrane water supply. These operating-condition observations provide more direct evidence that STE reduces retained bubble size and promotes earlier bubble departure. Their trend is qualitatively consistent with that indicated by the static bubble release angle. To further assess the water-delivery limitation inherent to cathode-fed operation, polarization curves under anode-fed and cathode-fed modes were compared at the same water flow rate (Fig. S4). The markedly poorer high-current performance under cathode-fed operation is consistent with an additional limitation in membrane-mediated water supply to the anode, highlighting the importance of maintaining cathode-side water access through bubble management. Taken together, the anode-fed/cathode-fed comparison identifies the additional water-delivery limitation inherent to cathode-fed operation, while the wettability measurements, time-resolved bubble statistics, and EIS results indicate how STE acts on this limitation. By reducing persistent cathode-side gas coverage, STE helps preserve continuous liquid contact with the MEA and lowers the low-frequency transport-related resistance.

These combined observations support the interpretation that improved cathode-side bubble removal stabilizes

membrane-mediated water supply to the anode and suppresses the associated voltage rise.

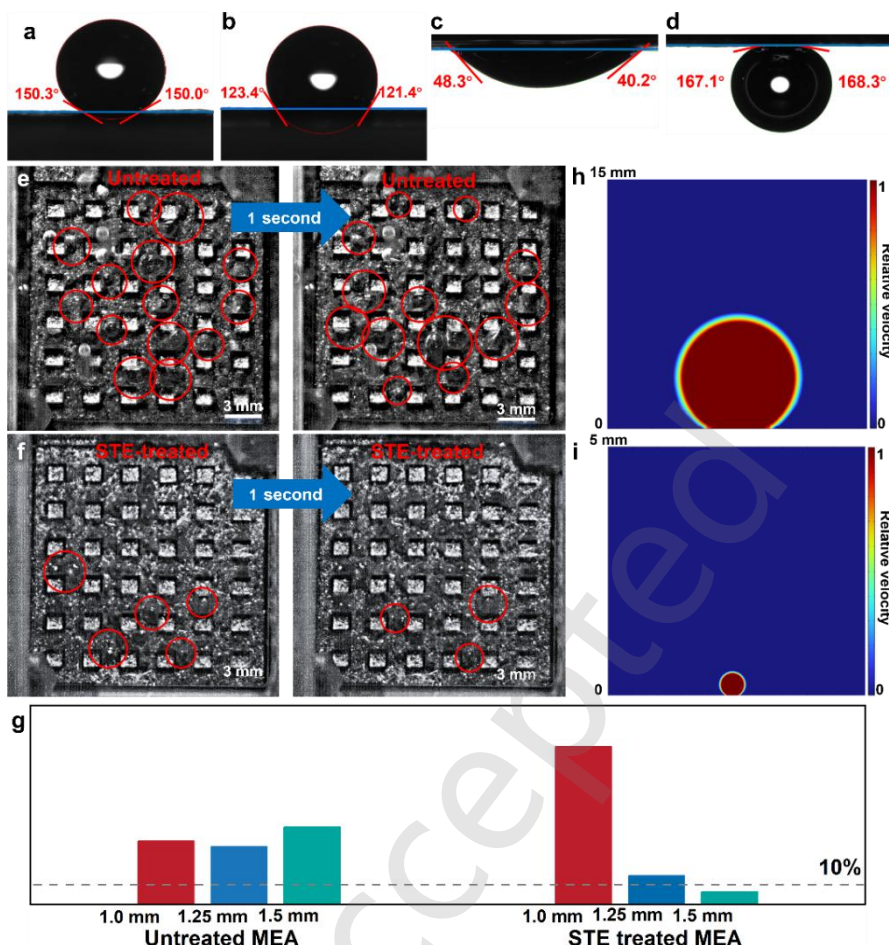


Figure 2. Bubble evolution and detachment behavior on the MEA surface before and after STE treatment. (a, b) Water contact angle measurements before (a) and after STE treatment (b). (c, d) Static apparent bubble release-angle measurements before (c) and after STE treatment (d). (e, f) Images within a 1 s time window during cathode-fed PEMWE, showing bubble growth/coalescence and detachment on the untreated MEA (e) and the STE-treated MEA (f). Red circles highlight larger bubbles captured in the field of view. (g) Bubble-size distribution ($D > 1.0$ mm) obtained from time-resolved tracking of 500 consecutive frames for each MEA during cathode-fed operation. (h, i) Quasi-static bubble-detachment simulations for the untreated (h) and STE-treated (i) cathode surfaces, illustrating the reduced critical detachment size after STE treatment.

Quasi-static bubble-detachment simulations further support this mechanistic interpretation from a force-balance perspective. The static apparent bubble angles measured in Fig. 2c, 2d were used as comparative interfacial inputs. The simulation results show that the untreated surface requires an equivalent bubble diameter greater than 7.00 mm to reach the detachment condition, whereas the STE-treated surface can achieve detachment at an equivalent diameter of approximately 0.50 mm (Fig. 2h, 2i). The key simulation parameters and assumptions are summarized in Table S2. Because the model does not explicitly reproduce the dynamically evolving contact angle, continuous gas generation, flow-field shear, bubble coalescence, or local structural nonuniformity during electrolysis, the calculated diameters should be interpreted as comparative trend indicators rather than exact predictions of the operating detachment diameter. Together with the transparent-cell observations, the simulations support the conclusion that STE reduces the effective bubble-solid contact region, weakens contact-line pinning, and lowers the characteristic

retained bubble size. We next examined how the coupled variation in in-plane pattern periodicity and out-of-plane deformation affects cathode-fed operating stability.

Optimization of Coupled STE Pattern under Cathode-fed Operation

After confirming that the patterned cathode interface can promote H_2 bubble detachment, three Ti meshes with nominal pore sizes of 0.8×1.6 , 1.0×2.0 , and 1.5×3.0 mm were compared under identical hot-pressing conditions to screen a suitable STE configuration. It should be noted that changing the Ti-mesh pore size simultaneously alters the in-plane periodicity of the transferred pattern and the resulting out-of-plane deformation amplitude of the MEA surface. Therefore, the present comparison does not independently isolate the effects of pattern scale and deformation amplitude, but evaluates their coupled influence on cathode-fed operating stability. The purpose of this comparison was

to identify a mild STE configuration that could introduce an effective interfacial texture without causing excessive deformation or structural damage to the MEA.

For cathode-fed PEMWE, surface patterning is not intended simply to increase surface roughness. Rather, the transferred topology is expected to divide bubble-solid contact regions, restrict lateral bubble spreading, and preserve pathways for liquid water to re-enter the catalyst-layer surface. A relatively sparse pattern may provide insufficient geometric boundaries to interrupt extended bubble-covered regions, whereas excessive out-of-plane deformation may introduce local transport nonuniformity, altered interfacial contact, or structural perturbations. The present experiment should therefore be regarded as a practical screening of coupled STE pattern parameters rather than as an orthogonal decoupling of the in-plane and out-of-plane structural factors.

Fig. 3a–i show that the three patterns differ not only in aperture size, but also in the resulting three-dimensional interfacial morphology. The 0.8×1.6 mm sample forms a relatively continuous and regular diamond-shaped topology, with clear local height variation but without excessive surface deformation; its maximum height, S_z , is $135.6 \mu\text{m}$. The 1.0×2.0 mm sample also shows a well-defined pattern, but the laser microscope (LM) images reveal stronger height variation, with S_z increasing to $188.3 \mu\text{m}$, indicating deeper local deformation of the MEA surface at this scale. In contrast, the 1.5×3.0 mm sample exhibits a much lower pattern density, a sparser surface topology, and weaker height variation, with an S_z value of only $82.8 \mu\text{m}$. These results demonstrate that the nominal Ti-mesh pore size cannot be treated as an independently varied in-plane

parameter, because it is accompanied by simultaneous changes in boundary density and out-of-plane deformation. Accordingly, the resulting bubble-management behavior and electrochemical response cannot be assigned exclusively to either the nominal pore size or S_z alone. This also suggests that the objective of STE optimization is not to maximize surface height difference, but to establish a topological window that can effectively interrupt bubble coverage while preserving liquid contact and interfacial integrity.

Fig. 3j, 3k summarize the starting and final voltages for the three topologies under cathode-fed operation. At 0.5 A cm^{-2} (Fig. 3j), the 0.8×1.6 mm topology maintains a low final voltage of 1.628 V after 1000 min with a total voltage increase of 17 mV , whereas the 1.0×2.0 mm topology exhibits a higher final voltage of 1.747 V and a larger increase of 29 mV . The 1.5×3.0 mm topology shows negligible voltage growth but remains at a slightly higher final voltage than the 0.8×1.6 mm case. At 1.0 A cm^{-2} (Fig. 3k), the 0.8×1.6 mm topology reaches 1.836 V after 250 min with a 69 mV increase, whereas the 1.0×2.0 mm topology shows a larger rise of 115 mV and the 1.5×3.0 mm topology reaches 2.043 V despite a smaller voltage increase of 17 mV . These trends indicate that the electrochemical response cannot be evaluated by voltage growth alone. The 1.5×3.0 mm pattern may appear stable because its voltage changes slowly, but its high absolute voltage suggests an initially unfavorable two-phase transport state; conversely, the 1.0×2.0 mm pattern combines high voltage with pronounced voltage growth. The 0.8×1.6 mm topology therefore provides the most balanced response, with relatively low voltage and moderate accumulated growth.

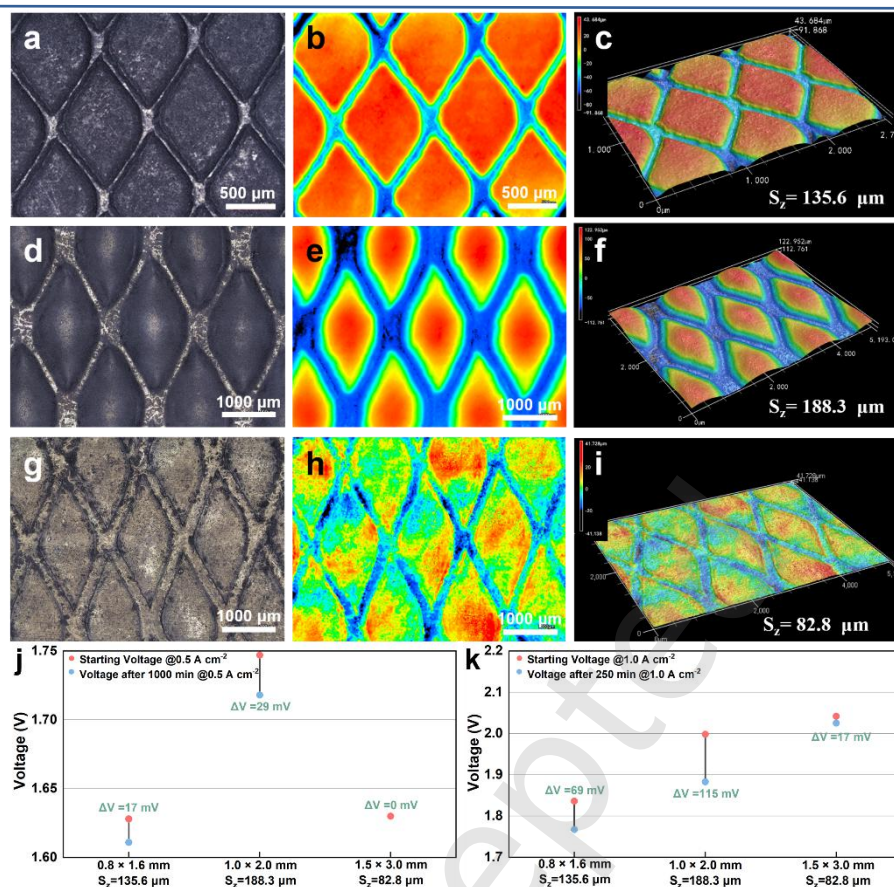


Figure 3. Surface morphology and electrochemical stability of MEAs treated with Ti meshes of different pore sizes.

SEM and LM images of MEAs treated using a Ti mesh with a pore size of 0.8×1.6 mm (a-c), 1.0×2.0 mm (d-f), and 1.5×3.0 mm (g-i), respectively, revealing distinct surface morphologies under identical conditions. (j, k) Starting and final voltages of MEAs treated with different mesh sizes under cathode-fed operation at 0.5 A cm^{-2} for 1000 min (j) and 1.0 A cm^{-2} for 250 min (k); ΔV values are annotated. All reported data were obtained without iR correction.

Overall, Fig. 3 and Figs. S5 and S6 reveal a nonmonotonic performance response to the coupled variation in in-plane pattern periodicity, boundary density, and out-of-plane deformation, rather than an independently resolved pore-size effect. A sparse transferred pattern may provide insufficient boundaries to interrupt bubble-covered regions, whereas excessive deformation may introduce additional local transport or contact nonuniformity. The 0.8×1.6 mm configuration combines a relatively high pattern-boundary density with a moderate deformation amplitude and consequently exhibits the most balanced electrochemical response among the tested samples. The comparison was therefore used to screen coupled STE pattern parameters, and the 0.8×1.6 mm topology was selected as the representative configuration for the subsequent processing-window study.

Processing-Window-Dependent Topology-Performance Relationship

After selecting the 0.8×1.6 mm pattern as the representative configuration from the coupled-pattern comparison, the next question is how the deformation amplitude and surface development of the same topological

motif determine two-phase transport stability in cathode-fed PEMWE. For STE, an effective patterned interface must provide sufficiently defined geometric boundaries to divide bubble-solid contact regions and weaken contact-line pinning; however, this does not mean that larger deformation or higher roughness is necessarily beneficial. If the topology is too weak, bubbles can still spread and coalesce on the catalyst-layer surface without encountering effective detachment boundaries. If the surface is overdeveloped, excessively deep or complex local features may introduce new gas-retention sites, nonuniform liquid access, or perturbations to local MEA contact. Therefore, temperature and pressure should be viewed not simply as processing parameters, but as variables that tune the geometric constraint imposed by the cathode interface.

Fig. 4a-f, Fig. S7-S8 and Table S3 show that, under the same 0.8×1.6 mm pattern length scale, different processing windows produced distinctly different three-dimensional topologies. At 60°C , increasing the pressure from 5 to 15 MPa increased S_z from 125.6 to 138.0 μm , while S_a (arithmetic mean height) and S_{dr} (developed interfacial area ratio) remained nearly unchanged at approximately 22 μm and 0.146-0.148, respectively, indicating a controlled

increase in topological depth. In contrast, at 80 °C, the MEA surface became more deformable and more developed, with S_a increasing to approximately 25 μm and S_z reaching 151.7 μm . In particular, the S_{dr} value sharply increased to 0.282 at 80 °C-15 MPa, indicating a substantial increase in real

surface area and local morphological complexity. These results show that the purpose of STE is not to create the roughest or deepest surface, but to establish a moderate topological window that can constrain bubbles without introducing excessive interfacial heterogeneity.

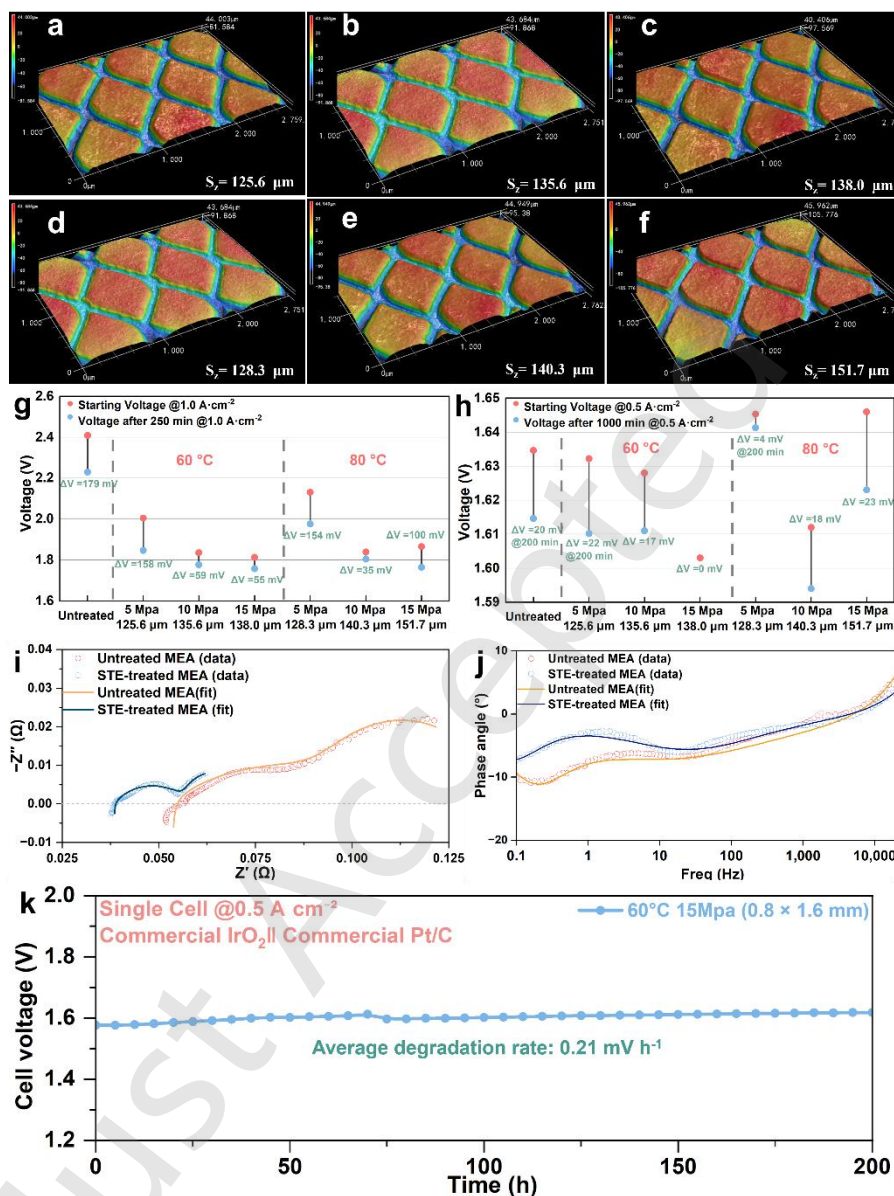


Figure 4. Surface topography and performance of membrane electrodes treated under various temperature and pressure conditions. (a-c) LM images of MEAs treated at 60 °C under 5, 10, and 15 MPa, respectively, showing variations in surface texture and height difference. (d-f) LM images of MEAs treated at 80 °C under 5, 10, and 15 MPa, respectively, illustrating the effect of higher temperature on STE depth. (g, h) Starting and final voltages, with ΔV annotations, at 1.0 A cm^{-2} for 250 min (g) and 0.5 A cm^{-2} for 1000 min (h). The first row below the x-axis gives treatment pressure, and the second row gives S_z values. (i, j) Nyquist (i) and Bode phase (j) plots of the untreated and STE-treated (60 °C, 15 MPa) MEAs under cathode-fed operation. Symbols represent the experimental data, and solid lines represent the equivalent-circuit fitting results using the L-R $-(R_1 \parallel CPE_1)-(R_{tr} \parallel Ctr)$ model. The equivalent circuit used for fitting is shown in Fig. S9. (k) Stability test of the MEA treated at 60 °C and 15 MPa in cathode-fed PEMWE at 0.5 A cm^{-2} . All reported electrochemical data were obtained without iR correction.

The electrochemical results further demonstrate that cathode-fed performance responds strongly to this topological window and does not vary monotonically with roughness or deformation depth. At 1.0 A cm^{-2} (Fig. 4g), the untreated MEA reaches 2.409 V after 250 min with a total voltage increase of 179 mV , reflecting pronounced accumulation of transport losses. Low-pressure treatments reduce the voltage relative to the untreated MEA but still show large voltage increases, reaching 2.086 V for 60°C -5 MPa and 2.127 V for 80°C -5 MPa after 250 min. When the topology enters a moderate morphology window, both the final voltage and the accumulated voltage increase are reduced. The 60°C -10 MPa, 60°C -15 MPa, and 80°C -10 MPa samples maintain low final voltages of 1.836 , 1.813 , and 1.837 V , respectively. Among them, the 60°C -15 MPa sample provides the lowest final voltage, while the 80°C -10 MPa sample shows the smallest voltage increase. At 0.5 A cm^{-2} (Fig. 4h), the 60°C -15 MPa sample maintains 1.600 V after 1000 min with negligible voltage increase, whereas the 80°C -10 MPa and 80°C -15 MPa samples increase to 1.612 and 1.645 V , respectively. The high-temperature/high-pressure condition therefore does not provide further improvement despite its larger S_z and sharply increased S_{dr} . This nonmonotonic behavior indicates that the performance enhancement induced by STE does not originate directly from increased roughness, but from the coordinated regulation of bubble detachment, liquid replenishment, and interfacial contact stability within an appropriate topological window.

Electrochemical impedance and long-term operation further support this topology-performance relationship as shown in Fig. 4i and 4j. Taking the 60°C -15 MPa sample as the representative optimized interface, the EIS spectra of the untreated and STE-treated MEAs were quantitatively fitted using an L-R $-(R_1\|CPE_1)-(R_{tr}\|C_{tr})$ equivalent circuit (Fig. S9). The equivalent circuit was selected as the minimum model capable of reproducing the high-frequency inductive response and the two distinguishable relaxation regions observed in the Nyquist and Bode plots. This selection is consistent with previous PEMWE impedance studies that separate series-ohmic, interfacial-polarization, and low-frequency mass-transport-related contributions. Garcia-Navarro et al. represented the low-frequency contribution using a finite diffusion impedance, whereas Lickert et al. employed two $R\|CPE$ relaxation branches and introduced a series inductance when required by the high-frequency response.[51, 52] The inductance L accounts for the high-frequency response of the testing leads and fixture, while R_s represents the combined ohmic contribution of the membrane, electrodes, current collectors, and cell contacts. The depressed intermediate-frequency arc was described by $R_1\|CPE_1$, because the heterogeneous porous catalyst-

layer/MEA interface exhibits a distributed, non-ideal polarization response rather than ideal capacitive behavior. The additional low-frequency relaxation was represented by $R_{tr}\|C_{tr}$ as a minimal phenomenological description of transport-related processes, including gas accumulation, liquid-water redistribution, and interfacial two-phase transport. To avoid overinterpretation of the whole-cell spectra, R_1 and R_{tr} are therefore referred to as interfacial-polarization-related and low-frequency transport-related resistances, respectively, rather than as uniquely isolated elementary kinetic parameters. As shown in Fig. 4i, 4j, and Table S4, the fitted high-frequency series resistance, R_s , decreased from 0.05238Ω for the untreated MEA to 0.03834Ω for the STE-treated MEA. The interfacial-polarization-related resistance, R_1 , decreased from 0.05368 to 0.01943Ω , while the low-frequency transport-related resistance, R_{tr} , decreased from 0.03326 to 0.01510Ω , corresponding to a reduction of 54.6%. Consequently, the total polarization resistance, $R_p = R_1 + R_{tr}$, decreased from 0.08694 to 0.03453Ω . Consistently, the measured real impedance at 0.100 Hz decreased from 0.12128 to 0.06217Ω . These results indicate that STE substantially reduces the low-frequency transport-related impedance, although reductions are also observed in the high-frequency series resistance and interfacial-polarization-related contribution. Therefore, the improved impedance response cannot be attributed solely to a change in ohmic resistance and is consistent with alleviated gas accumulation, improved liquid-water access, and enhanced cathode-side two-phase transport. During the 200-hour stability test at 0.5 A cm^{-2} , the cell voltage increased from 1.576 to 1.618 V . The overall average degradation rate was therefore calculated from the total voltage increase as 0.21 mV h^{-1} for the 60°C -15 MPa MEA. These results indicate that a moderately developed topology can maintain a relatively stable interfacial state during prolonged cathode-fed operation (Fig. 4k). Overall, this section establishes a central design conclusion: cathode surface topology has a functional morphology window. The topology must provide sufficient geometric boundaries to promote bubble detachment, while avoiding excessive surface development that could introduce new local transport heterogeneity. Accordingly, gas-liquid management in cathode-fed PEMWE can be partially shifted from external system components to the cathode-side MEA interface, enabling passive two-phase transport regulation through manufacturable surface topology.

Conclusion

In this work, a cathode-side surface topology engineering strategy was developed to address the interfacial water-access limitation and voltage growth caused by H_2 bubble retention in cathode-fed PEMWE. By introducing patterned topologies onto the cathode catalyst layer, STE regulated the

gas-liquid-solid contact state and reduced bubble anchoring and contact-line pinning on the catalyst surface. Wettability measurements, bubble-release tests, transparent-cell visualization, and quasi-static detachment simulations showed that STE enabled H₂ bubbles to detach from the cathode surface at smaller retained sizes, thereby suppressing large-bubble residence and gas coverage. Further regulation of the topology length scale and processing window revealed that the effectiveness of STE depends on an appropriate surface-morphology window rather than on simply increasing roughness or deformation depth. Under the present conditions, the MEA patterned with a 0.8 × 1.6 mm topology at 60 °C and 15 MPa exhibited low operating voltage and stable cathode-fed operation, with an average degradation rate of 0.21 mV h⁻¹ during a 200-h test at 0.5 A cm⁻². These results demonstrate that manufacturable cathode-interface topology design can improve two-phase transport stability in cathode-fed PEMWE without adding external water-management components, providing an effective interfacial strategy for lightweight oxygen generation systems. While the present study establishes the feasibility of STE at the laboratory MEA scale, the template-assisted process also provides a practical basis for future scale-up studies involving larger MEA areas, batch consistency, and additional commercial MEA platforms.

Electronic Supplementary Material: Supplementary Material (details of materials, STE treatment, measurements, characterization, additional figures, videos, and tables, additional Figs. S1-S9, Videos S1 and S2, and Tables S1-S4) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909066>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and Supplementary Material.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Qi Fu, Jichen Zhao, Liming Cheng, Xuyan Zhao: Data curation, validation, writing manuscript.

Yawen Jiang, Lin Zu, Lili Ling: project administration.

Yu Zhang, Zhenqiang Yu, Yuen Wu: Project administration, writing manuscript, experimental design.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Just Accepted

Surface topology engineering of cathode catalyst layers for bubble management in cathode-fed PEM water electrolysis

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1. Materials and Methods

1.1 Materials

Deionized (DI) water produced using a Milli-Q system (Millipore, Billerica, MA) was used in all experiments. The membrane electrode assembly (MEA) was a commercial product, with IrO₂ as the anode catalyst and 40% Pt/C as the cathode catalyst. Three types of commercial Ti mesh were used: 0.8 × 1.6 mm, 1.0 × 2.0 mm, and 1.5 × 3 mm.

1.2 STE Treatment for MEAs

All MEAs were treated using a heat press instrument. The STE treatment temperature was controlled by setting the operating temperature of the heat press, while the pressure was adjusted using the pressure gauge on the instrument.

For example, during STE treatment at 60 °C and 5 MPa, the temperature of the heat press was first set to 60 °C. The MEA was placed in the instrument with thin transparent plastic films placed on both sides and a Ti mesh positioned on the top. The use of plastic films was intended to prevent the Ti mesh from adhering to the MEA after STE treatment, which could otherwise damage the electrode surface.

The heat press was then engaged to apply pressure, and once the pressure gauge indicated 5 MPa, the pressure was maintained for 3 minutes to complete the STE process. Afterward, the pressure was released, and the MEA was removed from the instrument. STE-treated MEAs under other temperature and pressure conditions followed the same procedure, with only the temperature and pressure parameters adjusted accordingly. For the hot-pressed control MEA, the same temperature, pressure and 3 min dwell time were used, but no Ti mesh template was placed on the MEA.

1.3 Characterizations

Scanning Electron Microscope (SEM) analysis was performed on JSM-6700F SEM. Laser microscope (LM) analysis was performed on Keyence VK-X1000.

2. Measurements

(1) Transparent Single-cell PEMWE Device

It should be noted that this transparent visualization cell is a customized, non-standard configuration designed for direct imaging; therefore, the results are used to compare relative bubble-release behaviors between MEAs rather than to report absolute polarization performance.

(2) Single-Cell PEMWE Test Method

The prepared MEA was assembled into a single-cell PEMWE unit. The assembled cell was connected to a single-channel PEMWE testing platform. The test data were monitored and recorded using the accompanying control software, and all reported data were obtained without iR correction.

During the tests, the operating temperature of the PEMWE single cell was maintained at 80 °C. Deionized water was supplied to the cathode at a flow rate of 40 mL min⁻¹, with the inlet water temperature controlled at 80 °C. All water used during the experiments was deionized water.

Electrochemical impedance analysis. The EIS spectra were quantitatively fitted using an $L-R_1-(R_1 \parallel CPE_1)-(R_{tr} \parallel C_{tr})$ equivalent circuit. This circuit was selected as the simplest model that reproduced the high-frequency inductive feature, the depressed intermediate-frequency arc, and the additional low-frequency relaxation observed in both the Nyquist and Bode plots without introducing unnecessary fitting elements. L accounts for the inductive response of the testing leads and fixture, whereas R_1 represents the combined high-frequency ohmic contribution of the membrane, electrodes, current collectors, and cell contacts. The $R_1 \parallel CPE_1$ branch describes the distributed non-ideal interfacial-polarization response of the porous catalyst-layer/MEA interface. A constant-phase element was used instead of an ideal capacitor because the heterogeneous porous interface produces a distribution of local time constants. The $R_{tr} \parallel C_{tr}$ branch represents the additional low-frequency relaxation associated with gas accumulation, liquid-water redistribution, and interfacial two-phase transport. Accordingly, R_1 and R_{tr} are conservatively assigned as interfacial-polarization-related and low-frequency transport-related resistances, respectively.

The real and imaginary components of the impedance were fitted simultaneously by modulus-weighted nonlinear least-squares fitting over the frequency range of 20 kHz–0.100 Hz. The same equivalent circuit, fitting range, parameter constraints, and weighting method were applied to the untreated and STE-treated MEAs.

(3) Time-resolved bubble-size analysis

Bubble-size distributions were obtained from Videos S1 and S2 recorded under the same cathode-fed operating conditions at 0.5 A cm^{-2} . For each MEA, one video recording corresponding to one fixed field of view was analyzed. A total of 500 consecutive frames, corresponding to a continuous period of 33.3 s, were processed for each sample. The spatial calibration was determined as 32.75 pixels = 1.5 mm.

Each frame was cropped to a fixed region of interest to minimize edge artifacts and then converted to grayscale. Image preprocessing sequentially included contrast-limited adaptive histogram equalization, median filtering, Gaussian background subtraction, and absolute-difference normalization. Bubble candidates were segmented using Otsu thresholding, followed by morphological closing and opening operations. The resulting contours were filtered according to contour area, circularity, and equivalent diameter, and the bubble diameter was calculated from the minimum enclosing circle of each accepted contour.

To avoid repeatedly counting the same bubble in consecutive frames, detected bubbles were associated into temporal tracks according to their center-to-center distance and size similarity. A maximum gap of three frames was allowed during track association, and tracks persisting for fewer than five frames were excluded as transient artifacts. For each retained bubble track, the maximum detected diameter was used for classification. The tracked bubbles were divided into three size ranges: 1.00–1.25 mm, 1.25–1.50 mm, and ≥ 1.50 mm. The raw bubble counts and corresponding percentages are summarized in Table S1.

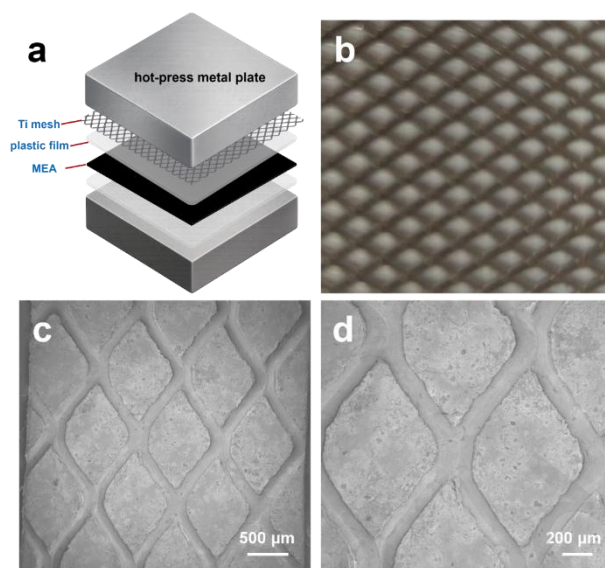


Fig. S1 (a) Schematic illustration of the STE process applied to the MEA. (b) Photograph of the 0.8×1.6 mm diamond-shaped Ti mesh used as the STE template. (c, d) SEM images of the MEA surface after STE treatment.

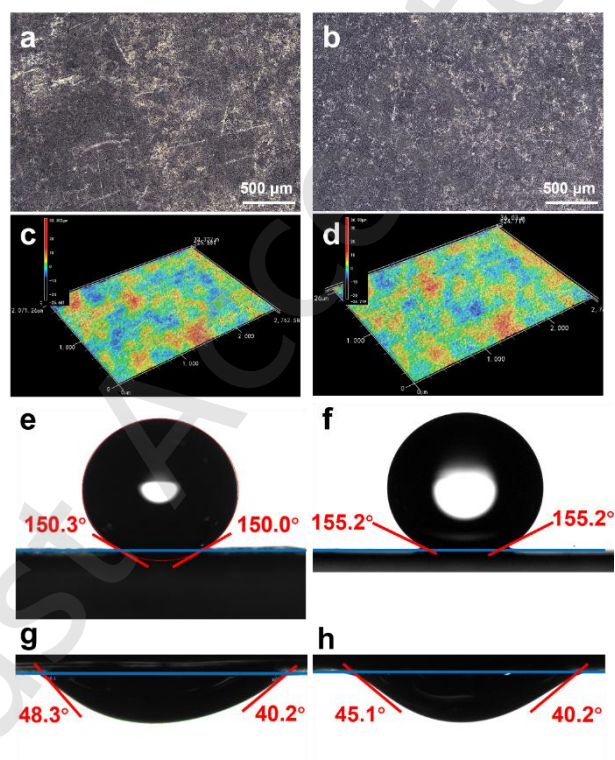


Fig. S2 (a, b) SEM images of the untreated MEA (a) and hot-pressed control MEA (b). (c, d) LM images of the untreated MEA (c) and hot-pressed control MEA (d). (e, f) Water-contact-angle measurements of untreated MEA (e) and hot-pressed control MEA (f). (g, h) Gas bubble detachment behavior of untreated MEA (g) and hot-pressed control MEA (h).

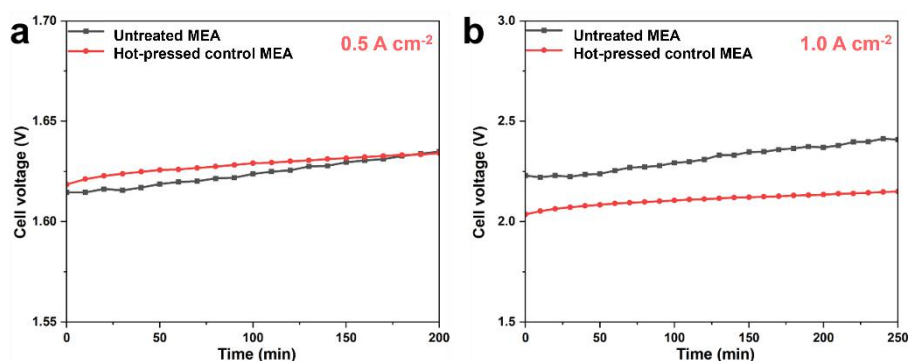


Fig. S3 Stability tests conducted at current densities of 0.5 A cm^{-2} (a) and 1.0 A cm^{-2} (b), respectively, comparing voltage evolution between the untreated MEA and hot-pressed control MEA.

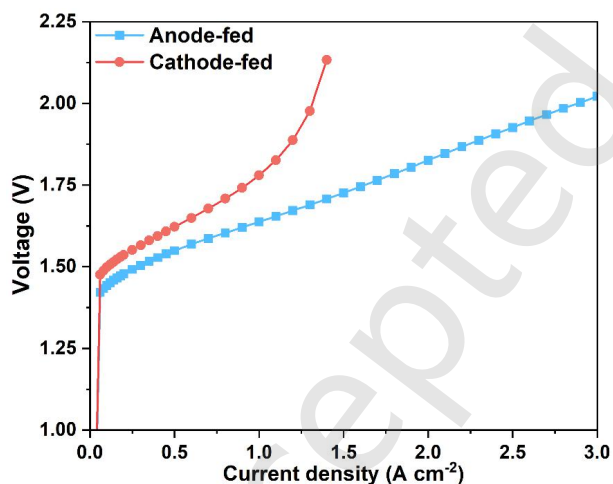


Fig. S4 Polarization curves of the PEM water electrolyzer operated in anode-fed and cathode-fed modes at an identical water flow rate of 40 mL min^{-1} .

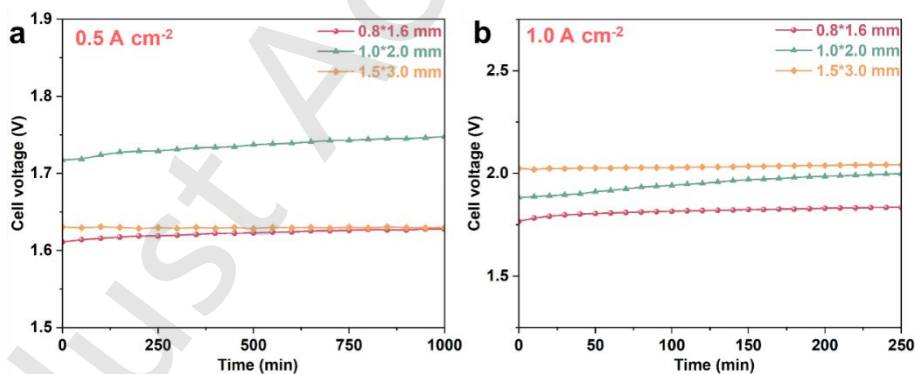


Fig. S5 (a, b) Stability tests conducted at current densities of 0.5 A cm^{-2} (a) and 1.0 A cm^{-2} (b), respectively, comparing voltage evolution among MEAs with different mesh sizes. All reported data were obtained without iR correction.

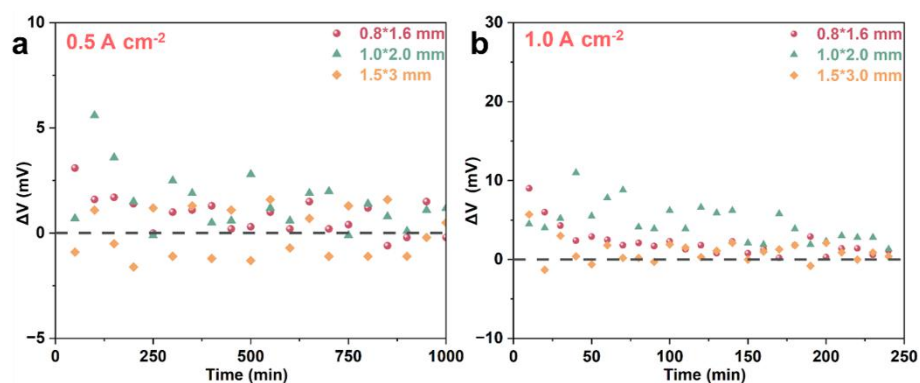


Fig. S6 (a) Incremental voltage change (ΔV) at 0.5 A cm^{-2} under cathode-fed operation, calculated in 50 min windows for STE-treated MEAs patterned with Ti meshes of different pore sizes. (b) ΔV at 1 A cm^{-2} under cathode-fed operation, calculated in 10 min windows for STE-treated MEAs patterned with Ti meshes of different pore sizes.

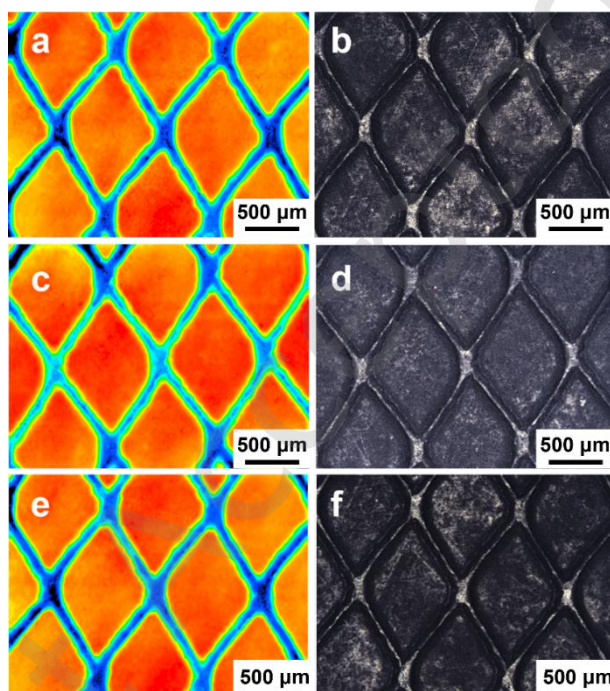


Fig. S7 Surface morphology of STE-treated MEA with Ti mesh size of 0.8×1.6 mm at 60°C . (a, b) Under 5 MPa. (c, d) Under 10 MPa. (e, f) Under 15 MPa.

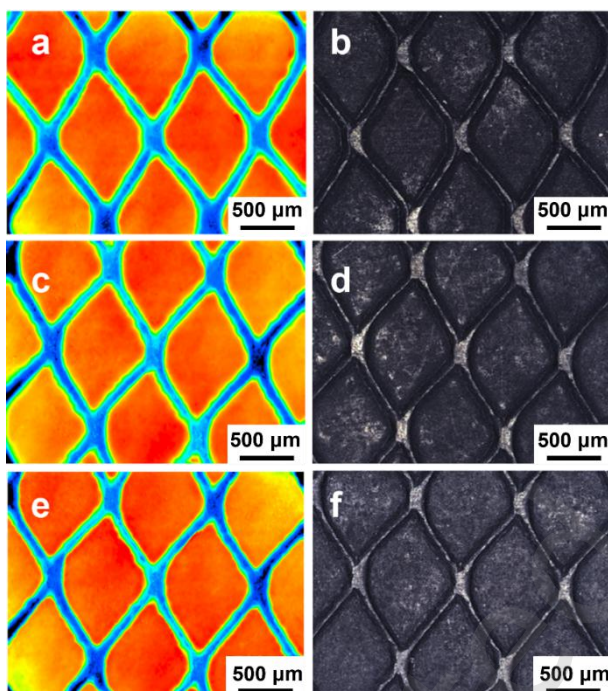


Fig. S8 Surface morphology of STE-treated MEA with Ti mesh size of 0.8×1.6 mm at 80 °C. (a, b) Under 5 MPa. (c, d) Under 10 MPa. (e, f) Under 15 MPa.

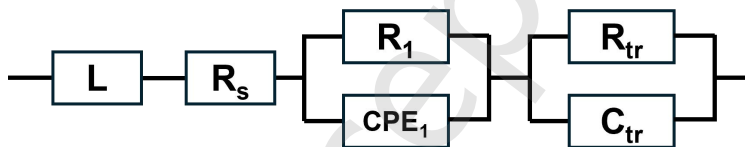


Fig. S9 Equivalent circuit used for fitting the EIS spectra

Table S1 Bubble counts and size distributions

Parameter	Untreated MEA	STE-treated MEA
1.00-1.25 mm	132 (31.8%)	240 (79.2%)
1.25-1.50 mm	121 (29.2%)	44 (14.5%)
≥ 1.50 mm	162 (39.0%)	19 (6.3%)
Total	415	303

Table S2. Parameters used in the quasi-static bubble-detachment simulation

Parameter	Setting / Value
Flow model	Two-phase flow
Gas phase	Hydrogen
Liquid phase	Water
Operating pressure	1 atm
Operating temperature	353.15 K
Gas-phase material properties	Based on the built-in Hydrogen material in COMSOL
Liquid-phase material properties	Based on the built-in Water material in COMSOL
Bubble-side contact angle for untreated MEA	44°
Bubble-side contact angle for STE-treated MEA	168°
Gravity condition	1g
Liquid density, ρ_L	Evaluated from the built-in Water material in COMSOL
Gas density, ρ_G	Evaluated from the built-in Hydrogen material in COMSOL
Gas-liquid surface tension, σ	Value specified in the COMSOL two-phase flow interface

Table S3. Surface roughness of MEAs treated by 0.8×1.6 mm Ti mesh under various temperature and pressure conditions.

Condition	S_a (μm)	S_z (μm)	S_{dr}
60 °C + 5 MPa	21.7	125.6	0.148
60 °C + 10 MPa	21.6	135.6	0.147
60 °C + 15 MPa	22.2	138.0	0.146
80 °C + 5 MPa	24.9	128.3	0.133
80 °C + 10 MPa	25.1	140.3	0.147
80 °C + 15 MPa	25.6	151.7	0.282

Table S4 Equivalent-circuit fitting parameters of the untreated and STE-treated MEAs

Parameter	Untreated MEA	STE-treated MEA	Physical assignment
R_s (Ω)	0.05238	0.03834	High-frequency series resistance
R_l (Ω)	0.05368	0.01943	Interfacial-polarization-related resistance
R_{tr} (Ω)	0.03326	0.01510	Low-frequency transport-related resistance
R_p (Ω)*	0.08694	0.03453	Total polarization resistance

* $R_p = R_l + R_{tr}$

All fitting parameters were obtained using the same equivalent circuit and modulus-weighted nonlinear least-squares procedure.