



Effect of metal–organic framework on hydrogen volume fraction in the oxygen-rich anode catalyst layer of proton exchange membrane water electrolyzer

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ABSTRACT

Hydrogen permeation through the membranes in proton exchange membrane water electrolyzers (PEMWEs) poses a significant safety risk, as the mixing of hydrogen with oxygen at the anode can lead to dangerous concentration levels and potential explosion hazards. This study investigates the modification of the anode catalyst layer (CL) within the membrane electrode assembly (MEA) to enhance the operational safety of PEMWEs by incorporating metal–organic frameworks (MOFs) with H₂-adsorbing capabilities. We evaluate the effects of MOFs with various functional groups on the H₂ concentration in O₂ stream and the electrochemical performance of the anode CL. The amine-functionalized MOF leads to the highest reduction in the H₂ concentration in O₂ stream. Additionally, the reversibility of the H₂ adsorption properties of the MOFs with temperature changes are verified. The amine-functionalized MOF leads to a H₂ volume fraction in O₂ of less than 1.2 mol% at the anode, which is well below the lower explosion limit of 4 mol% and thus, ensures PEMWE safety. In contrast, carboxyl and sulfonic acid-functionalized MOFs result in H₂ volume fractions in O₂ of 1.9 mol% and 2.2 mol%, respectively, at 50 mA cm^{−2}. These results provide crucial insights for developing safer anode CLs for PEMWEs.

1. Introduction

The proton exchange membrane water electrolyzer (PEMWE) has attracted considerable interest as a promising technology for H₂ production owing to its high efficiency, rapid response, and capability to generate high-purity H₂ [1,2]. A crucial element of a PEMWE is the membrane-electrode assembly (MEA), which is composed of a polymer electrolyte membrane (PEM), a catalyst layer (CL), and a porous transport layer (PTL). In the MEA, the PEM acts as a proton-conducting medium, and the CL—consisting of both catalyst particles and an ionomer—drives the electrochemical reactions [3–8]. The PTL plays a vital role in supplying water to the CL and facilitating the removal of the generated H₂ and O₂ gases.

H₂ crossover in PEMWE is a critical challenge because H₂ permeation

through the membrane can lead to the formation of an explosive H₂/O₂ mixture under operational conditions and reduce Faradaic efficiency [9]. This issue is particularly pronounced at low current densities, where the concentration of H₂ in O₂ at the anode CL becomes more significant than at high current densities due to the hydrophilic channels present in ionomers [10,11]. Moreover, the extent of H₂ crossover to the anode CL depends on factors such as the operating pressure, temperature, current density, and concentration of H₂ dissolved in the ionomer at the cathode CL [11–15]. Various strategies have been explored to address the issue of H₂ content in the O₂ stream of PEMWEs. One approach involves morphological modification of membranes through techniques such as increasing the membrane thickness, stretching, incorporating porous substrates, adding nanofillers, or synthesizing dense polymer structures [15–22]. The results of these previous studies generally suggest that

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enhancing the tortuosity of the gas transport pathways effectively reduces H_2 crossover. For instance, Lee et al. developed a biaxially stretched Nafion membrane to lower H_2 permeability [16]. Giancola et al. and Qelibari et al. used porous substrates or woven web layers to create reinforced membranes, and consequently reduce H_2 crossover while enhancing durability [17,19]. Klose et al. synthesized a sulfonated polyphenylene sulfide ionomer specifically for PEMWE and achieved a lower degree of gas crossover and better durability compared to the conventional Nafion 115 membrane [20]. In a different approach, Huang et al. created a hyperbranched imidazole-terminated ionomer blended with a perfluorinated acid ionomer, forming an acid-base crosslink reinforced with a poly(ether ether ketone) mesh [22]. This reinforced membrane reduced the H_2 fraction in O_2 at high current densities and pressure, while exhibiting a lower rate of voltage degradation. Another strategy involves electrode engineering: recombination layers that facilitate H_2 oxidation are fabricated within the MEA, which prevents H_2 accumulation in the O_2 stream at the anode [23–28]. Although these techniques can decrease H_2 permeability, they often adversely affect the cell performance and lead to higher costs owing to the addition of foreign materials. Moreover, these techniques do not ensure the complete elimination of H_2 crossover, which may ultimately compromise the overall H_2 production efficiency and increase operational costs.

Metal-organic frameworks (MOFs) have garnered considerable attention as promising sorbents and separation materials for various molecules [29–36]. The exceptional gas storage capacity and consistent performance of MOFs are largely due to their substantial pore volumes, extensive surface areas, and adaptable porosity [31–35]. In addition, MOFs demonstrate remarkable thermal and chemical stability owing to the strong covalent bonds between the metal centers and organic ligands, which enable them to withstand high temperatures. Hence, we propose the integration of MOFs into the anode CL of the MEAs in PEMWEs to effectively enhance H_2 adsorption. Moreover, nitrogen-functionalized molecules can have a significant effect on the gas storage capacity and selectivity via specific interactions with gas molecules. MOFs that contain paramagnetic metal ions offer additional electronic flexibility and spin coupling, which enhances the selective binding of guest molecules within the framework. The interactions between the metal centers and guest molecules are further affected by the functional groups within MOFs. Therefore, the integration of various functional groups and paramagnetic metal centers into MOFs has been widely investigated to optimize the performance of MOFs in gas storage and separation applications [37–42].

In this context, we focused on reducing the H_2 concentration in O_2

stream at the anode CL to enhance the safety of PEMWE operations by incorporating various functional groups into MOF structures and optimizing their concentrations within the anode CL (Fig. 1). We synthesized a functionalized MOF (f-MOF) with amine (MOF-NH₂), carboxylic acid (MOF-CO₂H), and sulfonic acid (MOF-SO₃H) groups and the effect of the f-MOFs on the H_2 adsorption properties through physical and electrochemical analyses. The H_2 fraction in O_2 was successfully reduced to 1.2 mol% at 50 mA cm⁻² upon MOF-NH₂ incorporation; this fraction is less than half of the lower explosion limit (LEL) of 4 mol%. This study demonstrates a practical approach to enhancing the operational safety of PEMWEs through MOF functionalization without requiring thicker membranes or expensive catalysts.

2. Experimental

2.1. Materials

1,2,4,5-benzenetetracarboxylic acid, ZrCl₄, acetone, acetic acid, 2-aminoterephthalic acid, 1-propanol, and N,N'-dimethylformamide (DMF) were purchased from Merck (Germany). NaSO₃-benzenedicarboxylate was obtained from TCI (Japan). NR212 Nafion membrane and dispersions (D2021 and D521) were sourced from Chemours (USA). Iridium oxide black was sourced from Boyaz Energy (Korea). Pt/C (10V50E, 46.7 wt% Pt) was supplied by Tanaka Kikinzoku Kogyo K.K. (Japan). A carbon-based gas diffusion layer (SGL, 39BC) was supplied by JNTG (Korea), while a titanium-based porous transport layer (PTL) was provided by LT Metal Ltd. (Korea). Deionized water (DI, 18 MΩ grade) was prepared using a Milli-DI water purification system (Germany).

2.2. Synthesis and characterizations of MOF-NH₂, MOF-CO₂H, and MOF-SO₃H

In a three-neck round-bottom flask fitted with a mechanical stirrer and condenser, 90 mmol of 1,2,4,5-benzenetetracarboxylic acid and 50 mmol of ZrCl₄ were dissolved in 300 mL of DMF at 25 °C. The mixture was transferred to an autoclave and heated to 120 °C and reacted for 24 h under a nitrogen atmosphere. After the reaction, the resulting white solid was filtered and thoroughly washed with deionized water and acetone to remove residual reactants. The final product, MOF-CO₂H, was dried in a vacuum oven at 25 °C [43]. MOF-NH₂ was synthesized using the same procedure, but with 2-aminoterephthalic acid replacing 1,2,4,5-benzenetetracarboxylic acid in the same molar amount [44]. For MOF-SO₃H preparation, a solution of NaSO₃-benzenedicarboxylate (0.33 g) in HCl (0.2 mL) was mixed with a solution of ZrCl₄ (0.29 g) in

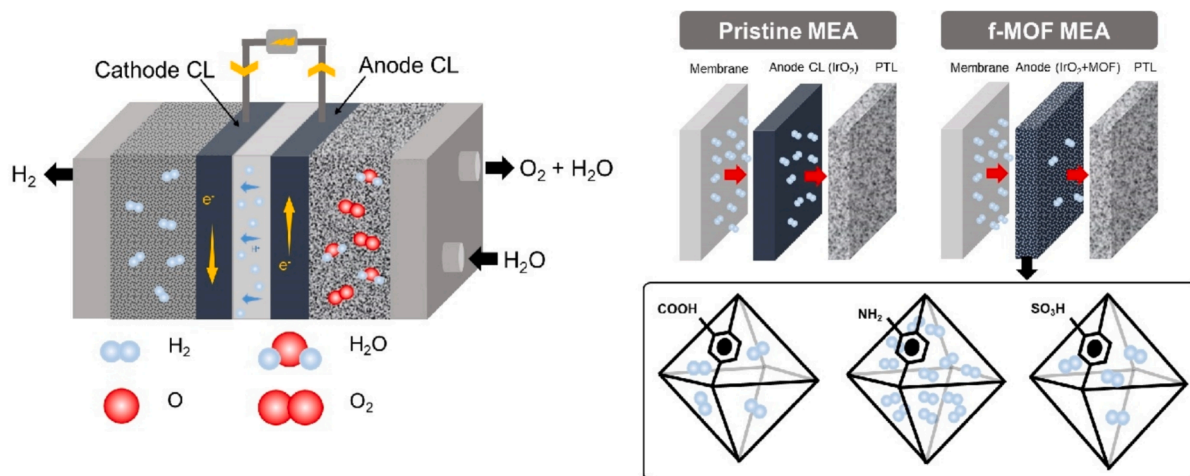


Fig. 1. Effect of incorporating a functionalized metal-organic framework (f-MOF) on the H_2 volume fraction in O_2 within the anode catalyst layer (CL) of a PEM water electrolyzer, including a schematic of the redox reactions in a PEMWE (Left) and a comparison of H_2 volume fraction changes in O_2 with and without f-MOF (Right).

15 mL of DMF, stirred for 30 min. and then heated to 120 °C, following the same procedure used for MOF-CO₂H [45]. The synthetic procedure was schematically illustrated in Fig. S1.

Powder X-ray diffraction (PXRD) analysis was conducted using a MiniFlex 600 diffractometer (Rigaku, Japan) in transmission geometry with Cu K α 1 radiation. The measurements were performed over a 2 θ range of 3–90° with a step size of 0.01°, using an accelerating voltage of 40 kV and a current of 15 mA.

The morphology and functional groups of f-MOF were analyzed via field-emission scanning electron microscopy (FE-SEM, SIGMA HD, Cal Zeiss), and its elemental composition was examined via energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax FlatQUAD). Functional groups of the f-MOF were characterized using FT-IR spectroscopy (Thermo Fisher Scientific, Nicolet 5700).

The thermogravimetric analysis (TGA, TA Instruments, TGA 5500) of the f-MOF was performed over a temperature range of 25 °C to 600 °C at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

Scanning transmission electron microscopy (STEM) images were obtained using an ultra-high resolution double Cs corrected TEM (FEI company, Titan cubed G2 60–300). For TEM sample preparation, the f-MOF was dispersed in ethanol and drop-cast onto molybdenum-based lacey carbon TEM grids.

2.3. CL fabrication and characterizations

The anode catalyst ink was prepared by mixing 0.8 g of IrO₂ black, 0.88 g of Nafion dispersion (D2021), 0.54 g of 1-propanol, and 0.48 g of DI water, and different amounts of f-MOF. The mixture was stirred mechanically at 500 rpm for 2 h using a magnetic stir bar; this was followed by an ultrasonic treatment for 150 s using a tip-type ultrasonicator. The f-MOF content was set at 0, 4, 8, 12, 16, and 20 wt%. The specified f-MOF ratio refers to its proportion relative to the combined mass of the catalyst and ionomer. For the cathode catalyst ink, 0.36 g of Pt/C and 3.7 g of ionomer (D521) were mixed in a similar manner, stirred at 500 rpm for 2 h and subsequently subjected to ultrasonic treatment for 210 s using a tip-type ultrasonicator. The resulting inks for anode or cathode were coated onto polytetrafluoroethylene (PTFE)-coated polyimide films using a 80 μ m-gap blade. The catalyst layers were initially dried at 35 °C for 30 min, followed by final drying at 80 °C for 2 h.

The morphology of the anode CLs was examined via field-emission scanning electron microscopy (FE-SEM, SIGMA HD, Cal Zeiss), while elemental composition was analyzed via EDS (Bruker Quantax FlatQUAD). The pore size distributions were determined using a mercury intrusion porosimeter (AutoPore V, Micromeritics).

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

The CCM was fabricated by transferring the anode or cathode CL onto an NR212 Nafion membrane using the decal method, applying 30.0 MPa and 130 °C for 10 min. The catalyst loadings after detaching the polyimide substrate were 2.0 mg_{IrO₂} cm⁻² for the anode CL and 0.4 mg_{Pt} cm⁻² for the cathode CL. A single cell was assembled with the CCM, GDL, Ti-PTL, flow fields featuring three serpentine channels, and end-plates; a clamping torque of 60 kgf cm⁻¹ was applied during the assembly.

The cell's performance was assessed by scanning the voltage between 1.35 and 1.90 V using a water electrolyzer test system; ambient pressure and a DI water flow rate of 30 mL min⁻¹ at 80 °C (Fig. S2, CNL energy, Korea). The cell voltage was increased by 0.05 V increments every 30 s. The H₂ concentration at the anode was measured at a constant current density using an integrated H₂ sensor. Electrochemical impedance spectroscopy (EIS, HCP-803, BioLogics) was performed in range of 10 kHz–0.1 Hz frequency with a 10 % voltage amplitude. The proton transport resistance within the anode CL of CCMs was evaluated

using EIS, wherein H₂ and N₂ gases were supplied to the anode and cathode CLs at flow rates of 300 and 600 mL min⁻¹, respectively.

The reversibility of f-MOF adsorption and desorption was evaluated by measuring the H₂ concentration in O₂ stream during temperature cycling between 30 °C and 80 °C. Following these cycles, the changes in the properties of the MEA containing the f-MOF were further analyzed via EIS, polarization curves, and H₂ concentration in O₂ stream.

3. Results and discussion

3.1. Synthesis and characterizations of functionalized metal–organic framework

The f-MOF was synthesized in accordance with previously established procedures [43,45,46] and was then incorporated into the anode CL of the PEMWE. Powder X-ray diffraction (PXRD) analysis (Fig. 2a–c) confirmed that the f-MOF corresponds to a cubic unit cell in the *Fm-3m* space group. The PXRD patterns exhibited two major diffraction peaks in the 2 θ range, corresponding to the (111) and (200) crystal planes. This diffraction pattern reflects the fundamental structural characteristics of the pristine UiO-66 framework and demonstrates that the same symmetry is maintained even after introducing functional groups. This stability can be attributed to the robust Zr₆O₄(OH)₄ metal cluster and the strong coordination bonds with the benzenedicarboxylic acid (BDC) linker in the MOF.

The f-MOFs with different groups significantly impacts its lattice parameter (*a*) and overall structure by altering steric effects, electronic properties, and interactions with the Zr clusters. The incorporation of smaller groups like –NH₂ results in the largest lattice parameter (*a* = 20.96 Å) and volume (*V* = 9213 Å³), as the weaker steric hindrance allows the framework to expand more freely. In contrast, bulkier and highly electronegative groups like –SO₃H lead to the smallest lattice parameter (*a* = 20.39 Å) and volume (*V* = 8476 Å³) due to increased electrostatic interactions and framework contraction. Functional groups like –CO₂H introduce intermediate effects, causing slight reductions in *a* (*a* = 20.68 Å) through steric and electronic interactions [47–49]. These changes, as shown in Table S1, highlight how functional groups modulate MOF structures, providing a pathway to tailor their properties for specific applications.

The results of morphological examination via FE-SEM and EDS indicated that the f-MOF composed of secondary particles, each measuring few micrometers. These secondary particles result from the clustering of spherical primary particles, which have diameters between 20 and 50 nm (Fig. 2d–(i), e–(i), and f–(i)). EDS analysis confirmed the presence of Zr (Fig. 2d–(ii), e–(ii), and f–(ii)) and O (Fig. 2d–(iii), e–(iii), and f–(iii)), indicating that these elements originate from the common moieties of the starting materials. Moreover, C (Fig. 2d–(iv)), N (Fig. 2e–(iv)), and S (Fig. 2f–(iv)) were also detected, confirming that the –CO₂H, –NH₂, and –SO₃H functional groups remained intact during the synthesis. FT-IR spectroscopy results further validated the presence of these functional groups (Fig. 2g). Strong absorption peaks at 1174 cm⁻¹ and 1076 cm⁻¹, corresponding to the stretching vibrations of sulfonic acid groups, were observed in the FT-IR spectrum of MOF-SO₃H [50]. Peaks at 3466 cm⁻¹ and 3354 cm⁻¹, related to asymmetric and symmetric N-H vibrations were observed in the FT-IR spectrum of MOF-NH₂ [51]. The spectra of all three f-MOF samples showed distinctive peaks at 1572 cm⁻¹ and 1355 cm⁻¹, corresponding to the symmetric and asymmetric stretching vibrations of carboxyl groups [52].

The TGA results for the f-MOF (Fig. 2h) reveal three distinct weight loss regions, consistent with the results reported in previous studies [37]. In the first stage, occurring between 25 °C and 130 °C, weight losses of 19.3 wt% for MOF-CO₂H, 14.2 wt% for MOF-NH₂, and 19.6 wt% for MOF-SO₃H were observed; these weight losses were attributed to the removal of guest molecules that were physically adsorbed. The lower weight loss in MOF-NH₂ suggests a stronger binding affinity with these guest molecules. The weight losses in the second stage, between 130 °C

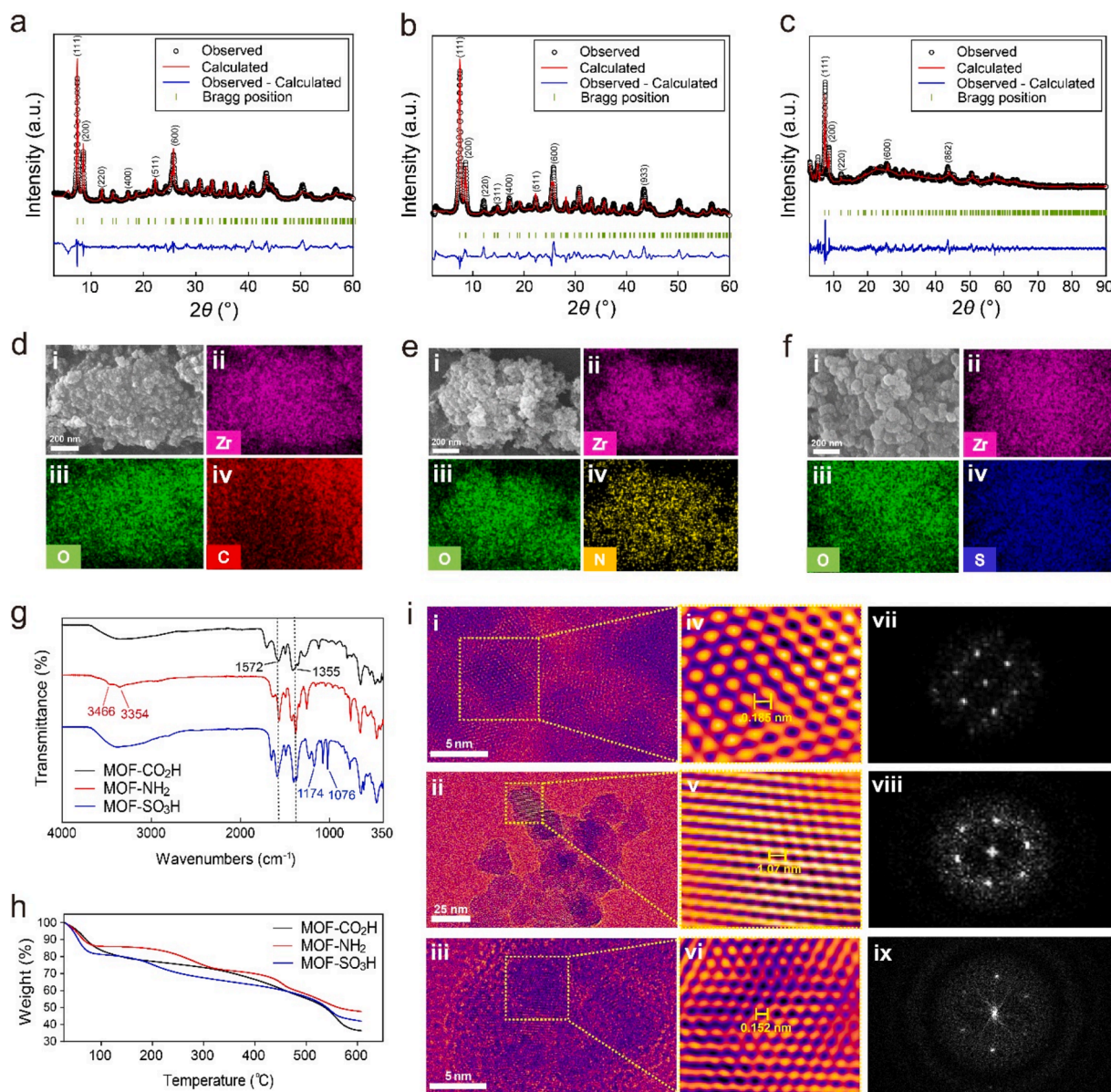


Fig. 2. Rietveld refinement of the powder X-ray diffraction patterns for (a) MOF-CO₂H, (b) MOF-NH₂, and (c) MOF-SO₃H. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of (d) MOF-CO₂H, (e) MOF-NH₂, and (f) MOF-SO₃H for Zr, C, O, N, and S. (g) FTIR spectra of the f-MOFs. (h) Thermogravimetric analysis (TGA) curves of the f-MOFs. (i) STEM image of the f-MOF along the [1 1 1] direction and fast Fourier transform analyses of the areas shown in Fig. 2(iv), (v), and (vi).

and 450 °C, were 19.6 wt% for MOF-CO₂H, 21.1 wt% for MOF-NH₂, and 20.0 wt% for MOF-SO₃H. The weight loss in the second stage is associated with the dehydroxylation of Zr clusters and the decomposition of functional groups (CO₂H, NH₂, SO₃H) within the MOF pores [53]. The third stage, occurring at temperatures above 450 °C, corresponds to the collapse of the MOF structure and the formation of ZrO₂. The guest molecule binding capacities of the f-MOF were further investigated via BET surface area (Fig. S3a), adsorption (Fig. S3a), and cumulative pore volume analyses (Fig. S3b). MOF-NH₂ exhibited a higher CO₂ adsorption capacity (3.5 mmol g⁻¹), surpassing MOF-CO₂H (1.2 mmol g⁻¹) and MOF-SO₃H (1.0 mmol g⁻¹). This enhanced CO₂ adsorption performance can be attributed to both chemisorption and physisorption mechanisms. Unlike other functional groups, the amino (-NH₂) group acts as a Lewis base, interacting with CO₂, which acts as a Lewis acid, to form a carbamate species (RNHCOO⁻) through acid-base interactions. This strong interaction provides selective CO₂ binding sites within the MOF framework, further enhancing adsorption. In addition, in terms of

physisorption, the high surface area (1072.9 m² g⁻¹) and large cumulative pore volume of MOF-NH₂ facilitate CO₂ adsorption. The cumulative pore volume of MOF-NH₂ (0.77 m³ g⁻¹) is approximately twice that of MOF-SO₃H (0.40 m³ g⁻¹) and more than three times that of MOF-CO₂H (0.21 m³ g⁻¹), indicating that MOF-NH₂ provides a more favorable environment for CO₂ adsorption.

Fig. 2i shows the structure of f-MOFs via STEM and fast Fourier transform (FFT) images. The low-magnification STEM images of MOF-CO₂H (Fig. 2i-(i)), MOF-NH₂ (Fig. 2i-(ii)), and MOF-SO₃H (Fig. 2i-(iii)) clearly reveal their porous structures. Among these, MOF-NH₂ exhibits a larger and wider pore structure compared to MOF-CO₂H and MOF-SO₃H. The distribution of pores is further examined in high-magnification STEM images with the pore diameters of MOF-CO₂H (Fig. 2i-(iv)), MOF-NH₂ (Fig. 2i-(v)), and MOF-SO₃H (Fig. 2i-(vi)) identified as 0.185, 1.070, and 0.152 nm, respectively, along the [111] direction. Moreover, the fast Fourier transform (FFT) images of these f-MOFs (Fig. 2i-(vii)–Fig. 2i-(ix)) confirm their well-developed cubic

crystal structure. The observed differences in pore sizes are attributed to the varying three-dimensional bulkiness of the linker compounds with functional groups, which react with ZrCl_4 during synthesis. In addition, the d-spacing analysis in the $[6\ 0\ 0]$ direction using STEM reveals trends consistent with changes in lattice parameters obtained from previous PXRD analysis (Fig. 2a–c, Fig. S4, Table S1) [54]. The variation in d-spacing values along the $[6\ 0\ 0]$ plane supports the idea that the differences in pore sizes induced by functional groups are directly related

to structural changes at the atomic level. These findings indicate that the structural variations caused by functionalized linkers influence both the crystallographic parameters and the resulting pore structures. Consequently, these distinct pore structures, confirmed by both PXRD and STEM analysis, are expected to affect the catalyst layer architecture and gas adsorption characteristics, which will be discussed in detail in the subsequent sections. The XPS spectra of f-MOF (Fig. 4g–i) revealed the C1s peak for MOF- CO_2H (283.1 eV), the N1s peak for MOF- NH_2 (397.1

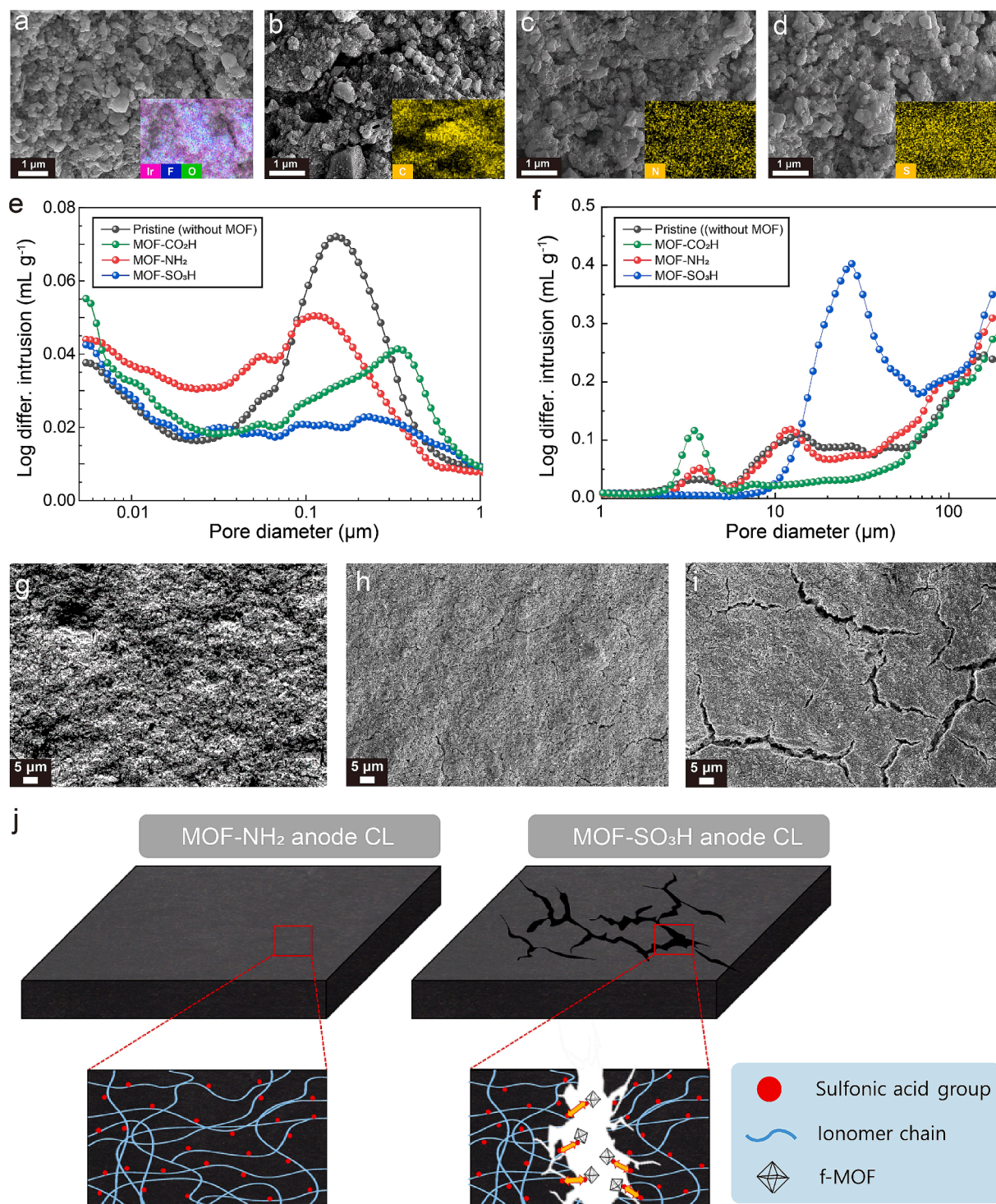


Fig. 3. High magnification SEM images and their EDS mapping (inset) of (a) the pristine anode CL and the anode CL with (b) MOF- CO_2H , (c) MOF- NH_2 , and (d) MOF- SO_3H . Pore size distributions for anode CLs containing f-MOF (e) below 1 μm pore diameter and (f) above 1 μm pore diameter. Low magnification SEM images of the anode CL with (g) MOF- CO_2H , (h) MOF- NH_2 , and (i) MOF- SO_3H . (j) Schematic illustration of crack formation in the catalyst layer.

eV), and the S2p peak for MOF-SO₃H (165.6 eV), demonstrating that the functional groups were successfully synthesized into the MOF.

3.2. Morphological properties of CLs

The morphological characteristics of the anode CLs were examined via SEM and EDS analyses (Fig. 3 and Fig. S5). Surface SEM images (Fig. 3a–c) reveal that the f-MOF-containing anode CLs forms agglomerates consisting of the catalyst, polymeric ionomer, and f-MOF, with sizes ranging from tens to hundreds of nanometers. The size of these agglomerates varies depending on the type of f-MOF, likely due to differences in interactions between the functional groups of the f-MOF and the ionomer. Furthermore, their low density results in them occupying a significant volume within the catalyst layer. The elemental mapping images (Fig. 3a–c inset) confirm the presence of C, N, and S elements in the anode CLs, corresponding to MOF-CO₂H, MOF-NH₂, and MOF-SO₃H, respectively, indicating that the f-MOF is uniformly distributed throughout the anode CL. Moreover, these images indicate uniform distribution of Ir and F in the anode CL (Fig. S5a–i), corresponding to the iridium oxide catalyst and Nafion ionomer, respectively, both evenly dispersed with the f-MOF in the anode CL.

The effect of f-MOF on the pore structure of the CL was examined by analyzing the pore size distribution via mercury intrusion porosimetry, with a focus on pores smaller than 1 μm (Fig. 3d). The results of pore size analysis, shown in Fig. 3d, indicate that the anode CL with MOF-NH₂ has a larger pore volume than the pristine anode CL, whereas the pore volumes were lower for the anode CLs with MOF-CO₂H and MOF-SO₃H.

This decrease is due to the lower density of f-MOF (0.43–1.05 g cm⁻³) compared to that of the Nafion ionomer (2.04 g cm⁻³). Consequently, the f-MOF occupies a significant volume within the ionomer matrix, thereby reducing the pore volume in anode CLs with MOF-CO₂H and MOF-SO₃H [32,54]. In contrast, the increased pore volume in the anode CL with MOF-NH₂ is attributed to its large surface area and internal pore volume (Fig. S3), which compensate for pore reduction via accommodation of additional ionomer volume. Fig. S6 shows that MOF-NH₂ has the largest average pore diameter (31.9 nm). In comparison, the average pore diameters of MOF-CO₂H and MOF-SO₃H were 5.7 nm and 11.3 nm, respectively. These results support the findings of pore size distribution trend for pores smaller than 1 μm . For pore size distributions measuring over 1 μm (Fig. 3e), the micropore volume of the MOF-SO₃H-containing CL was larger than those in other anode CLs. To confirm these results, low-magnification SEM images of the anode CLs containing MOF-CO₂H, MOF-NH₂, and MOF-SO₃H were acquired (Fig. 3f–h). Aligned with the pore size distribution shown in Fig. 3e, microcrack formation was minimal in the anode CLs with MOF-CO₂H and MOF-NH₂, whereas extensive microcracks were observed in the anode CL with MOF-SO₃H. This is attributed to the SO₃H group, which disrupts the entanglement of Nafion chains due to repulsion with the SO₃H side chain of Nafion, leading to microcrack formation (Fig. 3i). This indicates that the presence of f-MOF interferes with the ionomer chain connectivity in the micro-sized regions. Thus, the extensive internal nanopores in the f-MOF contribute to increased nanopore formation within the anode CL, which, in turn, plays a crucial role in enhancing its performance, as discussed in subsequent sections.

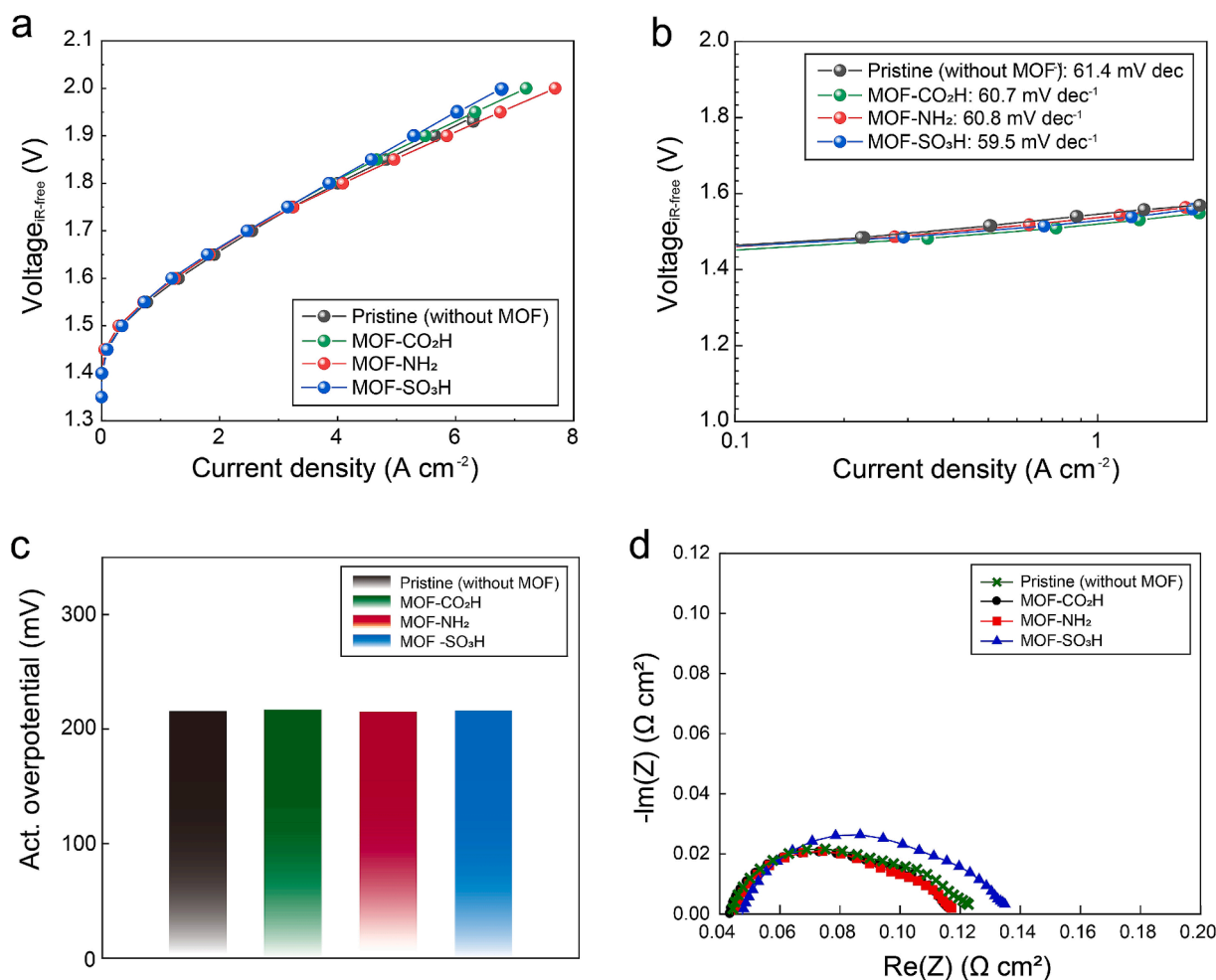


Fig. 4. (a) Polarization curves, (b) Tafel plots, (c) Activation overpotential at 0.1 A cm⁻², and (d) Nyquist plots for MEAs with MOF-CO₂H, MOF-NH₂, and MOF-SO₃H.

3.3. Effect of f-MOF on cell performance

The influence of f-MOF on cell performance was assessed through polarization curve measurements. At current densities below 3.5 A cm^{-2} , the polarization curves remained identical, regardless of the MOF functionalization groups (Fig. 4a). However, above 3.5 A cm^{-2} , marginal differences in the performance were observed. The increased voltage in the MEA containing MOF-SO₃H is likely due to the reduced nanopore volume within the anode CL, which hinders water and oxygen transport, as indicated in Fig. 3d.

The influence of the f-MOFs on the kinetic performance was further examined using iR-corrected polarization curves generated by measuring the ohmic resistance (R_{ohm}) at 1 kHz via EIS. The activation overpotential (η_{act}) of the cell was calculated from the iR-corrected polarization curves using the Tafel equation: $\eta_{\text{act}} = a \cdot \log(j) + b$, where a represents the Tafel slope. The activation overpotential was calculated in the current density range of $0.01\text{--}0.1 \text{ A cm}^{-2}$, where mass transport and ohmic overpotentials are negligible. As shown in Fig. 4b, the Tafel slopes for the MEAs with f-MOFs range between 59.5 mV dec^{-1} to 60.8 mV dec^{-1} , indicating that introducing f-MOFs into the anode CL have a minimal effect on the anodic kinetics of PEMWE. Furthermore, Fig. 4c and Table 1 reveal that the η_{act} at 0.1 A cm^{-2} for the different f-MOFs follows a similar trend, with a maximum variance of less than 2 mV, suggesting that differences in the MEA performance are not driven by changes in η_{act} .

The effect of f-MOF on the cell performance was further examined via EIS. In the Nyquist plots, the high-frequency intercept on the real axis represents the R_{ohm} , and the first and second semicircle intercepts correspond to the charge transfer resistance (R_{ct}) and mass transport resistance (R_{mt}), respectively. All MEAs exhibited nearly identical R_{ohm} values; however, the R_{mt} of the MEA containing MOF-SO₃H was than that of others (Fig. 4d and Table 1). This suggests that the slight incorporation of f-MOF has minimal impact on the proton conduction of MEA. These results are consistent with polarization curves wherein the performances were similar up to 3.5 A cm^{-2} . At current densities above 3.5 A cm^{-2} , MOF-SO₃H exhibited the highest R_{mt} . This may be due to the severe cracks in the MOF-SO₃H containing anode CL, as shown in Fig. 3h. These cracks might have hindered uniform water supply to the catalyst layer or the efficient release of produced oxygen. The influence of f-MOF on proton conduction resistance (R_{CL}) within the anode CL was further investigated via EIS of the MEAs with f-MOF using H₂ as the anode feed and N₂ as the cathode feed. The R_{CL} is usually calculated as three times the distance between the high-frequency intercept and the point where the tangent line from the sloped low-frequency region intersects the real axis (Fig. S7). The spectra were shifted to the origin to aid identification and comparison. The R_{CL} values for the pristine, MOF-CO₂H, MOF-NH₂, and MOF-SO₃H MEAs were 113.5, 118.9, 102.9, and 109.5 $\text{m}\Omega \text{ cm}^2$, respectively. The nearly identical R_{CL} values for the pristine, MOF-CO₂H, and MOF-NH₂ MEAs suggest that do not impede ion or electron transport within the anode CL despite being insulators. In addition, the limited effect of f-MOFs on the overall cell performance is due to the considerably smaller value of R_{CL} compared to the value of R_{ohm} .

3.4. Effect of f-MOF on H₂ content in O₂

The effect of f-MOF on the H₂ volume fraction in O₂ (Φ_{H_2}) was evaluated by measuring the Φ_{H_2} at the anode outlet while recording the polarization curve under varying current densities (Fig. 5a). The Φ_{H_2} was the highest for the pristine MEA at all current densities, and was greater than half of the LEL (2 mol%) for the H₂/O₂ gas mixture. In contrast, the Φ_{H_2} was the lowest for the MEA with MOF-NH₂. This effect is due to the larger pore volume and the wider surface area of MOF-NH₂, which facilitates the capture of a larger number of permeated H₂ molecules at the anode CL. Thus, MOF-NH₂ reduces the risk of explosion by preventing the mixing of H₂ with O₂ at the anode CL. Furthermore, although the cell performance decreases when using the thicker N115 membrane (Fig. S8a), the Φ_{H_2} reduction effect due to MOF-NH₂ (Fig. S8b) is still preserved.

The MEAs with MOF-CO₂H and MOF-SO₃H also exhibited a lower Φ_{H_2} than the pristine MEA, although the effect was worse than that of the MOF-NH₂. The H₂ adsorption capacity in the f-MOFs at different current densities was quantified as follows: the adsorption capacity was calculated by subtracting the Φ_{H_2} of the f-MOF MEAs from that of the pristine MEA (Fig. 5b). The MOF-NH₂ exhibited an H₂ adsorption capacity of approximately 1.0 % at 50 mA cm^{-2} , with the Φ_{H_2} reduced to 1.2 % (from 2.2 % for the pristine MEA); this corresponds to a 45.5 % reduction in Φ_{H_2} . Additionally, the H₂ adsorption flux as a function of the current density was calculated based on the H₂ adsorption capacity and total H₂ flux at the anode outlet, and the linear fitting results are shown in Fig. 5c and Table 1. The slopes for MOF-CO₂H, MOF-NH₂, and MOF-SO₃H were 4.6×10^{-4} , 25.3×10^{-4} , and $9.0 \times 10^{-4} \text{ mmol sec}^{-1} \text{ A}^{-1}$, respectively. These findings confirm that MOF-NH₂ exhibits a significantly higher adsorption rate than MOF-CO₂H and MOF-SO₃H owing to its larger surface area and a pore structure optimized for gas adsorption. To examine the influence of MOF-NH₂ on Φ_{H_2} under varying pressures, we measured the Φ_{H_2} values across different current densities at absolute pressures of 1 bar, 3 bar, and 5 bar. The results showed an increase in Φ_{H_2} values with rising pressure, with a particularly pronounced effect at low current densities. This phenomenon occurs because higher operating pressures lead to greater hydrogen crossover, and the effect becomes more noticeable at low current densities due to the lower oxygen production compared to high current densities (Fig. S9).

In summary, MOF-SO₃H exhibits the highest Φ_{H_2} value due to its smaller surface area compared to MOF-NH₂ and the bulky, three-dimensional structure of the SO₃H functional group, which impedes H₂ adsorption. Similarly, MOF-CO₂H shows a relatively high Φ_{H_2} value because of its lower surface area and pore volume compared to the other two MOFs. Due to these structural and physical properties, MOF-CO₂H has an H₂ heat of adsorption energy ranging from 6 to 20 kJ mol^{-1} [55,56], making H₂ adsorption more difficult compared to MOF-NH₂, which has a lower value of 8.2 kJ mol^{-1} [57]. Although MOF-SO₃H has a relatively low H₂ heat of adsorption energy of 5.5 kJ mol^{-1} , both adsorption and desorption are hindered by the bulkiness of its functional group [38,58]. The schematic representation of this is shown in Fig. 5d.

Table 1
Electrochemical data for MEAs with f-MOF.

	Voltage at 6 A cm^{-2} (V)	Tafel slop (mV dec^{-1})	Activation overpotential (mV)	R_{ohm} ($\text{m}\Omega \text{ cm}^2$)	R_{mt} ($\text{m}\Omega \text{ cm}^2$)	R_{CL} ($\text{m}\Omega \text{ cm}^2$)	Slop of fit curves of H ₂ adsorption flux ($\times 10^{-4} \text{ mmol s}^{-1} \text{ A}^{-1}$)
Pristine	1.91	61.4	216.4	44.1	44.6	113.5	—
MOF-CO ₂ H	1.92	60.7	217.0	43.4	47.0	118.9	4.6
MOF-NH ₂	1.90	60.8	217.9	44.8	45.5	102.9	25.3
MOF-SO ₃ H	1.95	59.5	216.0	45.4	53.5	109.5	9.0

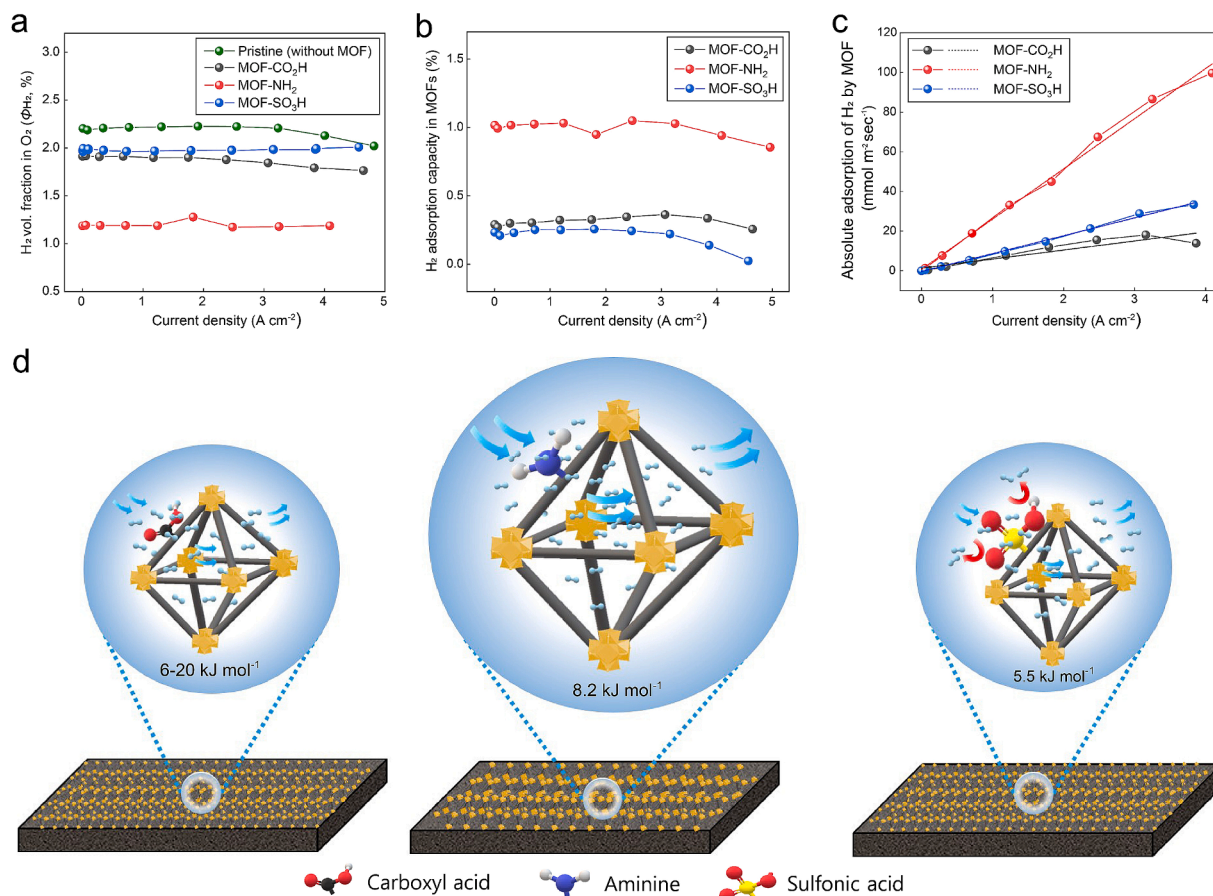


Fig. 5. (a) H_2 volume fraction in O_2 (Φ_{H_2}) for both pristine and f-MOF MEAs as a function of current density. (b) H_2 adsorption capacity in f-MOF. (c) Absolute amount of H_2 adsorbed by f-MOF at the anode outlet. (d) Schematic illustration of gas adsorption in f-MOF.

3.5. Cyclability of f-MOF and ex-situ analysis

The H_2 adsorption reversibility of the f-MOFs was analyzed as follows. The Φ_{H_2} of the MEAs with f-MOFs was measured by recording the polarization curves at both 30 °C and 80 °C over 10 cycles. The rate of increase in Φ_{H_2} was calculated based on the initial cycle at both temperatures under an operating current density of 100 mA cm⁻². As shown in Fig. 6a, the rate of increase in Φ_{H_2} is higher at 80 °C than at 30 °C. This difference can be attributed to the higher kinetic energy of the gas molecules at elevated temperatures, which reduces the H_2 adsorption efficiency of the f-MOFs at 80 °C. Moreover, with an increase in the number of cycles, the rate of increase in Φ_{H_2} increased at both temperatures, indicating a gradual decline in the H_2 adsorption capacity of the f-MOFs with repeated use. The MEA with MOF-NH₂ exhibited a lower rate of increase in Φ_{H_2} compared to the MEAs with MOF-CO₂H and MOF-SO₃H. Hence, MOF-NH₂ is more effective in reversible gas adsorption and desorption at both 30 °C and 80 °C. Moreover, the increase rate of Φ_{H_2} for the MEAs with MOF-NH₂ and MOF-SO₃H increased gradually over the 10 cycles, whereas the Φ_{H_2} for the MEA with MOF-CO₂H increased sharply up to the 5th cycle and stabilized thereafter until the 10th cycle. Fig. 6b shows the difference in Φ_{H_2} value between 30 °C and 80 °C depending on the cycle. The MEA with MOF-NH₂ exhibited a largely consistent difference in Φ_{H_2} , whereas other MEAs exhibited a reduced difference with an increase in the number of cycles. By the 10th cycle, the MEA with MOF-NH₂ sustained a difference of 0.25 %, whereas the MEAs with MOF-CO₂H and MOF-SO₃H exhibited differences of 0.14 % and 0.1 %, respectively. The smaller differences for the MOF-CO₂H and MOF-SO₃H MEAs indicate a reduction in the reversible adsorption/desorption efficiency, likely due to an incomplete desorption of the initially adsorbed gas during the temperature cycles.

This can result in the formation of dead zones within the internal pores and on the surface, thereby reducing the adsorption capacity over time. Moreover, H_2 molecules are physisorbed onto the MOF surface through weak van der Waals forces, without altering the electronic orbital structure in MOF-CO₂H and MOF-NH₂. On the other hand, MOF-SO₃H undergoes chemisorption due to interactions with the functional group, leading to lower cyclability compared to MOF-NH₂ because of reduced desorption capability [38]. The low cyclability of MOF-CO₂H is attributed to the limited surface area and the high heat of adsorption for H_2 , making desorption more difficult as mentioned previous section.

Ex-situ analyses after the cycling tests were conducted via polarization curve, EIS measurements, and SEM imaging. The polarization curves of MOF-CO₂H (Fig. 6c), MOF-NH₂ (Fig. 6d), and MOF-SO₃H (Fig. 6e), indicate a marginal performance decrease in the high current density region (>5 A cm⁻²) where R_{mt} has a significant effect. The current density regions affected by the R_{ohm} and R_{ct} exhibited minimal changes. The results of the EIS analysis (Fig. 6f and Table 2) revealed that the changes in the R_{ohm} , R_{ct} , and R_{mt} values before and after thermal cycling were the smallest for MOF-NH₂. In particular, R_{ohm} (1.0 mΩ cm²) and R_{ct} (10.5 mΩ cm²) remained almost unchanged. In contrast, although the R_{ohm} values of MOF-CO₂H (3.5 mΩ cm²) and MOF-SO₃H (1.4 mΩ cm²) showed minimal variation, their R_{ct} values (15.7 mΩ cm² and 13.5 mΩ cm², respectively) and R_{mt} values (9.4 mΩ cm² and 7.3 mΩ cm², respectively) exhibited considerable increases compared to the changes in R_{ohm} . This indicates that although f-MOF addition has minimal impact on the proton conductivity during durability testing, it has a significant effect on the R_{ct} and R_{mt} . The substantial increase in R_{mt} suggests that the morphological changes in the anode CL are the primary factor for durability. To confirm this, SEM images and EDS maps of the catalyst layers were obtained after cycling (Fig. 6g and Fig. S10). The

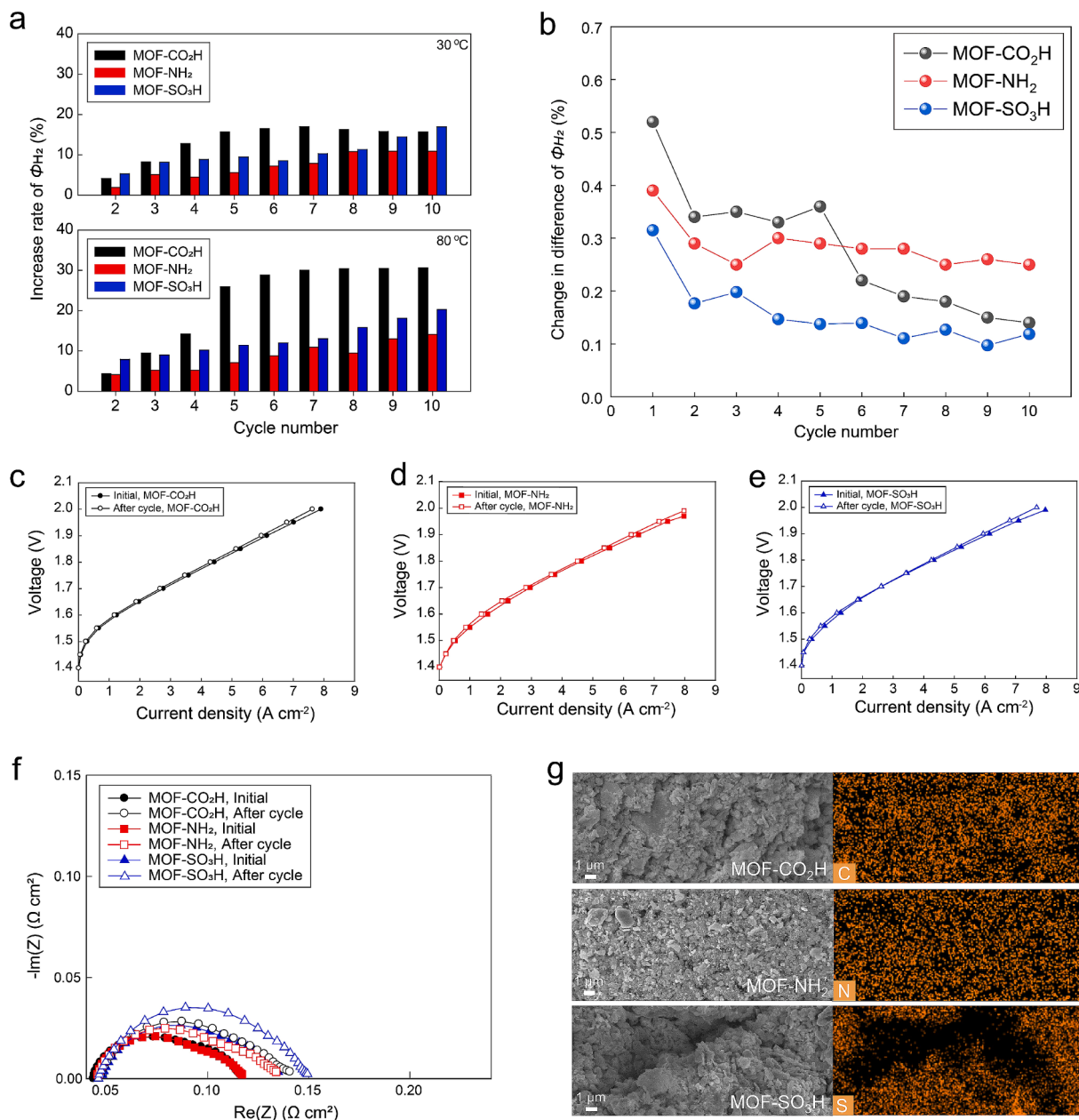


Fig. 6. (a) Variation of H_2 volume fraction in O_2 (Φ_{H_2}) during temperature cycling between 30 °C and 80 °C. (b) Change in the difference of H_2 volume fraction in O_2 (Φ_{H_2}) between 30 °C and 80 °C. Polarization curves of MEAs with (c) MOF- CO_2H , (d) MOF- NH_2 , and (e) MOF- SO_3H both before and after the temperature cycling. (f) Nyquist plots of MEAs with f-MOF before and after the temperature cycling. (g) SEM images of anode CLs after temperature cycling and their EDS map for C, N, and S elements.

Table 2

Voltage and resistance changes of MEAs with f-MOF during thermal cycling.

	ΔV at 6 A cm $^{-2}$ (mV)	ΔR_{ohm} (m Ω cm 2)	ΔR_{ct} (m Ω cm 2)	ΔR_{int} (m Ω cm 2)
MOF- CO_2H	11	3.5	15.7	9.4
MOF- NH_2	11	1.0	10.5	6.3
MOF- SO_3H	12	1.4	13.5	7.5

results revealed cracks on the surface of the anode CLs containing MOF- CO_2H and MOF- SO_3H . In particular, the anode CL with MOF- SO_3H exhibited more severe cracking compared to the initial state, leading to increased resistance during mass transport and subsequent performance

degradation. The formation of these cracks is attributed to the functional groups of MOF- CO_2H and MOF- SO_3H interfering with chain entanglement in the ionomer through repulsive interactions within the catalyst layer.

Furthermore, to assess the sustained effect of MOF- NH_2 under continuous operation at high current conditions, we performed a 91 h continuous operation at 1.8 V and measured the Φ_{H_2} values before and after the test (Fig. S11a). Over the 91-hour period, a performance decline of 156 mA h $^{-1}$ was observed, and after continuous operation, the Φ_{H_2} value at 1 A cm $^{-2}$ increased from the initial 1.19 % to 1.81 % (Fig. S11b). This increase is attributed to the possible degradation of MOF- NH_2 under high current density conditions or a decrease in the reversibility of hydrogen adsorption and desorption. We also measured the cell performance (Fig. S11c) and CV (Fig. S11d) before and after continuous operation. The results showed a decline in both low and high

current performance, along with a reduction in ECSA. While the effect of MOF-NH₂ diminished compared to the initial state, the Φ_{H_2} value remained below the LEL of 4 %, confirming that stable operation was maintained. To examine the changes in the MOF within the electrode after continuous operation, we measured the XPS (Fig. S11e–g) and XRF (Fig. S11h) of the anode catalyst layer. The XPS data indicated that the functional groups of the MOF were maintained even after high current continuous operation. However, the XRF-based quantitative analysis of the Zr element showed a notable reduction in its quantity. The amount of MOF-SO₃H decreased the most, while MOF-NH₂ experienced the least loss. This can be attributed to the formation of numerous cracks in the catalyst layer for MOF-SO₃H, as mentioned earlier, which led to a decline in its mechanical properties.

4. Conclusions

In this study, f-MOF containing –CO₂H, –NH₂, and –SO₃H groups were synthesized. The f-MOFs were introduced into the anode CL as a gas adsorbent, and its impact on the H₂ volume fraction in O₂ (Φ_{H_2}) was examined. The introduction of MOF-NH₂ resulted in the lowest Φ_{H_2} , which was consistently less than half of LEL (2 mol%). This indicates that the H₂ permeating from the cathode to the anode was partially adsorbed by the MOF-NH₂ molecules. The effectiveness of MOF-NH₂ is attributed to its large surface area and internal pores, which facilitate the adsorption and desorption of the permeated H₂ gas. Moreover, the reversible characteristic of the f-MOF were evaluated by measuring Φ_{H_2} during thermal cycling. The MEA containing MOF-NH₂ exhibited the slowest increase in Φ_{H_2} regardless of the temperature and maintained a relatively constant difference in Φ_{H_2} between 30 °C and 80 °C. This indicates that gas adsorbents with a high surface area and internal pores are essential to ensure the safe operation of PEMWEs under ambient pressure. Thus, this study provides important guidance for optimizing the CL to promote the safe operation of PEMWE. Furthermore, it has the potential to be expanded into future research on fuel cell or lithium-ion battery electrodes.

CRediT authorship contribution statement

Inku Kang: Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Sojin Lee:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Won-Jong Choi:** Validation, Formal analysis, Data curation. **Siyeon Lee:** Validation, Formal analysis, Data curation. **Soonyong So:** Formal analysis, Data curation. **Duk Man Yu:** Formal analysis, Data curation. **Sang Jun Yoon:** Formal analysis, Data curation. **Dong-Won Kim:** Writing – review & editing, Writing – original draft, Supervision, Data curation, Conceptualization. **Kwan Woo Nam:** Writing – review & editing, Writing – original draft, Supervision, Data curation, Conceptualization. **Keun-Hwan Oh:** Writing – review & editing, Writing – original draft, Supervision, Data curation, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.161094>.

Data availability

Data will be made available on request.

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