

Mitigation of H₂ crossover in PEM water electrolyzers via cathode catalyst layer engineering: Effects of pore former type, loading, and operating pressure

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ARTICLE INFO

Keywords:

Hydrogen crossover
Mass transport
Pore former
Cathode catalyst layer
Proton exchange membrane water electrolyzer

ABSTRACT

H₂ crossover through the membrane is a critical safety and efficiency concern in proton exchange membrane water electrolyzers (PEMWEs), particularly under pressurized operation. This study develops a cathode catalyst layer (CL) pore-engineering strategy using PEG as a pore-forming agent to regulate gas transport within the CL. The molecular weight of PEG governs its dispersion behavior in the catalyst ink and the architecture of the resulting pore network. An intermediate molecular weight additive generates a uniform and interconnected pore framework that facilitates rapid H₂ removal from the cathode CL. As a result, H₂ permeation through the membrane is suppressed while maintaining comparable electrochemical kinetics. Optimization of PEG loading identifies 60 wt% as the optimal condition, delivering reduced H₂ crossover, improved high-current-density performance, and enhanced durability. The engineered CL also maintains lower crossover levels under pressurized operation, highlighting pore-structure control as a strategy for improving the safety and stability of PEMWEs.

1. Introduction

One of the critical components influencing the performance and durability of proton exchange membrane water electrolyzer (PEMWE) is the membrane-electrode assembly (MEA). The MEA consists of a proton exchange membrane (PEM) sandwiched between a catalyst layer (CL) on each side, a gas diffusion layer (GDL) on the cathode side, and a porous transport layer (PTL) on the anode side. The primary role of the PEM is to conduct protons between the electrodes. The CLs, composed of ionomer and catalyst particles, serve as the sites for electrochemical reactions. The GDL and PTL function as pathways for electron conduction and facilitate the transport of gases and liquids in the MEA [1–3].

In PEMWE, a critical issue related to safe operation is how to ensure safety without compromising system performance. During electrochemical operation, hydrogen gas is generated at the cathode and oxygen gas at the anode. However, due to the inherent properties of the PEM, complete separation of these gases is not achievable, resulting in

partial mixing of H₂ and O₂ on either the anode or cathode side. When hydrogen and oxygen are mixed, an explosion can occur in the presence of an ignition source if the hydrogen concentration falls in the flammable range of 4–94 mol% (or 4–75 mol% when mixed with air) [4,5]. Therefore, H₂ production systems are typically designed with a safety margin, limiting the H₂ concentration to 50% of the lower explosion limit (2 mol%) [6]. In particular, the mixing ratio of H₂ and O₂ (H₂ in O₂) increases significantly in the low current density region of PEMWE operation. This value varies significantly depending on operating parameters such as temperature, pressure, and membrane thickness, and must be carefully controlled to ensure safe and reliable operation [7–11].

Using a thicker PEM can mitigate this issue; however, it also reduces the efficiency of PEMWE, ultimately increasing the cost of hydrogen production. To address this trade-off, extensive research has been conducted, primarily focusing on the synthesis of novel membrane structure or the modification of existing PEMs through composite or

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<https://doi.org/10.1016/j.ijhydene.2026.156712>

Received 18 March 2026; Received in revised form 16 July 2026; Accepted 19 July 2026

Available online 20 July 2026

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functionalization approaches. For example, Lee et al. reported a strategy to reduce the H_2 in O_2 by increasing the tortuosity of hydrophilic channels through biaxial stretching of the PEM [12]. Klose et al. used fully hydrocarbon based MEA with sulfonated poly(phenylene sulfone) as both the membrane and electrode ionomer, achieving significantly higher performance (3.5 A cm^{-2} at 1.8 V) and a lower hydrogen crossover current density (0.3 mA cm^{-2}) compared to Nafion (N115), which exhibited 1.5 A cm^{-2} at 1.8 V and 1.1 mA cm^{-2} , respectively [13]. Huang et al. developed a reinforced PEM incorporating an acid-base crosslinked network structure and a mechanical support layer, utilizing a hyperbranched polymer with imidazole terminal groups, perfluorinated sulfonic acid, and a poly(ether ether ketone) mesh. This strategy aimed to enhance performance, durability, and reduce hydrogen permeability. The resulting membrane demonstrated excellent performance (1.84 V at 3.0 A cm^{-2}), a low degradation rate ($6.2 \mu\text{V h}^{-1}$), and a reduced hydrogen crossover current density (1.06 mA cm^{-2}) [14]. Qelibari et al. fabricated a reinforced membrane by preparing a porous poly(ether ether ketone) matrix and infusing it with sulfonated polyphenylene oxide as the electrolyte. The resulting membrane showed reduced H_2 permeability and lower resistance compared to the fluorinated Nafion (N115) membrane, while also exhibiting excellent durability [15]. Tian et al. synthesized a highly sulfonated polybenzoxazine-based PEM via a Mannich reaction. This polymer demonstrated enhanced performance (1.29 A cm^{-2} at 1.95 V) compared to the N115 (1.02 A cm^{-2} at 1.95 V) and significantly reduced H_2 crossover in the range of 536 to 655 ppm compared to 965 ppm for N115 [16]. Additionally, various approaches have been investigated to suppress H_2 and O_2 , such as incorporating gas recombination layers into the PEM or CL, modifying the properties of the ionomer, engineering the CL structure in the cathode CL, and introducing gas-adsorbing materials into the anode CL to prevent the mixing of H_2 with the O_2 stream [5,9,17–20]. However, these approaches often involve additional processing steps, which can increase the overall cost of H_2 production. Moreover, hydrocarbon-based PEMs still exhibit lower durability compared to perfluorinated sulfonic acid-based PEMs, which hinders their practical application.

Meanwhile, the H_2 generated on the catalyst surface in the cathode CL tends to accumulate in the ionomer phase, and this H_2 can become

supersaturated depending on the ionomer's properties. When the H_2 generation rate exceeds the release rate, the H_2 was supersaturated in the ionomer phase and as its content increases, the H_2 permeation through the membrane also increases. Previous studies have experimentally demonstrated that higher H_2 supersaturation leads to increased H_2 crossover by imposing mass transfer [21–24]. Therefore, it is crucial to develop cathode CL structures that can suppress H_2 supersaturation in the ionomer phase to effectively minimize H_2 crossover. To this end, the specific aim of this study is to design a cathode CL structure that can effectively suppress H_2 supersaturation within the ionomer phase by optimizing the pore architecture, thereby minimizing H_2 crossover and reducing the H_2 concentration in the anode-side O_2 stream (H_2 in O_2) during operation of PEMWE. We hypothesize that engineering the pore structure of the cathode CL by introducing a pore former can facilitate rapid removal of generated H_2 from the ionomer and limit H_2 accumulation while suppressing supersaturation. This structural modification is expected to reduce the driving force for H_2 permeation through the membrane, ultimately lowering H_2 crossover and improving the safety margin of PEMWE operation without compromising performance.

In this study, the H_2 in O_2 was measured by varying the molecular weight of polyethylene glycol (PEG) in the cathode CL used as a pore former to investigate the effect of cathode CL structure on the safety of PEMWE (Fig. 1). As a result, the H_2 in O_2 was reduced by a factor of 2 when using PEG with a molecular weight of 2000 at a content of 60 wt%. This study demonstrates an effective strategy to enhance the safety of PEMWE without relying on thicker membranes by tuning the pore structure of the cathode CL through controlled PEG-based pore formation.

2. Experimental

2.1. Materials

Nafion membrane (NR212) and Nafion ionomer dispersion (D521 and D2021) were supplied by Chemours (USA). IrO_2 black and Pt/C (47.0 wt% Pt, 10V50E) were sourced from Boyaz Energy (Korea) and Tanaka Kikinzoku Kogyo K.K. (Japan), respectively. The carbon-based

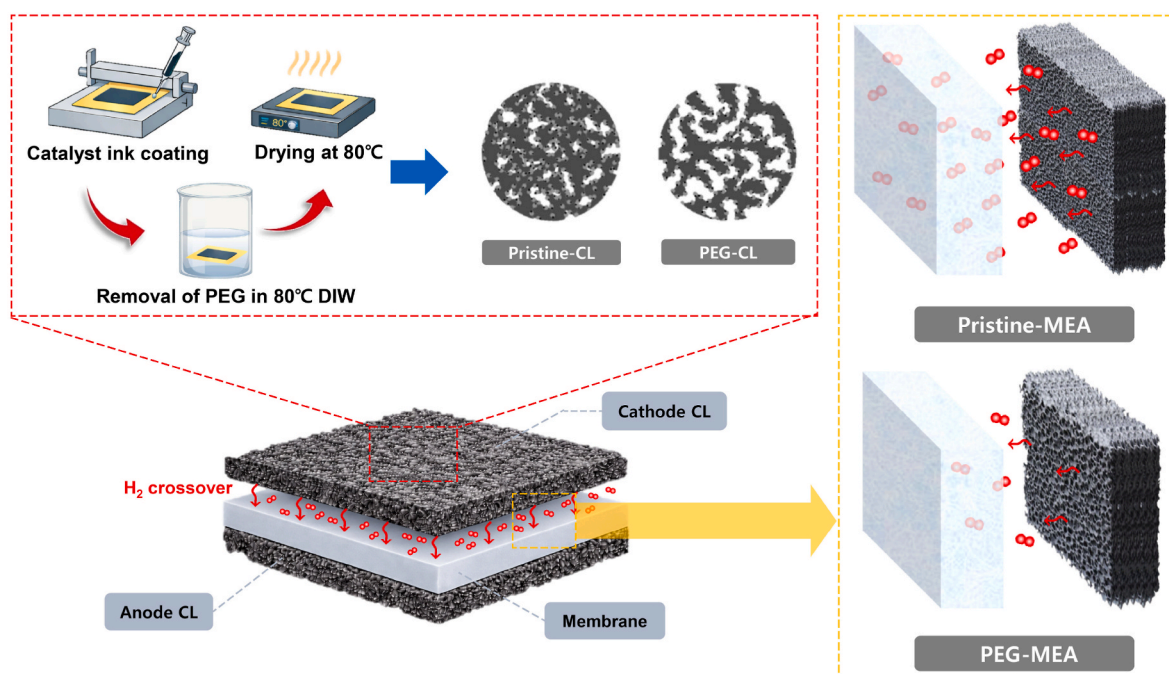


Fig. 1. Schematic illustration of the PEG removal procedure in the CL and its effects on the pore structure and H_2 crossover.

GDL (39BB) and titanium-based PTL were provided by SGL carbon (Germany) and LT Metal Ltd. (Korea). Deionized (DI) water (18 MΩ) was prepared using a Milli-Di water purification system (Germany). Polyethylene glycol (PEG) was purchased from Sigma-Aldrich (Germany) with different molecular weights PEG200, PEG2,000 (PEG2k), PEG20,000 (PEG20k), and PEG200,000 (PEG200k). All materials were used as received from the suppliers without any further modification.

2.2. CL fabrication and characterizations

To prepare the anode catalyst ink, 0.8 g of IrO₂ black was mixed with 0.56 g of 1-propanol, 0.5 g of DI water as a co-solvent, and 0.44 g of Nafion dispersion (D2021). The mixture was stirred mechanically at 500 rpm for 2 h, and subsequently treated using a probe-type ultrasonicator operated in a pulsed mode (5 s on/5 s off) for a total sonication time of 300 s. For the cathode catalyst ink, 0.35 g of Pt/C, 3.7 g of Nafion dispersion (D521) and PEG of varying molecular weights were combined and mechanically stirred at 500 rpm for 3 h with DI water/1-Propanol co-solvent. Ultrasonication was applied for 420 s using a tip sonicator. The PEG content was adjusted to 20, 40, 60, and 80 wt% relative to the total mass of Pt/C and Nafion ionomer, while the ionomer-to-carbon mass ratio was maintained at 1. The well-dispersed catalyst ink was coated onto a PTFE-coated polyimide film using a doctor blade with a 90 μm gap. The coated film was predried at 35 °C for 30 min and then thoroughly drying at 80 °C for 2 h. To remove the PEG embedded in the CL, a 5 cm² catalyst coated film was immersed in DI water at 80 °C and stirred continuously using a magnetic bar for 48 h.

The PEG size was measured using dynamic light scattering (DLS). The morphology of the CL was examined using field emission scanning electron microscopy (FE-SEM, Gemini 560, Carl Zeiss) equipped with energy dispersive X-ray spectroscopy (EDS). To investigate the through-plane structure of the CL, focused ion beam scanning electron microscopy (FIB-SEM; Crossbeam 550, ZEISS) was employed. Pore size distribution was characterized by mercury intrusion porosimetry (MIP, AutoPore V, Micromeritics). Surface property of the CL was measured with contact angle analyzer (PHX3000, Surface Electro Optics (SEO)).

2.3. Fabrication of catalyst coated membranes (CCMs) and electrochemical characterizations

CCMs were prepared by decal transfer of the anode and cathode CLs onto a Nafion NR212 membrane. The transfer was carried out at 130 °C under 40.0 MPa for 10 min. The fabricated CCMs were targeted to catalyst loadings of 2.0 mg_{IrO₂} cm⁻² for the anode CL and 0.4 mg_{Pt} cm⁻² for the cathode CL. The single cell was assembled using the CCM, carbon-based GDL, a Pt-coated titanium-based PTL, two non-Pt-coated graphitic bipolar plates with a triple-serpentine flow field, and two endplates. A clamping torque of 80 kgf cm⁻¹ was applied.

Electrolysis performance was tested using a PEM water electrolyzer test station (CNL, Korea). Measurements were conducted at 80 °C and atmospheric pressure while feeding DI water at 30 mL min⁻¹. Polarization data were collected by stepping the cell voltage from 1.35 to 1.90 V in 0.05 V increments, holding each step for 30 s. The H₂ in O₂ at the anode outlet was monitored at selected constant current densities under varying pressure conditions using an integrated hydrogen sensor. Electrochemical impedance spectroscopy (EIS, HCP-803, BioLogics) was performed from 10 kHz to 0.1 Hz with a perturbation amplitude of 10% applied voltage.

The durability of the MEAs was evaluated under a constant current density of 1 A cm⁻² using a single-cell PEMWEs. The cell was operated at 80 °C while feeding DI water at 30 mL min⁻¹. During the 500 h durability test, the cell voltage was continuously monitored to evaluate voltage degradation behavior.

The fluorine emission rate (FER) was measured to evaluate the chemical degradation of fluorinated components during long-term operation. During the durability test, the anode effluent water was

periodically collected and analyzed for dissolved fluoride ions. The fluoride concentration was quantified using ion chromatography (IC).

2.4. Calculation of H₂ permeation rate

The H₂ permeation rate (P_{H_2}) to the anode was calculated from the measured H₂ volume fraction in the anode O₂ stream (Φ_{H_2}) using a steady-state mass balance coupled with Faraday's law. The relationship among P_{H_2} , Φ_{H_2} , and the molar flux of oxygen evolution (N_{ev,O_2}) is expressed as follows [17]:

$$\Phi_{H_2} = \frac{P_{H_2}}{P_{H_2} + N_{ev,O_2}}, \quad (1)$$

where N_{ev,O_2} was obtained from the applied current density i assuming a four-electron oxygen evolution reaction:

$$N_{ev,O_2} = \frac{i}{4F}, \quad (2)$$

with F being Faraday's constant. Combining Eqs. (1) and (2), P_{H_2} can be expressed as

$$P_{H_2} = \frac{i}{4F} \frac{\Phi_{H_2}}{1 - \Phi_{H_2}}, \quad (3)$$

By rearranging the balance equation given in the literature [4], the supersaturation concentration of dissolved H₂ in the ionomer ($C_{H_2}^{super}$) was calculated using the following equation:

$$C_{H_2}^{super} = \frac{\frac{i}{2F} + k_L C_{H_2}^{sat}}{k_L + \frac{D_{mem,H_2}}{\delta_{mem}}}, \quad (4)$$

where k_L is the mass transfer coefficient, $C_{H_2}^{Henry}$ is the theoretical saturation concentration of dissolved H₂, $D_{H_2}^{eff}$ is the effective hydrogen diffusion coefficient of the membrane, and δ_m is the membrane thickness.

Eq. (4) can be inserted into Fick's first law of diffusion to calculate the H₂ permeation rate as follows:

$$P_{H_2} = D_{mem,H_2} \frac{C_{H_2}^{super}}{\delta_{mem}}, \quad (5)$$

3. Results and discussion

3.1. Physical characterizations of cathode CLs

To investigate the effect of PEG as a pore former on the catalyst layer (CL) morphology, the size of PEG in the mixed solvent used for CL fabrication was first analyzed by dynamic light scattering (DLS) as a function of PEG molecular weight (Fig. 2a). Because PEG is dissolved in a water/1-propanol mixed solvent, the size distribution exhibits two or more peaks. Moreover, the intensity of the main peak corresponding to smaller particles decreases with increasing molecular weight, accompanied by a shift toward larger particle sizes. In the mixed solvent, PEG chains do not maintain the random-coil conformation typically observed in water but instead gradually transition to a more contracted globular structure. In particular, high-molecular-weight PEG has longer chains that are more easily entangled, which increases the likelihood that neighboring PEG chains come into contact as the coils contract. As a result, loosely associated multi-chain aggregates are formed rather than isolated single-chain structures. This behavior arises because the presence of 1-propanol reduces PEG-water interactions; compared to PEG, 1-propanol is relatively hydrophobic, leading to diminished hydrogen bonding with water and promoting increased PEG-PEG interactions as a means of stabilization. This effect becomes more pronounced with increasing PEG chain length. Based on the particle size distributions as a function of molecular weight, PEG200, PEG2k, and PEG20k exhibit

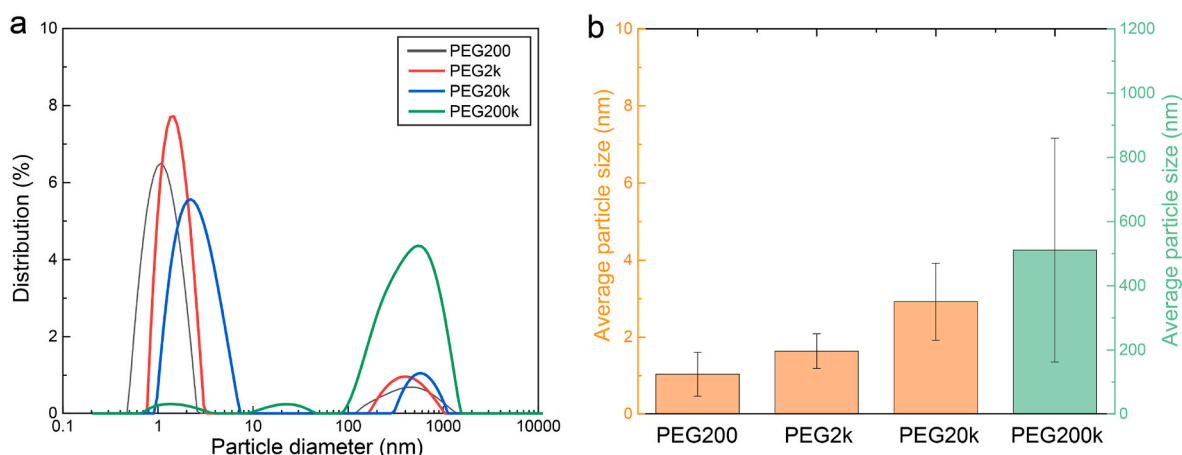


Fig. 2. (a) Dynamic light scattering (DLS) results of the mixed solution containing dissolved PEG and (b) variation in particle size in the mixed solution with molecular weight of PEG.

particle sizes smaller than 10 nm and are therefore expected to primarily affect pores within catalyst agglomerates (primary pores). In contrast, PEG200k shows particle sizes exceeding 100 nm, indicating that it predominantly influences the inter-agglomerate pores (secondary pores) within the CL (Fig. 2b).

To investigate how PEG of different molecular weights contributes to pore formation within the CL, the surface morphology of the CL was analyzed by SEM. Fig. 3a1–3d1 presents SEM images of CLs containing PEG with different molecular weights, showing the formation of Pt/C-ionomer agglomerates that are not significantly different from the

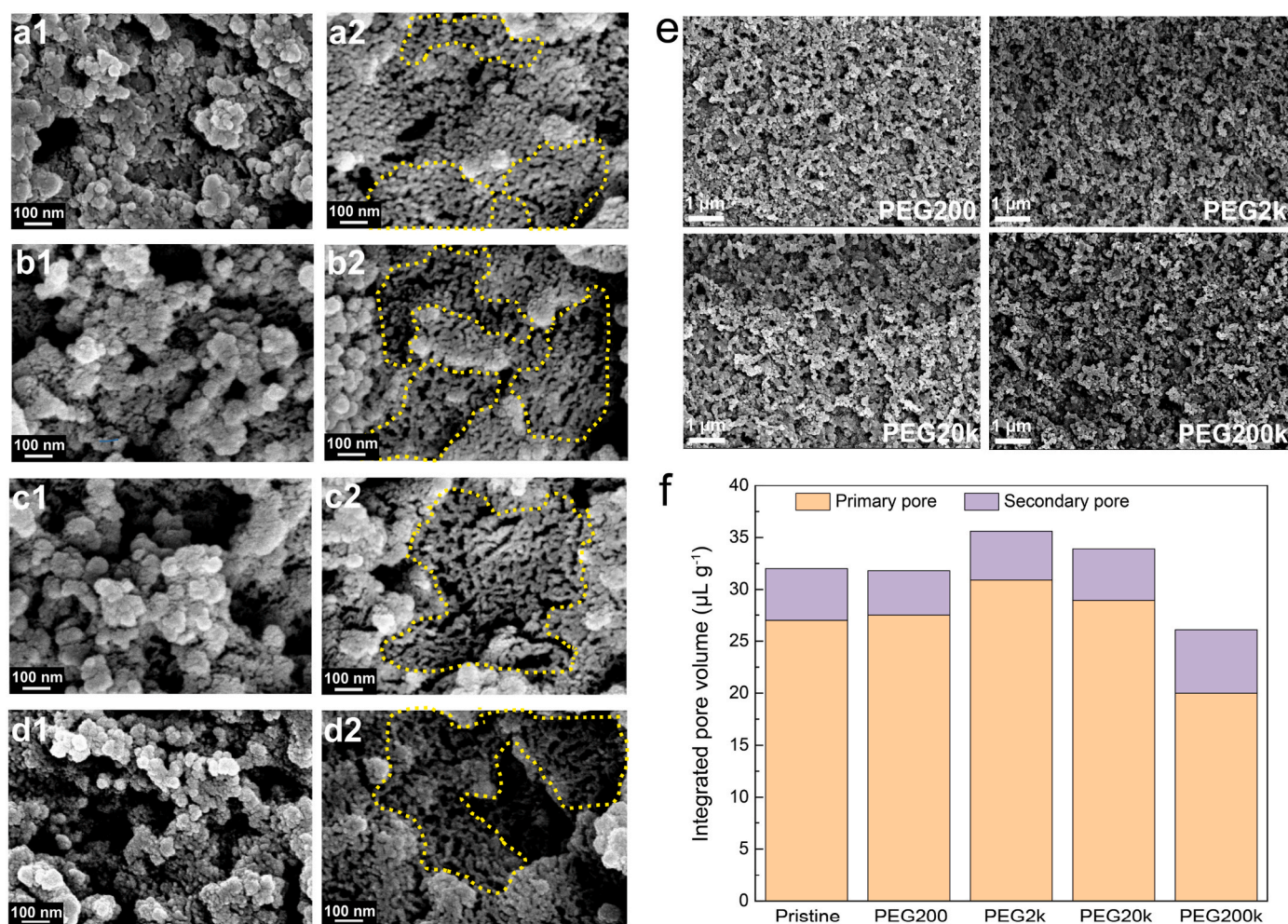


Fig. 3. Morphologies of the cathode CLs as a function of PEG molecular weight before removal (a1–d1) and after removal (a2–d2). (e) Low-magnification surface morphologies of the CLs after PEG removal for different PEG molecular weights. (f) Cumulative pore volume in the ranges of 7–50 nm (primary pores) and 50–1000 nm (secondary pores).

morphology of a pristine-CL without PEG (Fig. S1a). In contrast, the CLs after PEG removal (Fig. 3a2–3d2) clearly display localized pore formation (highlighted by the yellow dotted regions). For PEG200, PEG2k, and PEG20k, relatively small pores with comparable sizes are formed, whereas the CL from which PEG200k was removed exhibits significantly larger pores. In addition, low-magnification SEM images reveal that the surface roughness of the CL after PEG removal is significantly higher than that of the pristine-CL (Fig. 3e and Fig. S1b). As the surface roughness increases, a larger fraction of air pockets is formed at the CL surface, leading to an increase in the water contact angle from 109° (Pristine-CL) to 125° (PEG2k-CL) (Fig. S2). This observation further indicates that PEG removal induces the formation of a large number of pores, a trend that is consistent with the DLS results. In addition, EDS mapping and quantitative elemental analysis of the CLs before (Fig. S3a–S3d) and after PEG removal (Fig. S3e–S3h) showed that the oxygen content decreased after PEG removal for all four PEG types. This reduction in oxygen fraction further provides evidence that PEG was effectively eliminated from the CL.

To quantitatively analyze pore formation in the CL, pore size distribution analysis was performed using MIP (Fig. 3f and Fig. S4). From the MIP profiles and the calculated pore volumes divided by a threshold of 50 nm, it is evident that the CLs prepared with PEG200, PEG2k, and PEG20k exhibit an increase in pore volume smaller than 50 nm after PEG removal. In contrast, for PEG200k, the pore volume below 50 nm decreases, while the pore volume above 50 nm increases. Moreover, the largest increase in total pore volume is observed for the CL prepared with PEG2k. These results can be explained by the different dispersion behaviors of PEG in the solvent. PEG200 is finely dispersed, leading to the formation of only small and limited pores after removal and thus a modest increase in pore volume. PEG200k exists as large aggregates,

resulting in the formation of locally large pores; however, their nonuniform distribution and poor connectivity limit the overall pore volume. In contrast, PEG2k is uniformly dispersed in the catalyst ink, enabling the formation of continuous and well-connected pore structures upon removal, which leads to the largest pore volume. These findings demonstrate that the pore size distribution within the CL can be effectively tuned by controlling the molecular weight of PEG.

To evaluate the through-plane pore distribution within the bulk CL, cross-sectional SEM images were additionally acquired (Fig. S5). These cross-sectional observations reveal that the pores generated by PEG2k are uniformly distributed across the entire thickness of the CL, indicating the formation of an interconnected pore network throughout the electrode bulk. This finding is in good agreement with the results obtained from MIP.

3.2. Effect of CL pore structure on cell performance

The effect of PEG content on cell performance was evaluated by investigating polarization curves. As shown in Fig. 4a, the cell performance below 2 A cm^{-2} remained nearly identical regardless of the PEG molecular weight. In contrast, at 7 A cm^{-2} , the voltages of PEG-treated MEAs (PEG-MEAs) were lower than that of the pristine-MEA, indicating enhanced performance. Among them, the PEG2000-treated MEA (PEG2k-MEA) exhibited the lowest cell voltage (1.938 V) compared to the pristine-MEA (1.986 V) at 7 A cm^{-2} . The PEG200-treated MEA (PEG200-MEA), PEG20,000-treated MEA (PEG20k-MEA), and PEG200,000-treated MEA (PEG200k-MEA) showed voltages of 1.952 V, 1.962 V, and 1.970 V, respectively, at the same current density (Table 1). The reduced cell voltages of the PEG-MEAs compared with the pristine-MEA are attributed to the function of PEG as a pore former,

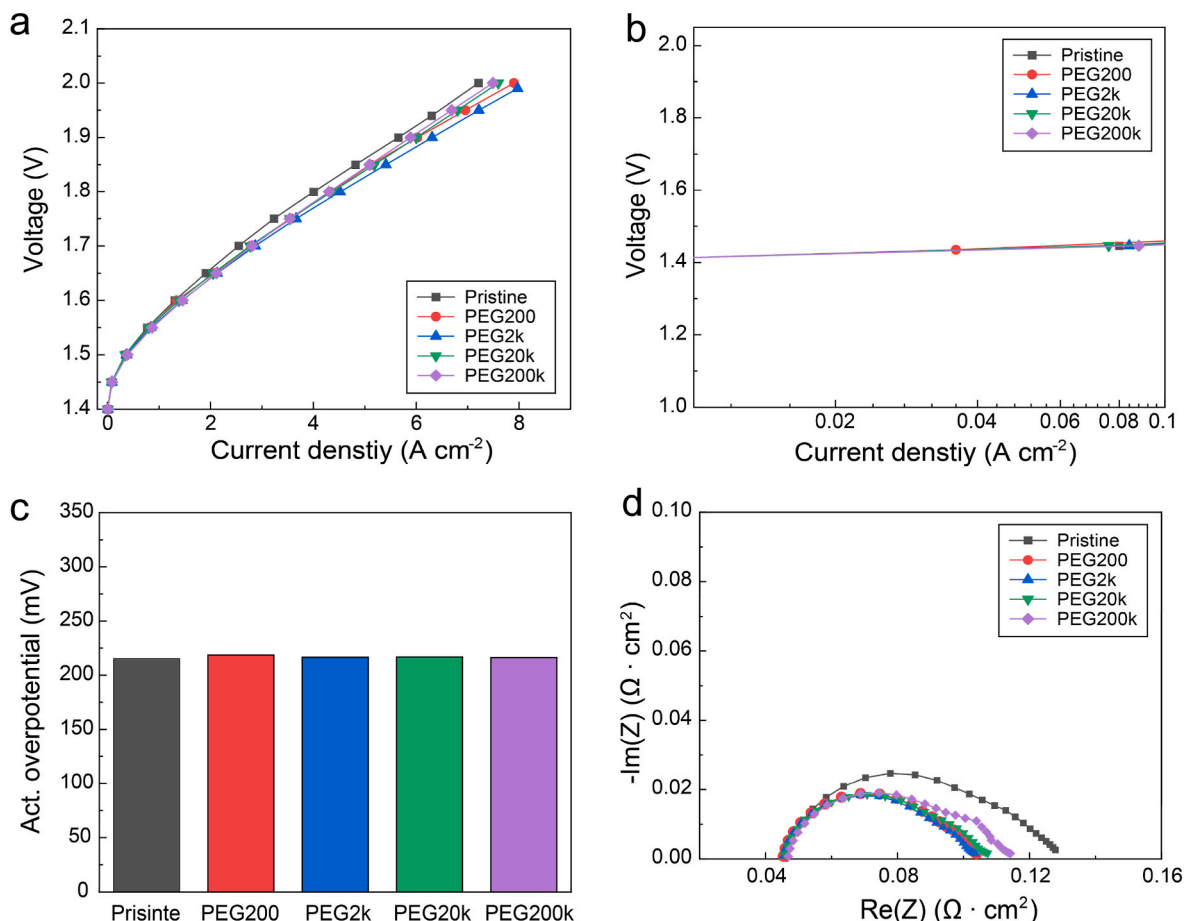


Fig. 4. (a) Polarization curves, (b) Tafel plots, (c) activation overpotentials, and (d) Nyquist plots of the MEAs with a PEG molecular weight.

Table 1

Various electrochemical data for MEAs with different PEG types.

MEA	Voltage at 7 A cm ⁻² (V)	Tafel slope (mV dec ⁻¹)	η_{act} (mV)	R_{ohm} (mΩ • cm ²)	R_{mt} (mΩ • cm ²)	Slope of permeation rate fit (mmol m ⁻² sec ⁻¹)/(A cm ⁻²)	k_L (mm s ⁻¹)
Pristine	1.986	61.9	215.4	46.3	48.4	0.56	5.3
PEG200	1.952	60.8	218.6	44.8	23.0	0.37	8.0
PEG2k	1.938	60.9	216.5	44.1	22.8	0.32	9.3
PEG20k	1.962	61.1	216.7	45.4	23.5	0.47	6.3
PEG200k	1.970	61.6	216.3	47.6	32.9	0.49	6.1

which improves mass transport in the cathode CL.

To evaluate the influence of PEG-induced pore formation on kinetic performance in the low-current-density region, iR-free polarization curves were obtained by correcting for ohmic resistance. Based on these curves, the operational activation overpotential (η_{act}) was calculated using the Tafel equation [25,26]. The relationship is expressed as $\eta_{act} = a + b \cdot \log(j)$, where b is the Tafel slope, which is typically evaluated in the current density range of 0.01–0.1 A cm⁻². This range is selected because the contributions from mass transport and ohmic overpotentials are negligible. As shown in Fig. 4b, the Tafel slopes of the PEG-MEAs range from 60.9 to 61.9 mV dec⁻¹, indicating that the introduction of PEG as a pore former in the cathode CL has a minimal impact on the cathodic kinetics of the PEMWE. Furthermore, as represented in Fig. 4c, the η_{act} at a current density of 0.1 A cm⁻² is comparable across all PEG-MEAs, with a maximum difference of less than 3.2 mV. These results confirm that the observed performance differences among the MEAs do not originate from variations in η_{act} . Moreover, the nearly identical Tafel slopes and activation overpotentials observed for all PEG-containing MEAs suggest that residual PEG does not adversely affect the Pt active sites, indicating its effective removal from the catalyst layer. This interpretation is further supported by the TGA (Fig. S6a and S6b) and CV (Fig. S6c) results, which provide direct evidence for the successful removal of PEG. Furthermore, the substantial increase in pore volume revealed by MIP and the comparable cell performance observed in the low-current-density region are both consistent with the complete elimination of PEG from the CL after fabrication.

The influence of PEG-induced pore engineering on cell performance was further evaluated by EIS (Fig. 4d and Table 1). In the Nyquist plots, the high-frequency intercept on the real axis corresponds to the ohmic resistance (R_{ohm}), while the low-frequency intercept of the second semicircle is associated with the mass transport resistance (R_{mt}). Only the PEG200k-MEA exhibited a value comparable to that of the pristine-MEA, while the other PEG-MEAs showed lower values than the pristine-MEA. In contrast, R_{mt} decreases in the order of pristine-MEA (48.4 mΩ cm²), PEG200k-MEA (32.9 mΩ cm²), PEG20k-MEA

(23.5 mΩ cm²), PEG200-MEA (23.0 mΩ cm²), and PEG2k-MEA (22.8 mΩ cm²), which is consistent with the observed cell performance trends. These results indicate that PEG-based pore formation enhances both proton conduction within the MEA and mass transport.

3.3. Effect of CL pore structure on H₂ permeation rate

To investigate the effect of PEG-induced pore formation on the H₂ permeation rate (P_{H_2}), the H₂ in O₂ (Φ_{H_2}) of PEG-MEAs was measured as a function of current density (Fig. 5a and Table S1). As shown, relatively high Φ_{H_2} values are observed in the low-current-density region, followed by a gradual decrease with increasing current density. This behavior arises because, at low current densities, a small amount of O₂ is produced, resulting in a higher concentration of permeated H₂, whereas at higher current densities, the increased O₂ production (N_{ev,O_2}) dilutes the permeated H₂, leading to lower Φ_{H_2} values. Notably, the pristine-MEA exhibits Φ_{H_2} values exceeding 2% even in the high-current-density region, indicating a higher risk with respect to explosion safety. Across the entire current density range, the PEG2k-MEA shows the lowest Φ_{H_2} values. As indicated by the MIP results, this behavior can be attributed to the formation of a large number of small pores, which facilitate H₂ transport out of the CL, thereby reducing the amount of P_{H_2} through the membrane. Furthermore, comparison with the Φ_{H_2} data of the PEG200k-MEA, which exhibits an increased volume of large pores (Fig. 3), indicates that the formation of smaller pores has a more pronounced effect on reducing the P_{H_2} . Based on the Φ_{H_2} values measured as a function of current density, the P_{H_2} was calculated using Eq. (3) (Fig. 5b). P_{H_2} increases with increasing current density, while the slope varies depending on the molecular weight of PEG, indicating that PEG modifies the structure of the cathode CL [27]. In particular, the PEG2k-MEA, which forms smaller pore structures, exhibits lower P_{H_2} values over the entire current density range compared with the PEG200k-MEA, which contains larger pores. This trend can be attributed to the combined effects of enhanced mass transport resulting from the increased pore volume and modifications to the ionomer coating morphology induced by PEG

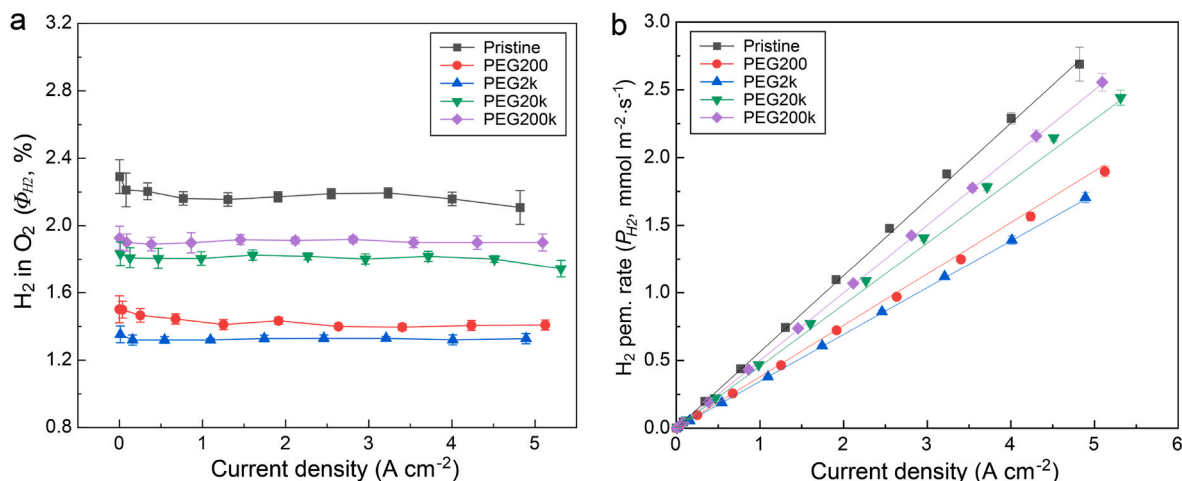


Fig. 5. (a) H₂ volume fraction in the O₂ stream (H₂ in O₂) at the anode and (b) H₂ permeation rate as a function of current density for PEG-MEAs.

during catalyst ink preparation. The incorporation of PEG during ink preparation influences the organization of the Nafion ionomer, resulting in a more uniform ionomer distribution and thinner ionomer films surrounding catalyst agglomerates after PEG removal. Evidence for this structural reorganization is provided by the significant increase in water contact angle from 109° to 125° (Fig. S2), suggesting changes in CL surface chemistry induced by ionomer redistribution rather than surface roughness effects alone [28]. The resulting ionomer morphology is expected to lower the effective H_2 solubility and diffusivity within the ionomer phase and alleviate local H_2 supersaturation by reducing

ionomer film thickness. Therefore, the decreased H_2 crossover observed in PEG containing CLs is attributed not only to enhanced pore connectivity and more efficient H_2 evacuation but also to ionomer phase reorganization that limits H_2 dissolution and transport through the ionomer [29,30].

It should be noted that the Pt-coated anode PTL used in this study may catalyze chemical recombination of crossover H_2 with O_2 prior to detection, potentially underestimating the absolute H_2 crossover flux relative to systems employing non-Pt-coated PTLs [31]. Nevertheless, since all MEAs were tested under identical hardware conditions, the

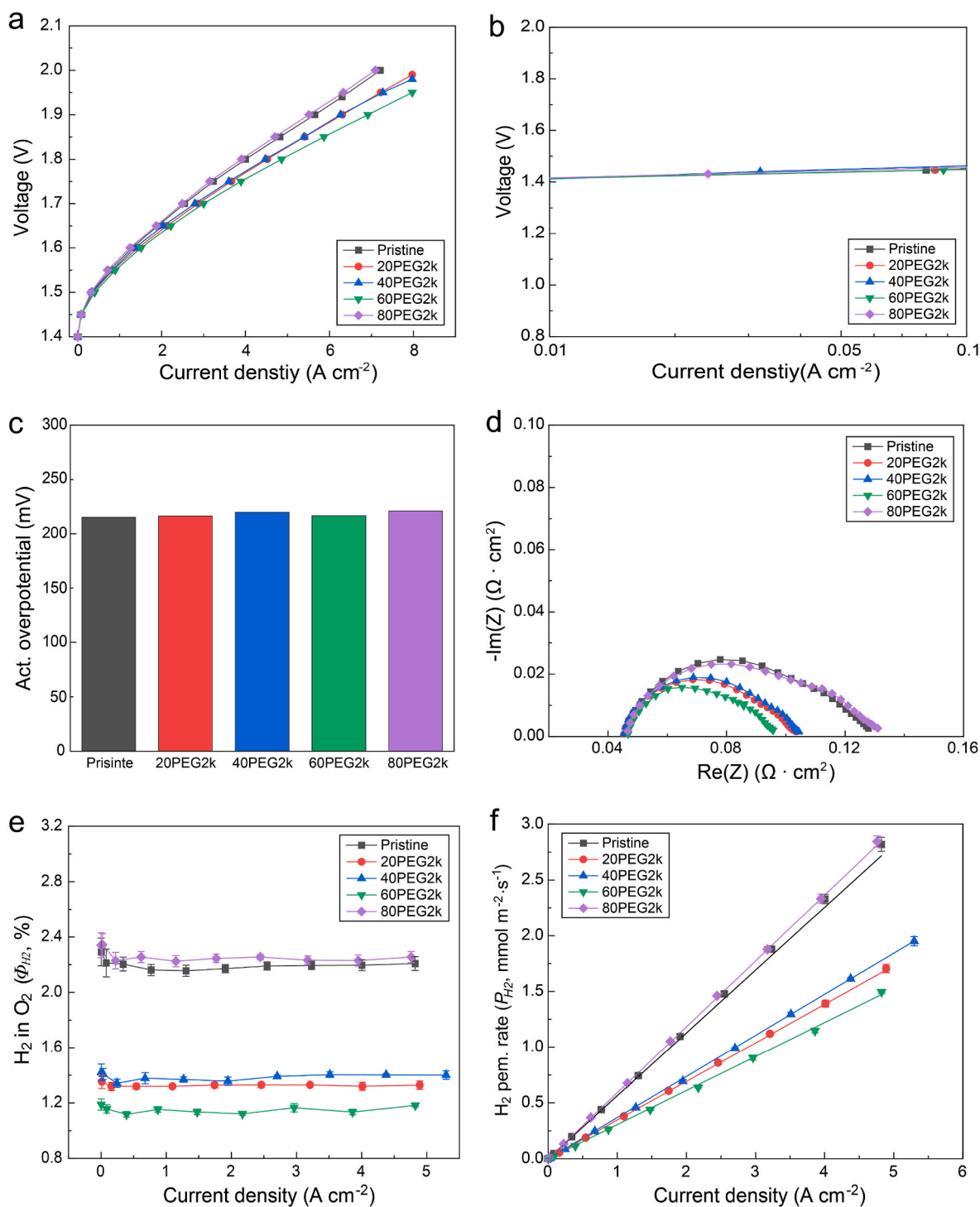


Fig. 6. (a) polarization curves, (b) Tafel plots, (c) activation overpotentials, (d) Nyquist plots, (e) H_2 volume fraction in the O_2 stream (H_2 in O_2), and (f) H_2 permeation rates with different PEG2k loadings.

relative differences in Φ_{H_2} among the MEAs reliably reflect the effect of cathode CL pore structure on H_2 permeation.

The trend lines shown in Fig. 5b were derived by combining Eqs. (4) and (5). The cathodic mass transfer coefficient (k_L) is the only fitting parameter, and its value for each PEG-MEA was determined using the corresponding mass balance equation (supporting information). The P_{H_2} data fitted using k_L exhibit good agreement with the experimentally measured trends (Fig. 5b and Table 1). The k_L values for PEG200-MEA, PEG2k-MEA, PEG20k-MEA, and PEG200k-MEA range from 6.1 to 9.3 mm s⁻¹, with the corresponding slopes varying from 0.32 to 0.49 mmol m⁻² s⁻¹ A⁻¹ cm². Furthermore, as summarized in Table 1, PEG-induced pore formation led to a progressive increase in the k_L accompanied by a corresponding decrease in R_{mt} , revealing a clear inverse relationship between these parameters across all MEAs. This systematic correlation demonstrates that k_L effectively reflects the enhancement of cathodic mass transport resulting from pore structure engineering and supports its validity as a physically meaningful descriptor of transport characteristics within the cathode CL. Consequently, the P_{H_2} can be reduced through combined optimization of pore architecture within the cathode CLs.

3.4. Effect of PEG loading on cell performance and H_2 permeation rate (P_{H_2})

To elucidate the effect of PEG loading on the P_{H_2} , electrochemical analyses were conducted using PEG2k with varying loadings. Fig. 6a presents the polarization curves with PEG content, showing that the MEA containing 60 wt% PEG (60PEG2k-MEA) exhibits the highest performance. In contrast, PEG loadings of 20 (20PEG2k-MEA), 40 (40PEG2k-MEA), and 80 wt% (80PEG2k-MEA) exhibit poorer performance in the high-current-density region than the 60PEG2k-MEA, suggesting adverse effects on mass transport. At low PEG loadings, pore formation is insufficient to induce a meaningful improvement in transport properties, whereas excessive PEG strongly interacts with the catalyst and ionomer, leading to agglomerate damage and detachment during the PEG removal process (Fig. S7). The Tafel slopes derived from the Tafel plots (Fig. 6b) are summarized in Table 2 and were determined to be 60.9, 60.5, 60.1, and 61.1 mV dec⁻¹ for the 20PEG2k-, 40PEG2k-, 60PEG2k-, and 80PEG2k-MEAs, respectively. Consistently, the activation overpotentials (Fig. 6c) were 216.5, 220.1, 216.9, and 221.3 mV at a current density of 0.1 A cm⁻², respectively. The variation was within 4.8 mV, indicating that the PEG content does not significantly affect the cathode kinetics.

The influence of PEG loading on cell performance was further investigated by EIS (Fig. 6d and Table 2). Up to a PEG2k loading of 60 wt %, favorable interactions with the ionomer promoted its uniform spreading within the CL, resulting in a reduced R_{ohm} of the MEA. In contrast, at a higher loading of 80 wt%, R_{ohm} became comparable to that of the pristine-MEA, indicating that this beneficial effect was no longer present. This behavior is attributed to the dominance of PEG self-aggregation in the ink, which lowers the surface energy than PEG-ionomer interactions at high loadings. The R_{mt} results further confirm that PEG effectively functions as a pore former, with R_{mt} decreasing from 48.4 to 22.8, 22.0, 20.2, and 49.8, respectively, and exhibiting an optimum at the 60PEG2k-MEA.

To analyze the effect of PEG loading on the P_{H_2} , the Φ_{H_2} was measured as a function of current density (Fig. 6e and Table S2). Among all samples, the 60PEG2k-MEA exhibited the lowest Φ_{H_2} values, remaining below 1.2 mol% over the entire current density range. The 20PEG2k-MEA and 40PEG2k-MEA also showed reduced Φ_{H_2} levels, below 2 mol%, compared with the pristine-MEA. In contrast, the 80PEG2k-MEA displayed Φ_{H_2} values exceeding 2 mol%, indicating that structural engineering via PEG was ineffective and did not improve the explosion safety of the PEMWE. Based on these data, the P_{H_2} was calculated using Eq. (3) (Fig. 6f and Table 2). P_{H_2} increased with increasing current density for all MEAs. The P_{H_2} data fitted using the k_L showed good agreement with the experimentally observed trends. The k_L values for the 20PEG2k-, 40PEG2k-, 60PEG2k-, and 80PEG2k-MEAs were 9.3, 8.8, 11.5, and 5.0 mm s⁻¹, respectively, all higher than that of the pristine-MEA (5.4 mm s⁻¹). In addition, the slopes of the fitted lines for the H_2 permeation rate with varying current density corresponding to each sample were 0.32, 0.34, 0.26, and 0.59 mmol A⁻¹ m⁻² s⁻¹ cm², respectively, which are lower than that of the pristine MEA (0.56 mmol mmol A⁻¹ m⁻² s⁻¹ cm²), indicating reduced H_2 permeation. These results suggest that the generated hydrogen is more effectively collected through the CL with improved mass transport rather than permeating through the membrane. Overall, these findings clearly indicate that an optimal PEG loading of 60 wt% provides effective guidance for enhancing the explosion safety of PEMWEs through pore former-induced structural engineering of the catalyst layer.

3.5. Effect of operating pressure on H_2 permeation rate (P_{H_2})

The effect of operating pressure on H_2 crossover behavior was systematically investigated by analyzing the Φ_{H_2} and the corresponding P_{H_2} under three different pressures (1, 3, and 5 bar_g). Fig. 7a–c shows the H_2 in O_2 at the anode as a function of current density at 1, 3, and 5 bar_g, respectively. In all pressure conditions, the pristine-MEA consistently exhibited the highest H_2 concentration in the O_2 stream across the entire current density range. As the operating pressure increased from 1 bar_g to 5 bar_g, the H_2 in O_2 increased for all samples. This behavior is primarily attributed to the increased H_2 partial pressure at the cathode side, which enhances the driving force for H_2 permeation through the membrane according to Fick's law. At higher pressures, the elevated H_2 concentration at the cathode-membrane interface increases the diffusive flux of H_2 across the membrane, leading to a higher level of H_2 contamination in the anode oxygen stream. Despite the overall increase in H_2 permeation with pressure, the PEG-MEAs exhibited consistently lower H_2 in O_2 compared with the pristine-MEA. Among the PEG2k-MEAs, the 60PEG2k-MEA showed the lowest H_2 concentration across nearly all operating conditions. In addition, the hydrogen permeation rates as a function of current density are shown in Fig. 7d–f at operating pressures of 1, 3, and 5 bar_g. The pristine-MEA exhibited the highest permeation rate under all pressures, with a steeper slope of permeation rate versus current density compared to the PEG2k-MEAs, indicating greater H_2 accumulation near the membrane interface. In contrast, PEG2k-MEAs showed reduced permeation rates across the entire current density range, with the 60PEG2k-MEA exhibiting the lowest values. This suggests that the PEG2k-induced pore architecture improves H_2 transport

Table 2
Various electrochemical data for MEAs with different PEG2k loadings.

PEG loading (%)	Voltage at 7A cm ⁻² (V)	Tafel slope (mV dec ⁻¹)	η_{act} (mV)	R_{ohm} (mΩ • cm ²)	R_{mt} (mΩ • cm ²)	Slope of permeation rate fit (mmol m ⁻² s ⁻¹)/(A cm ⁻²)	k_L (mm s ⁻¹)
0	1.986	61.4	215.4	46.3	48.4	0.56	5.3
20	1.938	60.9	216.5	44.1	22.8	0.32	9.3
40	1.937	60.5	220.1	44.1	22.0	0.34	8.8
60	1.904	60.1	216.9	44.3	20.2	0.26	11.5
80	1.994	61.1	221.3	46.1	49.8	0.59	5.0

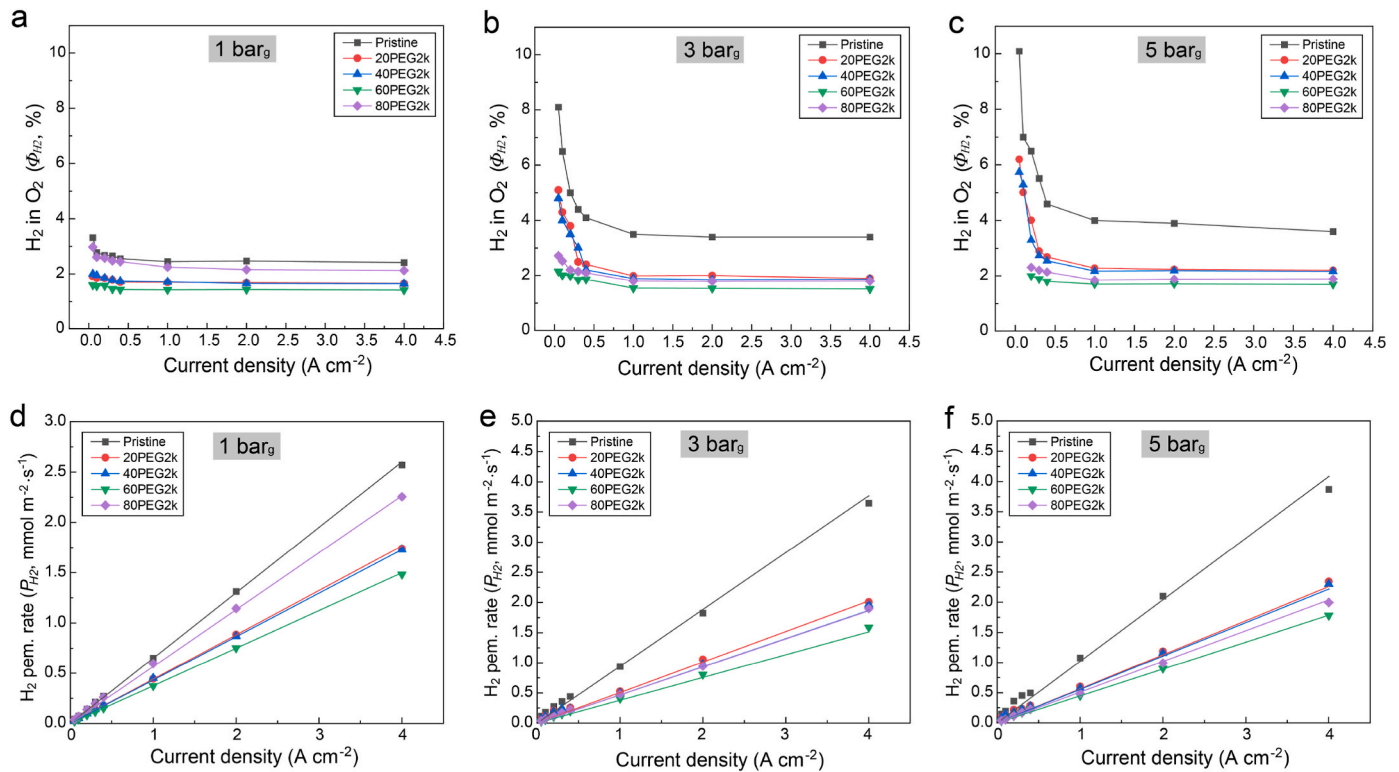


Fig. 7. H₂ volume fraction in the O₂ stream (H₂ in O₂) at the anode was a function of current density for different PEG2k loadings at (a) 1 bar_g, (b) 3 bar_g, and (c) 5 bar_g. The corresponding H₂ permeation rates at (d) 1 bar_g, (e) 3 bar_g, and (f) 5 bar_g.

within the CL, facilitating rapid H₂ removal and suppressing membrane crossover. Additionally, H₂ permeation increased with operating pressure due to the larger H₂ partial pressure gradient across the membrane, although the PEG2k-MEAs maintained significantly lower permeation rates even under pressurized conditions. The pressure-dependent trends observed in the Φ_{H₂} profiles can be comprehensively explained by the following mechanism. Under ambient pressure, the O₂ dilution effect dominates over the permeation enhancement effect across the entire current density range, resulting in a monotonically decreasing Φ_{H₂} profile. Under pressurized operation, the elevated cathode side H₂ partial pressure amplifies the crossover flux, allowing the permeation enhancement effect to overcome the dilution effect at higher current densities and restoring the conventional decrease followed by increase trend.

In particular, under operation at 5 bar_g, the pristine-MEA exhibited Φ_{H₂} values exceeding 4 mol% across the entire current density range, indicating a substantial explosion risk. The 20PEG2k-MEA and 40PEG2k-MEA showed lower Φ_{H₂} values than 4 mol% under 0.25 A cm⁻² operation; however, their values remained above 2 mol%, suggesting that explosion safety cannot be guaranteed during long-term operation at 5 bar_g operation. In contrast, the 60PEG2k-MEA and 80PEG2k-MEA exhibited Φ_{H₂} values below 2 mol%, except in the low-current-density region, demonstrating relatively superior explosion safety. Notably, the 60PEG2k-MEA provided a wider operable low-

current-density window (0.18–4 A cm⁻²) compared to the 80PEG2k-MEA (0.66–4 A cm⁻²), indicating a broader allowable operating current density range especially for low current density. This characteristic suggests that the 60PEG2k-MEA is particularly well suited for direct integration with renewable energy systems that require a wide and flexible operating current density range. Accordingly, the P_{H₂} values calculated as a function of current density show trends consistent with the Φ_{H₂} data (Fig. 7d–f and Table 3). The slopes extracted from the graph of H₂ permeation rate increase with operating pressure, indicating that P_{H₂} is strongly influenced by pressure; however, the 60PEG2k-MEA exhibits the smallest pressure dependence among all samples. Although the *k_L* generally decreases with increasing operating pressure, the optimized 60PEG2k-MEA (6.7 mm s⁻¹) maintains the highest *k_L* at 5 bar_g compared with the pristine-MEA (2.9 mm s⁻¹). These results indicate that appropriate pore engineering within the cathode CL can enhance gas mass transport and reduce H₂ crossover through the membrane even under pressurized operation.

3.6. Durability evaluation and post-test analysis

To evaluate the impact of PEG incorporation on durability, the long-term stability of the pristine-MEA and the 60PEG2k-MEA was assessed under a constant current density of 1 A cm⁻² for 500 h (Fig. 8a). The pristine-MEA exhibited a voltage decay rate of 153.3 μV h⁻¹, whereas

Table 3
Various electrochemical data for MEAs with different PEG2k loadings.

PEG loading (%)	Slope of permeation rate fit (mmol m ⁻² s ⁻¹)/(A cm ⁻²)	<i>k_L</i> at 1 bar _g (mm s ⁻¹)	Slope of permeation rate fit (mmol m ⁻² s ⁻¹)/(A cm ⁻²)	<i>k_L</i> at 3 bar _g (mm s ⁻¹)	Slope of permeation rate fit (mmol m ⁻² s ⁻¹)/(A cm ⁻²)	<i>k_L</i> at 5 bar _g (mm s ⁻¹)
0	0.65	4.6	0.94	3.1	1.02	2.9
20	0.44	6.7	0.51	5.9	0.56	5.3
40	0.43	6.9	0.47	6.5	0.55	5.4
60	0.37	8.0	0.38	7.9	0.44	6.7
80	0.57	5.4	0.47	6.5	0.51	5.8

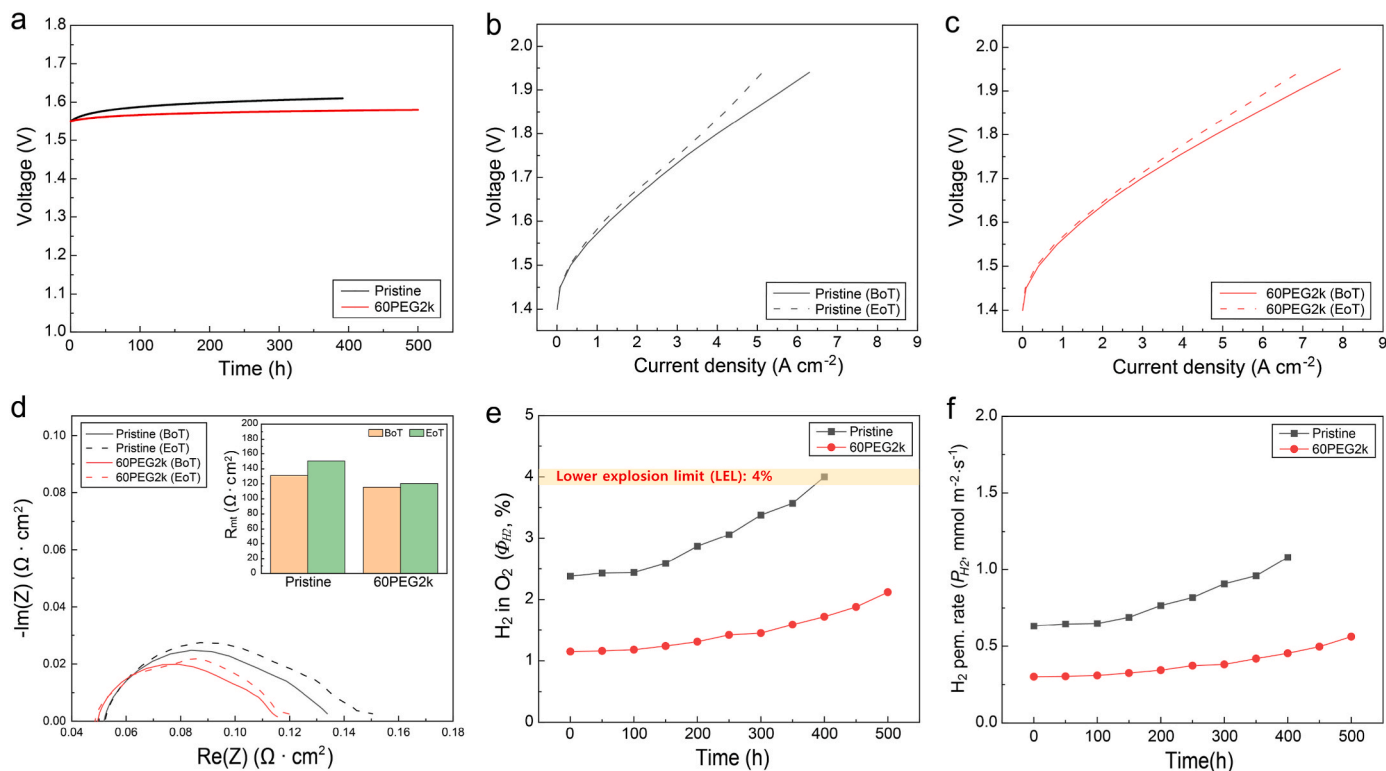


Fig. 8. Durability and electrochemical performance comparison between pristine-MEA and 60PEG2k-MEA. (a) Cell voltage profiles during constant current operation of 1 A cm^{-2} over time. Polarization curves of (b) pristine-MEA and (c) 60PEG2k-MEA measured at the beginning of test (BoT) and end of test (EoT). (d) Nyquist plots with corresponding mass transport resistance (R_{mt}) at BoT and EoT (inset). (e) H_2 volume fraction in the O_2 stream (H_2 in O_2) at the anode over time, with the lower explosion limit (LEL, 4%) indicated. (f) H_2 permeation rate as a function of operation time.

the 60PEG2k-MEA showed a lower decay rate of $60.0 \text{ } \mu\text{V h}^{-1}$, corresponding to an approximately 2.6-fold improvement in durability. In addition, the performance degradation (Fig. 8b and c) and resistance increase (Fig. 8d) after the durability test were significantly larger for the pristine-MEA, whereas only minor changes were observed for the 60PEG2k-MEA (Table 4). In particular, the increase in R_{mt} was substantial for the pristine-MEA ($19.2 \text{ m}\Omega \text{ cm}^2$ increase), while the 60PEG2k-MEA showed a much smaller increase of $2.6 \text{ m}\Omega \text{ cm}^2$. This behavior can be attributed to the role of PEG not only as a pore former but also in dissolving the fluorinated ionomer, thereby promoting the formation of a thinner and more continuous structure [28]. In contrast, the pristine-MEA likely experienced greater structural disruption of the CL during continuous operation, which hindered gas diffusion. The fluorine emission rate (FER) measured during the durability test (Fig. S8) further supports this interpretation. As shown in Fig. S8, the pristine-MEA exhibits a rapid increase in fluorine emission with operating time, indicating accelerated degradation of fluorinated components. In contrast, the 60PEG2k-MEA shows a much slower increase in FER throughout the test, suggesting improved structural stability of the CL and reduced degradation during long-term operation. Although the lower voltage decay rate observed for the 60PEG2k-MEA is primarily attributed to enhanced ionomer continuity and improved pore structure

stability, we recognize that the initially more porous CL also play a role by undergoing less severe mechanical compaction during operation. The significantly lower FER (Fig. S8) and the negligible increase in R_{mt} (Table 4) support the hypothesis of suppressed chemical degradation. Nevertheless, post-mortem investigations would be necessary to distinguish the relative contributions of chemical degradation and mechanical compaction, thereby enabling a more definitive determination of the mechanisms responsible for the enhanced durability.

Furthermore, during the durability test, the Φ_{H_2} and corresponding changes in P_{H_2} were monitored. As shown in Fig. 8e, the H_2 in O_2 gradually increased with operating time for both MEAs. However, the pristine-MEA exhibited a much higher H_2 concentration, approaching the lower explosion limit (LEL, 4%) after prolonged operation, whereas the 60PEG2k-MEA maintained significantly lower values throughout the operation. A similar trend was observed for the H_2 permeation rate (Fig. 8f), where the pristine-MEA showed a continuous increase over time, while the 60PEG2k-MEA exhibited substantially lower permeation rates. The accelerated increase in H_2 crossover for the pristine-MEA is likely associated with progressive structural degradation of the cathode CL during long-term operation, which can hinder H_2 transport and promote H_2 accumulation near the membrane interface, thereby increasing membrane permeation. In contrast, the 60PEG2k-CL maintains more stable mass transport pathways due to its optimized pore structure. These results highlight the critical role of pore-structure engineering in improving both operational safety and long-term stability of PEMWEs.

4. Conclusions

This study demonstrates that PEG is an effective pore former for the cathode CL of PEMWEs, improving mass transport, suppressing H_2 crossover, and enhancing durability. PEG dispersion in a water/1-

Table 4
Durability results and performance changes of pristine-MEA and 60PEG2k-MEA.

MEA	Voltage decay rate ($\mu\text{V h}^{-1}$)	Current density loss at 2.0 V (%)	R_{mt} increase ($\text{m}\Omega \text{ cm}^2$)	H_2 in O_2 increase at 1 A cm^{-2} (%)	H_2 permeation increase at 1 A cm^{-2} ($\text{mmol m}^{-2} \text{ s}^{-1}$)
Pristine	153.3	17.0	19.2	1.62	0.45
60PEG2k	60.0	11.2	2.6	0.57	0.26

propanol solvent strongly depends on molecular weight, which determines the resulting pore structure. PEG2k forms a uniformly distributed, well-connected pore network, whereas high-molecular-weight PEG200k produces large but poorly connected pores, enabling systematic control of cathode CL pore architecture. Electrochemical analyses show that PEG-induced pore engineering significantly improves high-current-density performance ($\geq 3 \text{ A cm}^{-2}$) by reducing mass transport resistance, while cathodic kinetics remain nearly unchanged. H_2 in O_2 results further indicate that small, well-connected pores are more effective in suppressing H_2 crossover, with PEG2k-MEAs exhibiting 20–30% lower H_2 permeation rates over the entire current density range compared to pristine-MEA. Optimization of PEG loading identifies 60 wt% PEG2k as the optimal condition, delivering the best balance of performance, H_2 crossover suppression, and durability. Long-term operation at 1 A cm^{-2} for 500 h shows a reduced voltage decay rate by approximately 30% relative to the pristine-MEA. Overall, this work provides practical design guidelines for cathode CL pore engineering to enhance the efficiency, safety, and durability of PEMWEs.

CRedit authorship contribution statement

Inku Kang: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization. **Won-Jong Choi:** Investigation, Methodology. **Eun-Sun Oh:** Investigation, Methodology. **Eunseo Kang:** Investigation, Methodology. **Jung Kyu Jang:** Investigation, Methodology. **Soonyong So:** Investigation, Methodology. **Duk Man Yu:** Investigation, Methodology. **Sang Jun Yoon:** Investigation, Methodology. **Dong-Won Kim:** Investigation, Methodology, Supervision. **Keun-Hwan Oh:** Conceptualization, Data curation, Formal analysis, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the Korea Research Institute of Chemical Technology (KRICT) Core Research Program (KS2622-10) and by the Project of Technology Independence for Green Hydrogen through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (RS-2025-02316898).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2026.156712>.

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