*Chinese Journal of*
**POLYMER SCIENCE**

REVIEW

https://doi.org/10.1007/s10118-026-3638-1
*Chinese J. Polym. Sci.*

# Covalent Organic Frameworks Modified Composite Proton Exchange Membranes towards Advanced Fuel Cells

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**Abstract** The urgent global demand for clean energy has positioned proton exchange membrane fuel cells (PEMFCs) as a pivotal technology owing to their high efficiency and environmental friendliness. Their performance critically relies on the proton exchange membranes (PEMs). Recently, integrating covalent organic frameworks (COFs) into conventional proton-conducting polymers has gained increasing, as this strategy is expected to combine the structural advantages of COFs with polymer flexibility to develop advanced PEMs. This review briefly outlines the current types of PEMs and the COF design for proton conducting. Then the fabrication strategies and evaluation methods are introduced. The design of COF-modified Nafion and sulfonated polyetheretherketone (SPEEK) for low-humidity proton conduction, as well as COF-modified polybenzimidazole (PBI) for high-temperature proton conduction were summarized, with particular emphasis on COFs forming continuous "proton highways" within polymer matrices for enhanced conduction while leveraging molecular sieving to suppress fuel crossover and thus improve cell efficiency and safety. Finally, critical challenges and outlook of COF-modified PEMs are discussed, such as interfacial compatibility, COF agglomeration, and the long-term stability and scalability under harsh conditions, which severely hinder the practical applications. Potential solutions are proposed, including *in situ* growth, hierarchical pore design, and gradient doping, to improve interfacial compatibility while maintaining excellent mechanical properties, as well as the development of intelligent and multifunctional PEMs.

**Keywords** Covalent organic frameworks; Proton exchange membranes; COF-modified PEMs; Interfacial compatibility

**Citation:** Ban, M. H.; Wu, J. L.; Han, Y. M.; Yang, A. P.; Ding, Q.; Xu, F. Covalent organic frameworks modified composite proton exchange membranes towards advanced fuel cells. *Chinese J. Polym. Sci.* https://doi.org/10.1007/s10118-026-3638-1

## 1 INTRODUCTION

The continuous depletion of fossil fuels such as coal and petroleum, has triggered great threats to environmental and development of mankind. Consequently, there is an urgent need to seek renewable and sustainable fuel sources such as solar, wind, and hydroenergy, which however faces challenges of intermittency and discontinuity. Developing and deploying of highly efficient clean energy utilization technologies is therefore essential for the future economy and society. Proton exchange membrane fuel cells (PEMFCs), which enable the direct conversion of chemical energy to electricity *via* electrochemical reactions between hydrogen and oxygen, have been recognized as a groundbreaking innovation to offer a highly efficient and environmentally friendly pathway for clean energy. By fundamentally moving beyond the inefficiencies of conventional combustion, this technology represents a pivotal shift in power generation. The electrochemical conversion process enables a remarkably efficient pathway for energy release, achieving near-zero emissions of greenhouse gases and eliminating the associated release of airborne pollutants common to fuel-burning systems. This emerging technology directly addresses the dual challenges of energy efficiency and environmental sustainability, positioning it as a cornerstone for the development of a truly clean and modern energy infrastructure.

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Special Topic: Porous Polymers
Received December 24, 2025; Accepted March 1, 2026; Published online April 16, 2026

As the central and indispensable component within PEMFCs, proton exchange membranes (PEMs) are a type of proton conductive polymers that selectively facilitate proton conduction from the anode to the cathode while effectively separate reactant gases and serve as an electrical insulator. Therefore, the inherent properties of the PEM directly set the theoretical ceiling for the device-level efficiency and long-term operational stability. As multifunctional modules, advanced PEMs are required to meet two competing operational demands simultaneously: they must create high-efficiency, direction-specific pathways for proton transport from anode to cathode, while also provide strong resistance against gas permeation.

The past decades have witnessed the significant advancements of polymer-based PEMs,[1] which can be categorized into three types based on conduction groups: (1) Nafion and sulfonated polyetheretherketone (SPEEK) which operates *via* sulfonic acid group conduction, (2) poly(vinylphosphonic acid) (PVPA)[2] and phosphoric acid-doped quaternary ammonium salt-grafted polystyrene (PA-QASOH)[3] based on phosphate-mediated conductivity, and (3) polybenzimidazole (PBI) membranes whose conductivity is facilitated by nitrogen-containing groups. DuPont's Nafion membranes, currently hold a dominant position in the commercial market, which are distinguished by their relatively high proton conductivity, typically exceeding 0.1 $S\cdot cm^{-1}$ at temperatures below 90 °C.[4] However, Nafion-type membranes are still restricted by substantial deterioration in proton conductivity under harsh elevated temperature above 100 °C.[5] Therefore, the development of PEMs that are capable of stable operation at high temperatures remains to be challenge.[6] Meanwhile, the precise regulation of the self-assembled hydrophilic microdomains in polymer chains is still elusive due to the complex influencing factors.[7] Therefore, increasing research interest has been focused on the design and synthesis of novel materials with precisely controlled and tunable architectures, which can maintain efficient proton conduction even under harsh operational environments (*e.g.*, high temperatures and low humidity levels).

Since the pioneered work by Yagi research group in 2005,[8] covalent organic frameworks (COFs) show unique advantages of low framework density, ultrahigh porosity[9,10] and atomic-level structural tunability,[11] benefiting from their lightweight organic building blocks connected *via* strong covalent bonds. Therefore, COFs are regarded as promising candidates for a wide range of applications, including photocatalysis,[12−15] molecular sieving,[10,16] energy storage.[17−21] Particularly, COFs have garnered significant attention as novel porous materials for proton conduction, due to the designable functional groups,[22] periodic structural alignment,[23] hydrophilic/hydrophobic nanoconfinement,[24, 25] optimal interlayer spacing,[26] and robust thermal stability.[27] The proton conductivity of proton-conducting COFs is primarily achieved by their various functional groups, such as sulfonic acid groups, phosphoric acid groups and nitrogen-containing groups as well as pore confinement of proton conducting guests, which has been reviewed.[20,28,29] For example, COF confined excess $H_3PO_4$ demonstrates high anhydrous conductivity of 0.191 $S\cdot cm^{-1}$.[30] An even higher conductivity of 1.4 $S\cdot cm^{-1}$ was achieved by extending the structural dimensionality of COFs.[31] However, considering the difficult processability into commercially required flexible membranes,[32] possible degradation and carrier loss,[33] the introduction of these conductive COFs into conventional proton-conducting polymer matrices could not only allow flexible processability, but also strengthen the mechanical properties and dimensional stability of the conventional membranes. Meanwhile, the integration of highly ordered and functionalized nanochannels from COFs helps to construct an efficient "proton highway" within the proton-conducting polymers.[30] Such "ordered-continuous" composite structure not only significantly enhances proton conductivity, especially under low humidity conditions, but also effectively suppresses fuel penetration by utilizing the sieving effect of COF channels, realizing a synergistic optimization of proton transport and barrier performance.

In 2016, Jiang's group developed $H_3PO_4$@SNW-1/Nafion composite membranes with improved interfacial compatibility and optimized hydrophilic domains, thus creating ordered and efficient proton transfer pathway.[34] In 2019, Zhang's group exfoliated sulfonic acid-functionalized materials into nanosheets (SCONs), which can shorten ion channels and facilitate proton diffusion; the uniform ion channels formed *via* electrostatic interactions endowed Nafion-SCONs composite membranes with enhanced proton conductivity and suppressed methanol permeability.[35] In 2024, Wang's group designed a proton exchange membrane material composed of Nafion and COFs linked by $\alpha$-aminoketone. This composite system not only significantly enhances the water retention capacity of the catalyst layer and accelerates the proton conduction rate, but also effectively ensures gas permeability; in fuel cell tests, compared with the system using pure Nafion as the proton exchange membrane, its power density is increased by 1.9 times.[36] Despite these achievements, COF-modified PEMs still face several critical challenges in practical applications, such as poor interfacial compatibility between COFs and polymer matrices, structural degradation and performance deterioration caused by severe agglomeration of COFs as well as the ambiguous proton conduction mechanism in composite membranes. In addition, the long-term operational stability of COFs against hydrolysis and degradation within the polymer matrix remains a critical challenge, and relevant post-operation device validation has been rarely reported. These shortcomings collectively hinder the practical application of COF-modified PEMs from material properties to device.

This review will systematically summarize the synthetic strategies for COF-modified multifunctional PEMs using Nafion, SPEEK, and PBI as the polymer matrices (Figs. 1a−1c). While few works using proton-conductive polymer based on phosphoric acid functional groups (*e.g.*, PVPA or PA-QASOH). Focusing on the key issue of improving the proton conductivity of PEMs under low humidity and high temperature conditions, this work mainly clarifies the mechanism by which COFs enhance proton conductivity and water retention, with an emphasis on the construction of molecular-level precise channels to optimize the proton conduction pathways. Furthermore, the performance of the COF-modified composite PEMs within practical membrane electrode assembly (MEAs) will be evaluated to assess their potential applications. Finally, the relationship between the structures of PEMs (including dimensions, sizes, chemical properties, *etc.*) and their properties (proton conductivity, stability, water retention, *etc.*) will be established, which is expected to provide a theoretical foundation for the design and development of the next-generation high-performance PEMs.

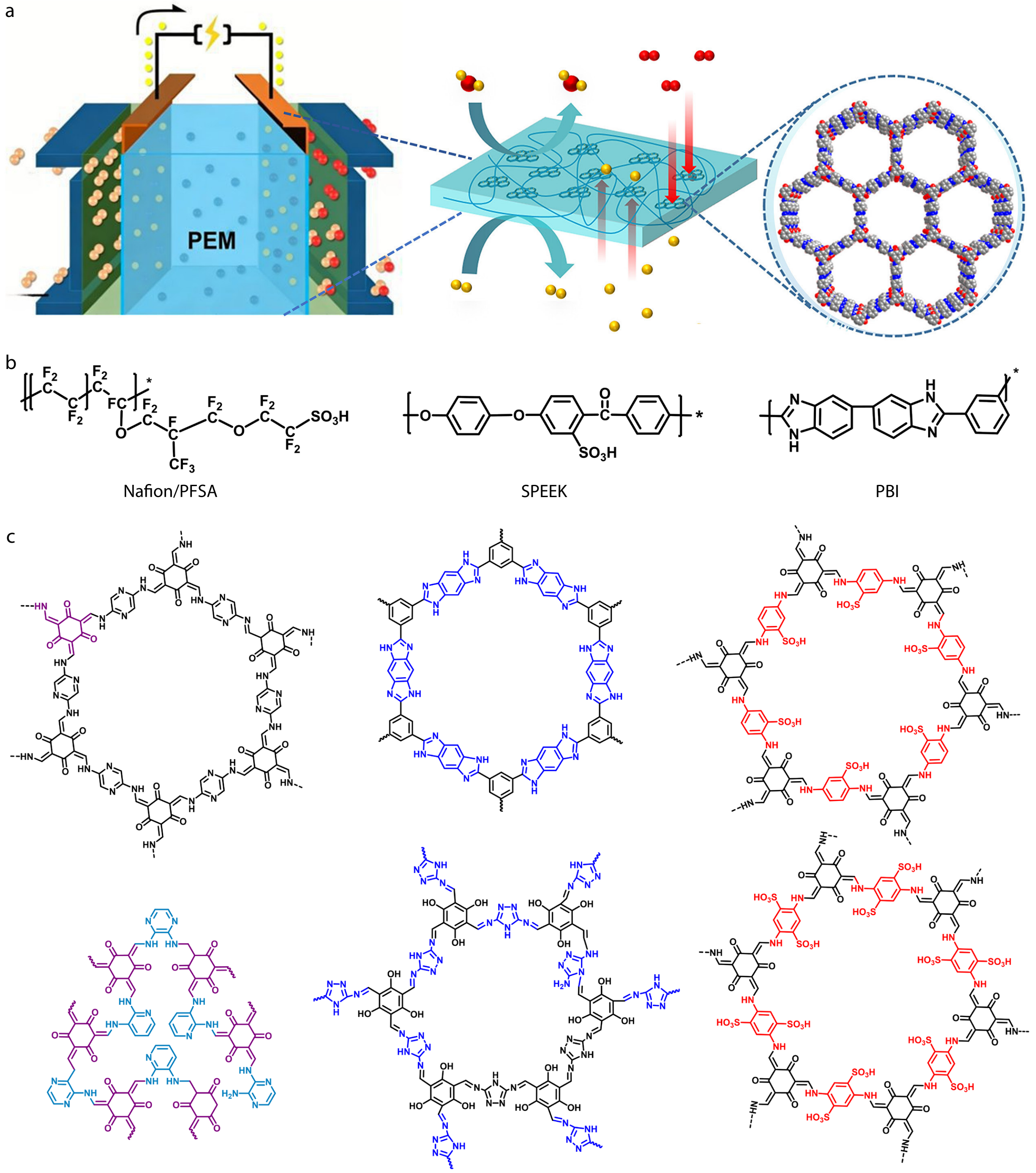

**Fig. 1** (a) Schematic diagram of COF-modified multifunctional membrane for fuel cell applications (Reproduced with permission from Ref. [24]; Copyright (2022), American Chemical Society), including (b) the formulas for linear polymer (Nafion/PFSA[37], SPEEK[38] and PBI[39]) and (c) structures of COFs for membranes.

# 2 DESIGN, PREPARATION AND EVALUATION OF COF-MODIFIED COMPOSITE PEMS AND DEVICES

## 2.1 Design Principles of Proton-conductivity on COFs

COFs have a remarkable structural designability, offering great potential for proton-conductivity performance enhancement. Proton-conductive building blocks, such as monomers containing sulfonic acid groups, phosphoric acid groups, and nitrogen-containing groups, are strategically designed for synthesizing COFs.

Through rational functional monomer design, Zhao *et al.*[40] developed sulfonic acid-functionalized COFs, which were blended with binders to form mixed-matrix membranes with proton conductivity. Dai's group[41] introduced irreversible *α*-phosphonic acid groups into COFs *via* asymmetric hydrophosphonylation, achieving a proton conductivity of $1.25\times10^{-3}$ S·cm$^{-1}$ under mild conditions. Nitrogen-rich COFs also enable efficient proton conduction through abundant nitrogen-containing functional groups and hydrogen-bond networks, making them well-suited as high performance PEMs.[42] Since the above-mentioned COFs incorporate intrinsic proton carriers and rely on water as the proton donor under practical conditions, they are classified as intrinsic proton-conducting COFs (Fig. 2). In addition, proton carriers such as phosphoric acid are often confined within COF pores to further boost proton conductivity. For example, Banerjee *et al*.[32] synthesized the Tp-Bpy COFs with pyridine rings, which functioned effectively in MEAs after confining phosphoric acid. Furthermore, the performance of COF-modified PEMs in PEMFCs can be enhanced by integrating proton-conductive COF frameworks with proton carriers or donors and impregnating them with phosphoric acid.[43] Molecular intercalation of water or other proton carriers into COFs leads to a remarkable enhancement in proton conductivity, which can be attributed to the intrinsically charged COF frameworks that is charge-compensated by mobile ions. This provides the fundamental motivation for us to employ COFs in the design of advanced composite PEMs.

## 2.2 Design and Preparation of COF-modified Composite PEMs

Proton-conducting polymer membranes such as sulfonated polymers (Nafion, SPEEK, *etc.*) currently represent the state-of-the-art PEM technology. Nevertheless, the intrinsic limitations of these polymers have driven the development of composite membranes incorporating functional materials. Among porous materials, COFs are particularly attractive: their covalent bonding confers superior thermal and chemical stability to composite PEMs, and their high specific surface area supports effective water management.[44] Together, these features promote durability under extreme operating conditions. Despite these advantages, conventional direct casting or coating approaches for fabricating COF-containing PEMs suffer from several critical shortcomings. Firstly, COFs tend to distribute inhomogeneously within the polymer matrix, producing spatial heterogeneity. Secondly, the resulting membranes are often thicker than required for practical operation. Thirdly, these techniques frequently yield membranes with poor dimensional uniformity.

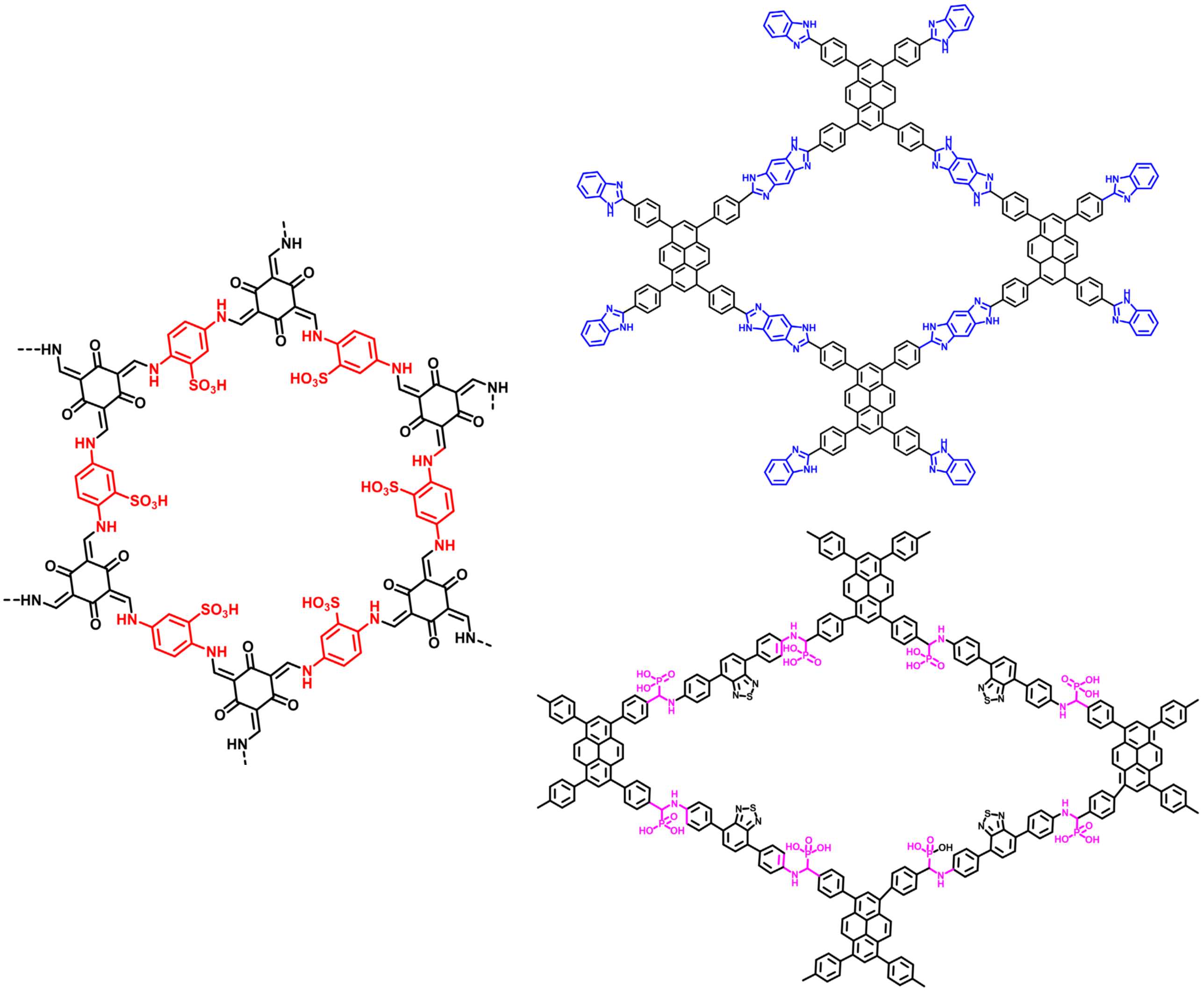

**Fig. 2** Classification of the intrinsic proton conducting structures of the COFs membrane.

To address the interfacial incompatibility between COF networks and polymer matrices, two complementary strategies have been developed recently. The first strategy, nanoconfinement dispersion engineering (Fig. 3a), aims to generate COF phases smaller than 100 nm-either by top-down exfoliation (for example, liquid-phase shearing) or by bottom-up methods such as confined crystallization-in order to substantially enhance their dispersibility within polymer matrices. Yao *et al*.[35] exfoliated COF nanosheets using the micromechanical cleavage technique. They produced Nafion-based composite PEMs by incorporating well-dispersed nanosheets into Nafion through a solution casting method. Additionally, the strong electrostatic interactions between the nanosheets and Nafion improved the dispersion of the ionic clusters. The second approach is *in situ* synthesis (Fig. 3b), in which the polymerization of the COF occurs in the polymer solutions so that COFs nucleate and grow spontaneously inside the polymer matrix. This route not only promotes uniform distribution but also enhances interfacial compatibility between the composite phases, yielding COF-polymer membranes that combine high loading with homogeneous spatial distribution and a dense morphology. Zhang *et al*.[45] produced well-dispersed COF oligomers/partially polymerized short-chain species through precise control of monomer ratios and reaction time. These oligomers enabled solution coating of large-area, uniform COF layers on SPEEK membranes, thereby substantially improving the processability of COF films. Consequently, the *in situ* synthesis route constitutes a promising paradigm for fabricating COF-polymer composite membranes with broad application potential. Moreover, membranes prepared by either nanoconfinement dispersion or *in situ* synthesis can exhibit a variety of microscale interconnections, a consequence of selecting COF building blocks and polymer matrices that present different functional groups. For example, introducing COFs bearing basic functional groups (*e.g.*, amino ($-NH_2$), hydroxyl ($-OH$)) enables the formation of ionic cross-linking networks with sulfonic acid groups ($-SO_3H$) in sulfonated polymers such as Nafion.[34] In the present study, from the viewpoint of practical application, nanoconfinement dispersion engineering can effectively enhance the dispersibility of COFs in polymer matrices by reducing their particle size, yet its improvement on interfacial compatibility remains limited. In contrast, *in situ* synthesis enables more uniform COF distribution, higher loading, better interfacial adhesion and superior processability, although it relies on the precise regulation of reaction parameters.

## 2.3 The Evaluation of COF-modified Composite PEM and Devices

PEMs are fundamental to the operation of PEMFCs, as their performance directly influences the efficiency, stability, and lifespan of the cells.[46] Consequently, a thorough evaluation of PEM performance is essential for determining its practical effectiveness in fuel cells. This evaluation necessitates a systematic, multi-dimensional analysis that combines core functionalities, such as proton conductivity, gas barrier capability, and operational tolerance with real-world application scenarios, including low-, medium-, and high-temperature environments. For membranes modified with COFs to achieve large-scale commercial viability, attention must be directed towards three critical aspects: proton conduction kinetics, gas barrier resistance, and structural durability. The mechanical properties of the developed membranes are also crucial for their overall performance. Currently, the evaluation of COF-modified composite PEMs varies in different works, such as sample preparation, hydration state, electrode configuration, and environmental control. Thus, it requires the use of unified standards for reliable comparison across different studies to highlight true advantages of new materials, and guide rational material design.

### *2.3.1 Proton conductivity*

The proton conductivity ($\sigma$) of the composite membrane measurements is highly sensitive to various factors including temperature, humidity, membrane hydration, electrode configuration, sample dimensions, and testing parameters, leading to poor data comparability across studies, highlighting the necessity of standardized testing protocols. The proton-conductivity is measured by a two-point-probe AC impedance method using an electrochemical workstation, and the main difference among the current testing methods lies in the electrode materials. In addition to platinum and silver electrodes, other suitable electrode materials for proton conductivity measurements include gold, carbon-based materials (*e.g.*, graphite paper, carbon cloth, carbon paper), conductive silver/carbon pastes, and stain-

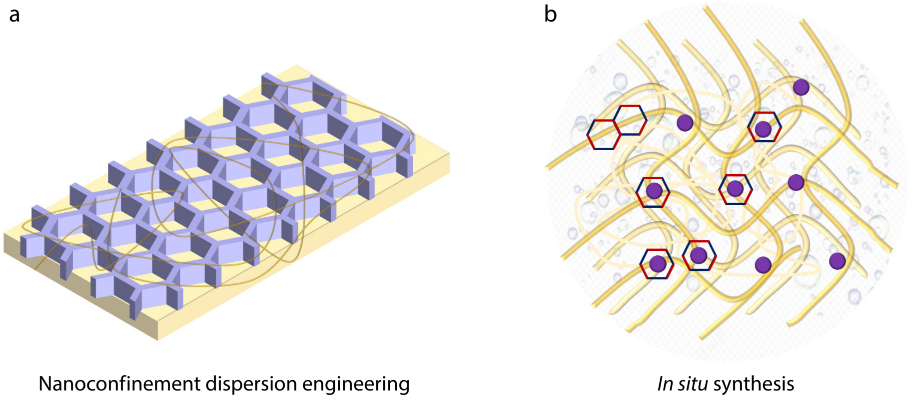

**Fig. 3** The preparation method of COF-modified composite proton exchange membranes. (a) Nanoconfinement dispersion improves COF dispersibility, but has limited interface improvement. (b) *In situ* synthesis enhances COF dispersion and interface, but requires precise reaction control.

less steel. Differences in electrode materials can lead to variations in the test results. All the membrane samples are fully hydrated prior to measurement. For the measurement of proton conductivity around gradient humidity below 100%, the temperature is controlled from 25 °C to 100 °C by water vapor. The proton conductivity of the membranes was calculated according to Eq. (1).

$$\sigma = \frac{l}{AR} \tag{1}$$

where $l$ is the distance between two electrodes, $A$ is the cross-sectional area of membrane and $R$ is the membrane resistance derived from the electrochemical workstation. The measurement was repeated three times and the standard deviation was within ±5.0%.

### *2.3.2 Water uptake and swelling degree*

The water uptake (WU) and swelling ratio (SR) are calculated by comparing the weight and size of the dry and wet membranes. Each membrane sample (*e.g.*, 6 cm × 6 cm) was dried at 60 °C until constant weight ($W_{\mathrm{DRY}}$, g), then its area ($A_{\mathrm{DRY}}$, cm$^2$). After immersing the membrane for 24 h in deionized water, the membranes are fully swelled and the weight of the wet membrane ($W_{\mathrm{WET}}$, g) and area ($A_{\mathrm{WET}}$, cm$^2$) are measured. The WU and SR are calculated by following Eqs. (2) and (3). The measurement is repeated three times and the standard deviation is within ±4.0%.

$$\mathrm{WU}\ (\%) = \frac{W_{\mathrm{WET}} - W_{\mathrm{DRY}}}{W_{\mathrm{DRY}}} \times 100\% \tag{2}$$

$$\mathrm{SR}\ (\%) = \frac{A_{\mathrm{WET}} - A_{\mathrm{DRY}}}{A_{\mathrm{DRY}}} \times 100\% \tag{3}$$

### *2.3.3 Mechanical property*

Prior to testing, all of the membranes should be dried in vacuum for 24 h. Then, the membranes are cut into 2 mm × 15 mm strips. The mechanical properties of the membranes are investigated by evaluating the tensile stress-strain curves.

### *2.3.4 Single PEMFC performance*

To assess the feasibility of COF-modified PEMFCs, it is crucial to incorporate these membranes into complete MEAs for thorough single-cell electrochemical performance evaluation. Few studies have systematically integrated COF-modified PEMs into MEAs for rigorous performance assessment, leaving a significant research gap.

The MEA, the core power-generating component of PEMFCs, features a symmetric sandwich structure. A COF-modified PEM serves as the central electrolyte, flanked by anode and cathode catalytic layers (CL), with gas diffusion layers on the outer surfaces. For CL fabrication, catalyst ink is made by dispersing an electrocatalyst (*e.g.*, 60 wt% Pt/C) in a solvent with around 5 wt% Nafion ionomer binder using ultrasonic homogenization (*e.g.*, 30 min at 200 W).

To test the COF-modified PEMs under challenging conditions, single-cell tests were conducted with optimized parameters. The operating temperature ranged from 80 °C to 120 °C, suitable for high-temperature, low-humidity conditions where traditional Nafion membranes struggle with proton conductivity loss. The anode ($H_2$ or MeOH) and cathode (ambient air or high-purity $O_2$ for baseline comparison) were humidified to 30%–50% relative humidity (RH) using a dew-point-controlled system.

The testing protocol comprised four stages: (1) an activation stage (2–4 h) at a constant voltage (0.6 V) to activate the electrocatalyst and redistribute ionomer within the CLs, ensuring strong interfacial contact between the COF-modified PEMs and CLs; (2) a stabilization stage (30–60 min) post-activation, maintaining conditions until voltage stability within ±5 mV was achieved to eliminate transient effects and ensure data reproducibility; (3) a performance testing stage (60–90 min per MEA) involving scanning the polarization curve, deriving power density, and monitoring short-term stability; and (4) repeatability validation, with each sample tested three times under identical conditions, reporting the average as the final result.

For polarization curve testing, scans were conducted from 0.9 V (open-circuit voltage, OCV, recorded for 5 min before scanning) to 0.2 V (to avoid excessive electrocatalyst degradation at low potentials) using a stepwise mode: a voltage step of 50 mV, a dwell time of 30–60 s per step, and a scanning rate of 5–10 mV·s$^{-1}$. Power density ($P$) was calculated using $P=V\times J$, where $V$ is the cell voltage in volts ($V$) and $J$ is the current density in milliamperes per square centimeter (mA·cm$^{-2}$), with maximum power density as the key performance metric. Short-term operational stability was assessed by maintaining the cell at a constant current density of 500 mA·cm$^{-2}$ for 5–10 h, measuring the voltage decay rate (mV·h$^{-1}$) to evaluate long-term interfacial compatibility between the COF-modified PEM and CLs.

## 3 DESIGN OF LOW-HUMIDITY COF-MODIFIED COMPOSITE PEMS

In hydrated Nafion membranes, protons ($H^+$) dissociate from —$SO_3H$ groups and become associated with water molecules to form $H_3O^+$. Because proton conduction relies on these hydrated species, Nafion requires near-saturated humidity (100% RH) to remain effective conductivity. At low relative humidity (RH), the proton-conducting channels in commercial PEMs, such as Nafion, as well as in alternative polymers like sulfonated SPEEK, collapse due to a substantial reduction in water content. However, at temperatures exceeding 100 °C, rapid evaporation leads to water loss, restricting proton conduction to the Grotthuss mechanism, which relies on continuous hydrogen-bond network *via* $H_3O^+$ intermediates.[47] However, the proton-conducting performance of these membranes deteriorates drastically under elevated operating temperatures (particularly above 100 °C) or low relative humidity (RH<30%), primarily due to their strong dependence on water molecules to mediate proton transport.[48,49] Currently, modifying membranes with COFs to fine-tune and optimize membrane hydration represents a highly effective strategy for overcoming the intrinsic limitations of Nafion-based PEMs and for extending the operating temperature range (80–120 °C) of fuel cells.[50]

### 3.1 COF-modified Nafion-based Composite PEMs for Improving Low-humidity Performance

Low-temperature PEMs typically refer to perfluorosulfonic acid membranes, represented by DuPont's Nafion® series. These membranes operate below 80 °C (typically 50–80 °C), and consists of a tetrafluoroethylene-based molecular backbone and

—$SO_3H$ side group. The TFE-derived framework imparts excellent mechanical and chemical stability, while the —$SO_3H$ groups serve as charged sites to facilitate proton conduction. However, their performance is primarily limited by the hydration-dependent characteristics of the —$SO_3H$ groups. Incorporating particular COFs into Nafion improves proton conductivity under low-humidity conditions while concurrently reducing the water swelling ratio.[36] These benefits arise from uniformly dispersed COFs interacting strongly with Nafion chains through electrostatic forces, which promotes the formation of evenly distributed ion channels and thus permits more precise control of proton-transport pathways within PEMs.

The dispersion of COFs critically determines the overall performance of composite PEMs: when COF particles agglomerate, they interrupt the continuity of proton-transport pathways and create interfacial defects. To overcome these problems and to strengthen the synergistic interaction between COFs and the polymer matrices, reducing COFs to the nanoscale has therefore become a promising approach. Nanoscaling suppresses particle aggregation, increases the specific surface area and improves interfacial compatibility with Nafion, thereby promoting the formation of more efficient proton-conducting channels. Zhang's group[35] fabricated sulfonated covalent organic nanosheets using a micromechanical exfoliation technique and incorporated them into Nafion membranes to prepare Nafion-SCONs composite membranes (Fig. 4a). When the SCONs content in the composite membrane is 0.6 wt%, the nanosheets are well-dispersed within Nafion, achieving a higher proton conductivity. However, increasing the content of SCONs to 2 wt% leads to significant agglomeration, thereby reducing the proton conductivity of the PEM (Fig. 4b). The uniform distribution of SCONs within the membrane establishes abundant microscopic ionic channels, enabling rapid proton transport. Furthermore, the lower swelling ratio reduces methanol permeability (Fig. 4c). When applied to methanol fuel cells, the Nafion-SCONs membrane exhibits a 44% higher energy density (118.2 mW·cm$^{-2}$) compared to pure Nafion at 60 °C (Fig. 4d). This study assessed the proton conductivity of the composite membrane only at 80 °C, leaving uncertainties regarding its behavior at high temperatures. Moreover, the continuity of proton-conducting channels within the exfoliated COF component of the membrane has not been established and therefore is worthy of further investigation.

To improve the interfacial compatibility between COFs and Nafion, the Jiang group[34] incorporated amino-containing Schiff base COF networks (SNW-1) loaded with phosphoric acid into the Nafion matrix (Fig 5a). In practice, the preweighed $H_3PO_4$-impregnated SNW-1($H_3PO_4$@SNW-1) was added to the Nafion/DMAc solution, and the resulting mixture cast onto a glass plate to form composite membranes. The fabricated composite membranes were labeled as Nafion/$H_3PO_4$@SNW-1-*X*, with *X* representing the weight percentage of SNW-1 networks. All membranes had thickness in

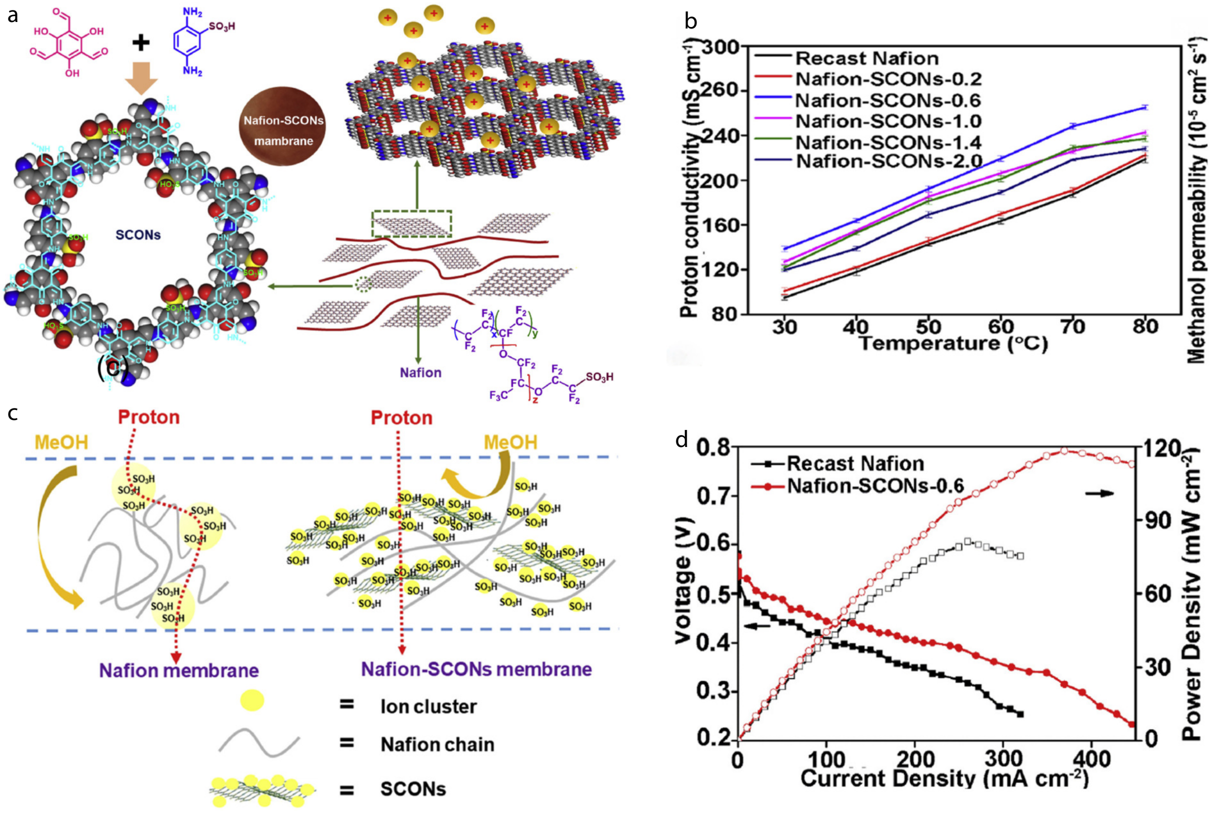

**Fig. 4** (a) Structural illustration of SCONs and Nafion molecule; (b) Proton conductivities of Nafion and composite membranes; (c) Schematic illustration for transfer proton and methanol through Nafion membrane and Nafion-SCONs membrane; (d) Polarization curves and power density of the DMFCs with Nafion and Nafion-SCONs-0.6 composite membrane in 60 °C. (Reproduced with permission from Ref. [35]; Copyright (2019), Elsevier).

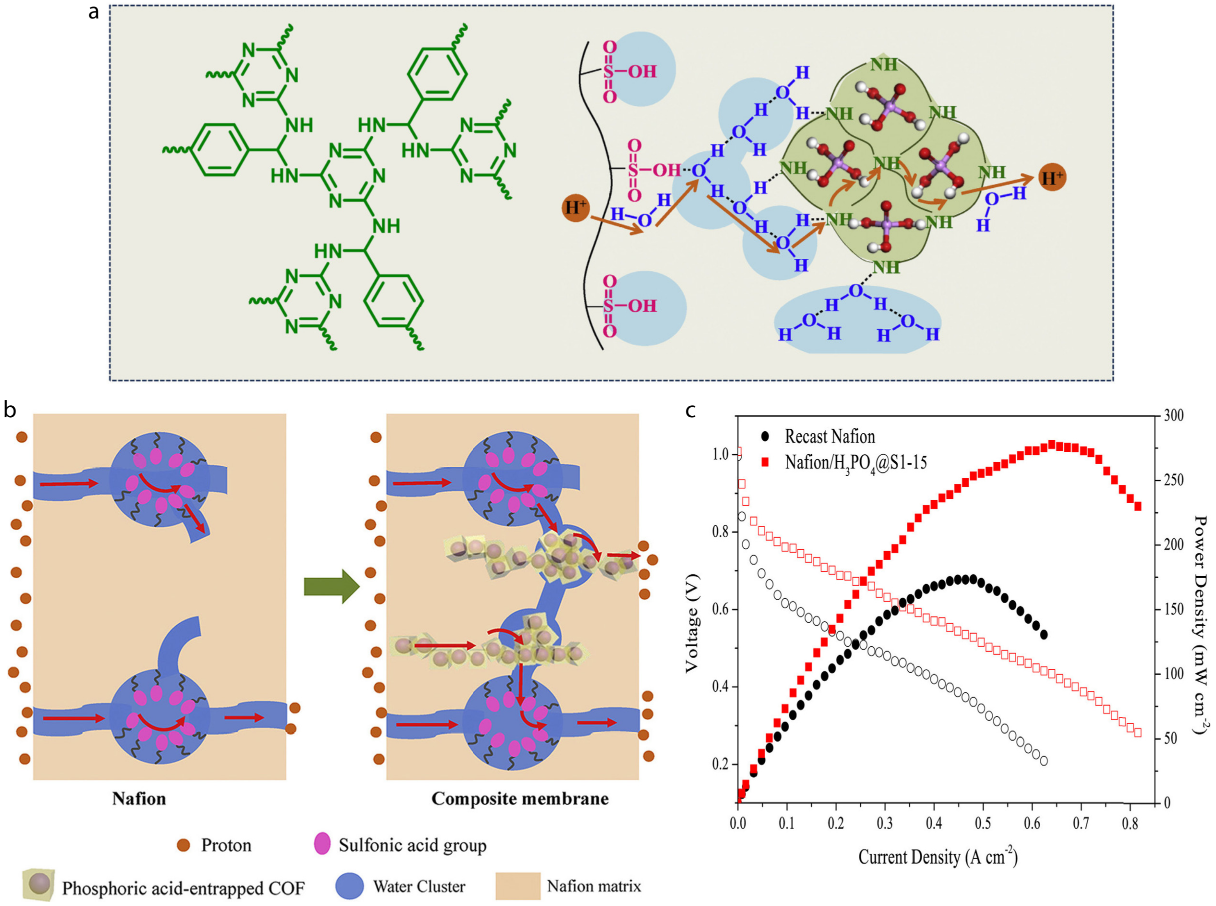

**Fig. 5** (a) Illustration of proton transfer along the hydrogen-bonded network within the composite membranes; (b) Schematic diagram of the abundant proton transfer sites provided by acidic —$PO_3H_2$ groups; (c) Single PEMFC performances of the recast Nafion membrane and Nafion/$H_3PO_4$@S1-15 with hydrous $H_2/O_2$ operated at 60 °C. (Reproduced with permission from Ref. [34]; Copyright (2016), Elsevier).

the range 90–100 μm. At the molecular level, the N—H moieties in the SNW-1 framework interact with Nafion's-$SO_3H$ groups, improving dispersion of SNW-1-*X* throughout the polymer matrix. Concurrently, acid-base pairing between the SNW-1 network and Nafion strengthens interfacial interactions and enlarges hydrophilic domains (Fig. 5b). The acidic-$PO_3H_2$ groups confined within the $H_3PO_4$@SNW-1 pores furnish abundant proton-transfer sites, thereby lowering the energy barrier for continuous proton conduction. Introducing $H_3PO_4$@SNW-1 also increases water uptake while limiting dimensional swelling. When the SNW-1 COFs content is below 15 wt%, Nafion chain mobility is effectively constrained, suppressing polymer swelling. In terms of low-humidity performance, the composite membrane Nafion/$H_3PO_4$@SNW-1-15 containing 15 wt% SNW-1 achieves a proton conductivity of 0.0604 S·cm$^{-1}$ at 80 °C and 51% relative humidity. In single-cell tests this membrane delivers a maximum power density of 277.8 mW·cm$^{-2}$ (Fig. 5c), a 60.3% improvement relative to pristine Nafion membrane. As amorphous COF, SNW-1 exhibits superior proton conduction under low humidity, which mainly originates from the synergistic advantages of water retention, proton-conductive sites and transport channels endowed by structural disorder, thereby compensating for the conduction shortcomings of crystalline SNW-1 at low humidity. Through a post-modification strategy, SNW-1 was zwitterion-functionalized with 1,3-propanesultone, which facilitated the attachment of sulfonic acid moieties. The Nafion-Z-COF-10 composite membrane exhibited a proton conductivity of 0.22 S·cm$^{-1}$ at 80 °C and 100% RH, alongside a 45.7% enhancement in maximum power density relative to the pure recast Nafion membrane.[51]

Mi *et al.*[52] synthesized hydrophilic two-dimensional ZUT-COF-$SO_3H$ functionalized with sulfonic acid, characterized by high crystallinity and a large specific surface area. These COFs were integrated into Nafion using a solution casting technique to produce composite membranes (Fig. 6a). Water uptake assessments demonstrated that augmenting the COFs doping level from 0% to 10% increased the membrane's water absorption from 7% to 21.57% (Fig. 6b). In an environment with 60% relative humidity, the 10 wt% ZUT-COF-$SO_3H$@Nafion composite membrane exhibits a proton conductivity of 5.782×10$^{-2}$ S·cm$^{-1}$. When the humidity is increased to 80%, the conductivity rises to 1.338×10$^{-1}$ S·cm$^{-1}$, by contrast, the proton conductivity of commercial Nafion is 5.566×10$^{-2}$ S·cm$^{-1}$. When evaluated in PEMFCs at 80 °C, it exhibited an OCV of 0.97986 V, a maximum current density of 640.179 mA·cm$^{-2}$, and a peak power density of 304.056 mW·cm$^{-2}$ (Figs. 6c and 6d).

Nafion's proton conductivity relies on water content, yet excessive humidity may result in liquid water buildup and

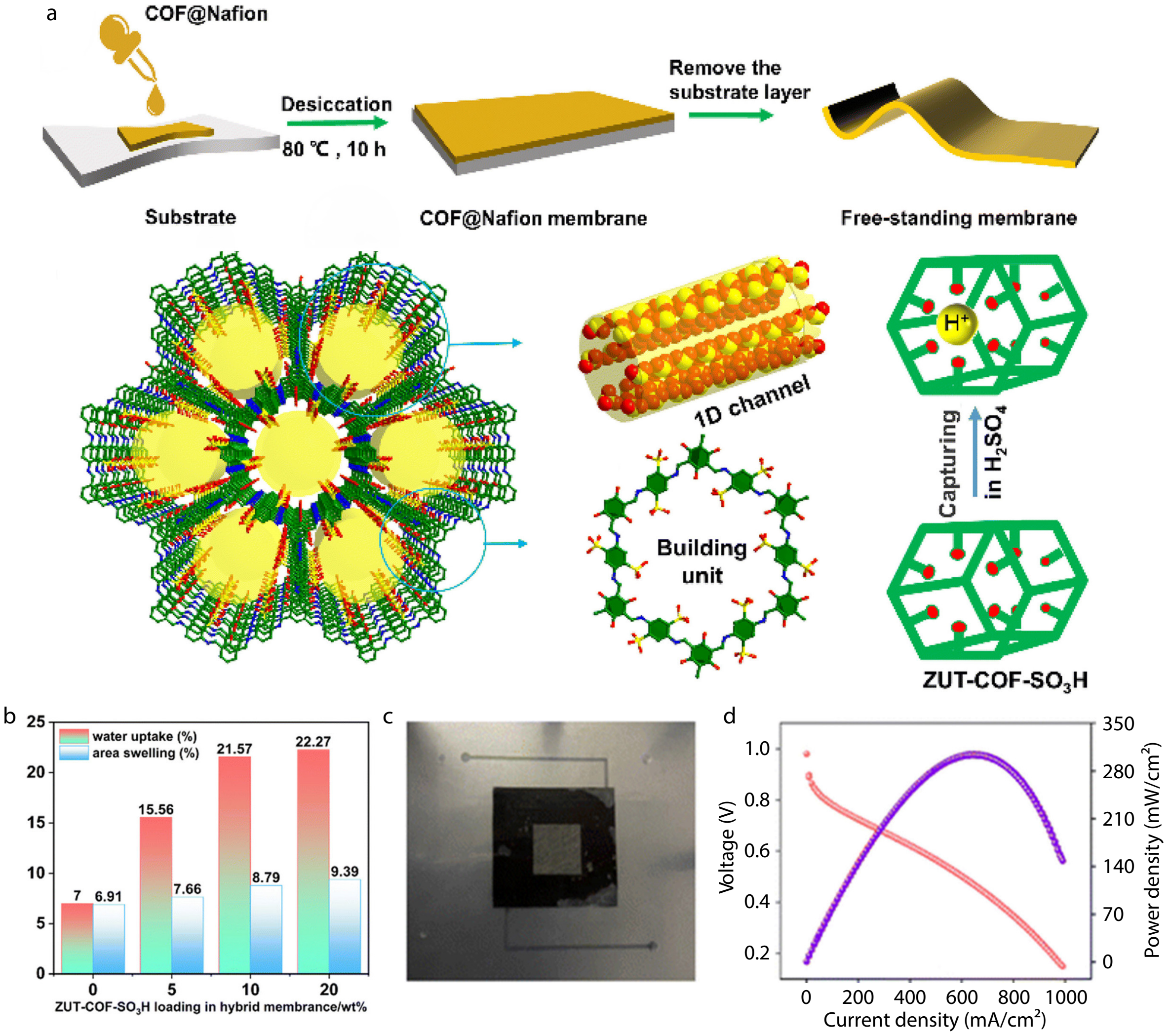

**Fig. 6** (a) Preparation of proton conductive membrane *via* solution casting technique; (b) Membrane water absorption and area expansion of ZUT-COF-$SO_3H$@Nafion hybrid membranes as a function of ZUT-COF-$SO_3H$ loading; (c) Preparation of fuel cell components; (d) Single $H_2/O_2$ fuel cell performances of the hybrid membrane at 80 °C. (Reproduced with permission from Ref. [52]; Copyright (2023), The Royal Society of Chemistry).

block gas pathways. By integrating COFs with improved water retention properties, the aforementioned problem is alleviated, which in turn boosts the water content and retention capacity within proton exchange membranes. This improved hydration control allows PEM systems to operate effectively in low-humidity, high-temperature environments. To probe the water-retention abilities of COFs more thoroughly, Wang's group[36] synthesized a series of $\alpha$-aminoketone-linked COFs (Am-COF) *via* a linker-exchange approach. In this method the original imine bonds in the parent COFs were replaced by $\alpha$-aminoketone linkages (Fig. 7a), introducing carbonyl (C=O) groups capable of forming hydrogen bonds with water and thereby enhancing molecular water retention. To improve film processability, composite PEMs were prepared by co-casting Am-COF-3-$SO_3H$ with Nafion at a mass ratio of 1:3. In contrast to the aqueous suspension, Am-COF-3-$SO_3H$ remained dispersed with no settling for at least three days (Fig. 7b). Because retained water is central to facilitating proton transport by the Grotthuss mechanism, the authors first examined water-binding using *in situ* diffuse reflectance FTIR spectroscopy. A stretching vibration at 3450 cm$^{-1}$ attributable to water hydrogen-bonded to the C=O moieties in Am-COF-3-$SO_3H$ was observed at 105 °C and 80% RH. By contrast, Nafion exhibited no comparable bound-water signature, although its first hydration shells may still be present (Fig. 7c). The investigators further observed that the water sorption capacity of Am-COF-3-$SO_3H$ increased with temperature at low humidity. They ascribed this counterintuitive temperature dependence to enhanced framework flexibility at elevated temperature, which facilitates the formation of multiple hydrogen bonds between the host and guest water molecules (Fig. 7d). Proton-conduction measurements indicate outstanding performance in PEMFCs operated at 100–120 °C. At 105 °C and 80% RH, the Am-COF-3-$SO_3H$/Nafion membrane delivered peak power densities of 1.87 W·cm$^{-2}$ with pure $O_2$ and 1.36 W·cm$^{-2}$ with air, corresponding to improvements of 32% and 94% relative to membranes lacking the COF additive (Figs. 7e and 7f).

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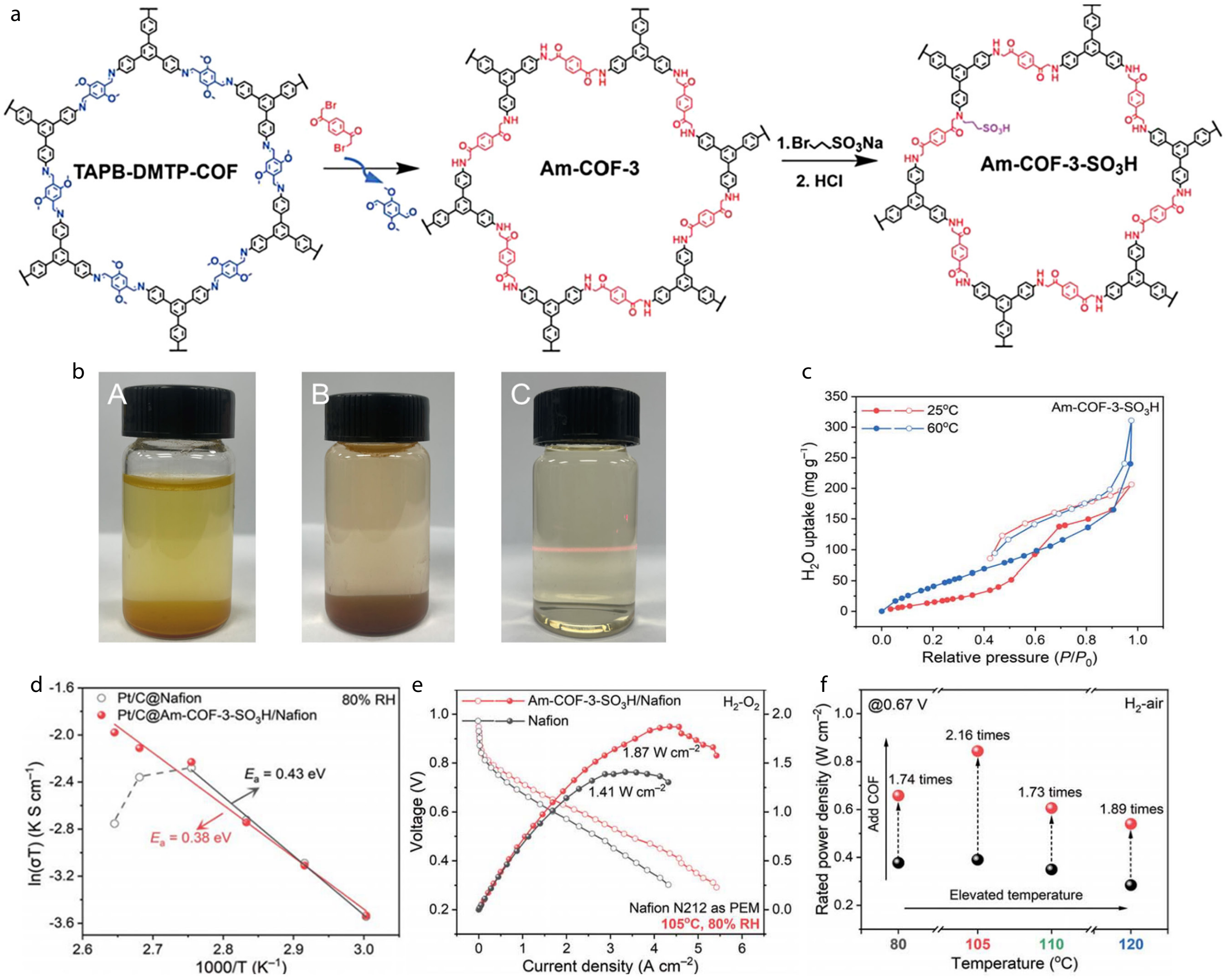

**Fig. 7** (a) Synthetic route of Am-COF-3-SO$_3$H; (b) The Tyndall phenomenon produced by (A) TAPB-DMTP-COF, (B) Am-COF-3, and (C) Am-COF-3-SO$_3$H aqueous solution. The Tyndall phenomena were examined after subjecting the solutions to a 2-h ultrasonic treatment in ice water, followed by a 72-h standing period. (c) $H_2O$ sorption isotherms of Am-COF-3-SO$_3$H at 25 and 60 °C; (d) Arrhenius plots of composite membranes; (e) $H_2$-$O_2$/air fuel cell I-V polarization and power density plots with Pt/C@Nafion and Pt/C@Am-COF-3-SO$_3$H/Nafion (1:3) measured at 105 °C and 80% RH under 150 kPa (Nafion N212 as PEM); (f) Comparison of the rated power densities of MEAs evaluated under $H_2$-air conditions at 80 °C. (Reproduced with permission from Ref. [36]; Copyright (2024), American Association for the Advancement of Science).

## 3.2 COF-modified SPEEK-based Composite PEMs for Improving Low-humidity Performance

The complex synthesis and consequent high cost of Nafion limit its broader application; as a result, polymers with aromatic backbones have been widely investigated because they are easier to prepare and can achieve proton conductivities comparable to Nafion. In particular, sulfonated poly(arylene ether ketone) variants have been proposed as alternatives, since their conduction mechanisms closely resemble those of Nafion. These materials offer lower production costs and superior barrier properties relative to Nafion, yet they are fundamentally constrained by a persistent trade-off between the degree of sulfonation and the swelling ratio. A representative example, SPEEK, typifies this compromise. Proton conductivity in SPEEK increases with the concentration of —SO$_3$H on the polymer backbone, but enhancing —SO$_3$H content inevitably undermines the mechanical integrity of the polymer matrix by promoting excessive water uptake and dimensional expansion. Thus, balancing the opposing demands of high proton conductivity and dimensional stability in SPEEK membranes remains a central and unresolved challenge.

Jiang *et al.*[53] prepared sulfonic acid-functionalized TpPa-SO$_3$H nanosheets by a surface-polymerization method and incorporated them into a SPEEK matrix to produce composite membranes (Fig. 8a). The densely populated sulfonic acid groups on the framework created continuous proton-conducting pathways within the SPEEK matrix (Fig. 8b), while the covalent network of the COF improves the dimensional stability of the composite membrane. Characterization demonstrated that the TpPa-SO$_3$H COF nanosheets had lateral dimensions of approximately 30 μm and exhibited smooth surfaces. Their high aspect ratio provided effective platforms for both in-plane and through-plane proton conduction. Optical images of the as-prepared membranes indicated that the pristine SPEEK membrane was light yellow, with the color deepening as the volume of TpPa-SO$_3$H nanosheets increased (Fig. 8c). Furthermore, the surfaces of all hybrid membranes were notably smooth and dense, suggesting that the TpPa-$SO_3H$ nanosheets were well-dispersed within the SPEEK matrix. Mechanically, the SPEEK/TpPa-$SO_3H$-5 membrane exhibited a tensile strength of reached 74.5 MPa. The authors attribute this reinforcement primarily to electrostatic interactions between the abundant —NH— groups on the TpPa-$SO_3H$ skeleton and —$SO_3H$ on the SPEEK. In single-cell testing, the SPEEK/TpPa-$SO_3H$-5 membrane outperformed pristine SPEEK, delivering a higher open-circuit voltage of 1.01 V and an increased power density of 86.54 mW·cm$^{-2}$.

Recent work shows that introducing alkaline functional groups into polymer matrices can foster acid-base interactions that both reinforce the polymer network and limit excessive water uptake, thereby reducing undesirable dimensional changes.[54] COFs featuring C═N, C—N, and N═N linkages are inherently basic in nature, and when incorporated into SPEEK matrices, can therefore improve proton conductivity and dimensional stability. However, because fuel cells operate in acidic media (pH=1–4),[55] the basic components must be chosen with care: their pKa values need to be compatible with the operating pH, since pKa will chiefly determine the protonation state of the basic groups under conditions of substantially reduced external water content.[56] Jiang *et al*.[57] prepared a homogeneous composite membrane by incorporating triazole-functionalized COFs into a SPEEK matrix. The formation of interfacial acid-base pairs between the triazole moieties and the —$SO_3H$ groups promoted uniform dispersion. Under reduced hydration, the protonation state of basic sites is governed by their pKa values: triazole residues whose pKa lies within the operating pH window of fuel cells can undergo reversible deprotonation-protonation cycles and thus serve alternately as proton acceptors and donors, enabling rapid proton transfer at low humidity. Notably, the SPEEK/HPW@COF-15 membrane exhibits a proton conductivity of 6.2×10$^{-3}$ S·cm$^{-1}$, which is 35.5 times higher than that of pristine SPEEK and 11.6 times higher than SPEEK/COF-15 (4.9×10$^{-4}$ S·cm$^{-1}$) (Fig. 9a). The ability of triazole to act as both proton donor and acceptor, given its pKa within the fuel-cell operating range[58], underpins the observed enhancement in proton mobility under low relative humidity. Furthermore, encapsulating phosphotungstic acid within the COF channels (HPW@COF) provides an additional, significant increase in proton conductivity. The proposed proton-conduction mechanism is illustrated in (Fig. 9b). This study is one of the few to examine the long-term stability of COF-modified composite PEMs and to draw conclusions from such observations. After 15 days in water, the composite membrane exhibits only a slight decrease in conductivity (from 0.088 S·cm$^{-1}$ to 0.081 S·cm$^{-1}$) (Fig. 9c), suggesting the excellent HPW retention ability of the composite membrane. This could be ascribed to the formation of ionic bonding between triazole and HPW by protonating the basic N sites, thus forming strong electrostatic interactions between HPW and tria-zole ring. As a nitrogen-rich polymer network, SNW likewise engages SPEEK through acid-base interactions between its abundant amine groups and the sulfonate groups of SPEEK. Tang *et al*.[59] prepared a series of SPEEK composite membranes with various amounts of SNW doping *via in situ* method and further sulfonated by immersion.

## 4 DESIGN OF HIGH TEMPERATURE COF-MODIFIED COMPOSITE PEMs

High-temperature PEMFCs (HT-PEMFCs), which operate at 100–200 °C, have attracted considerable attention relative to low-temperature PEMFCs because they offer higher electrode reactivity, improved CO tolerance and simplified water management.[60] Increasing the operating temperature of PEMFCs offers multiple performance enhancements: (i) catalytic activity and electrochemical kinetics,[4] (ii) the CO tolerance of cells is enhanced, thereby broadening the application of hydrogen

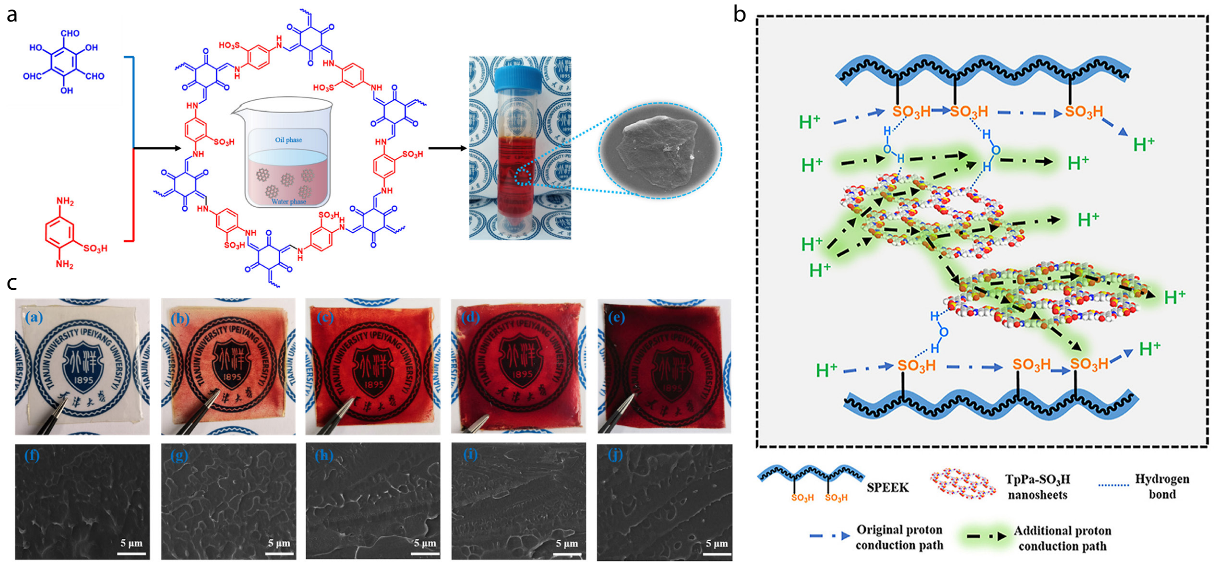

**Fig. 8** (a) Synthetic route of TpPa-$SO_3H$ nanosheets; (b) The proton-conducting pathways in the hybrid membranes; (c) The optical images and SEM cross-section images of (a, f) SPEEK, (b, g) SPEEK/TpPa-$SO_3$-1, (c, h) SPEEK/TpPa-$SO_3$-3, (d, i) SPEEK/TpPa-$SO_3$-5, (e, j) SPEEK/TpPa-$SO_3$-7. (Reproduced with permission from Ref. [53]; Copyright (2021), Elsevier).

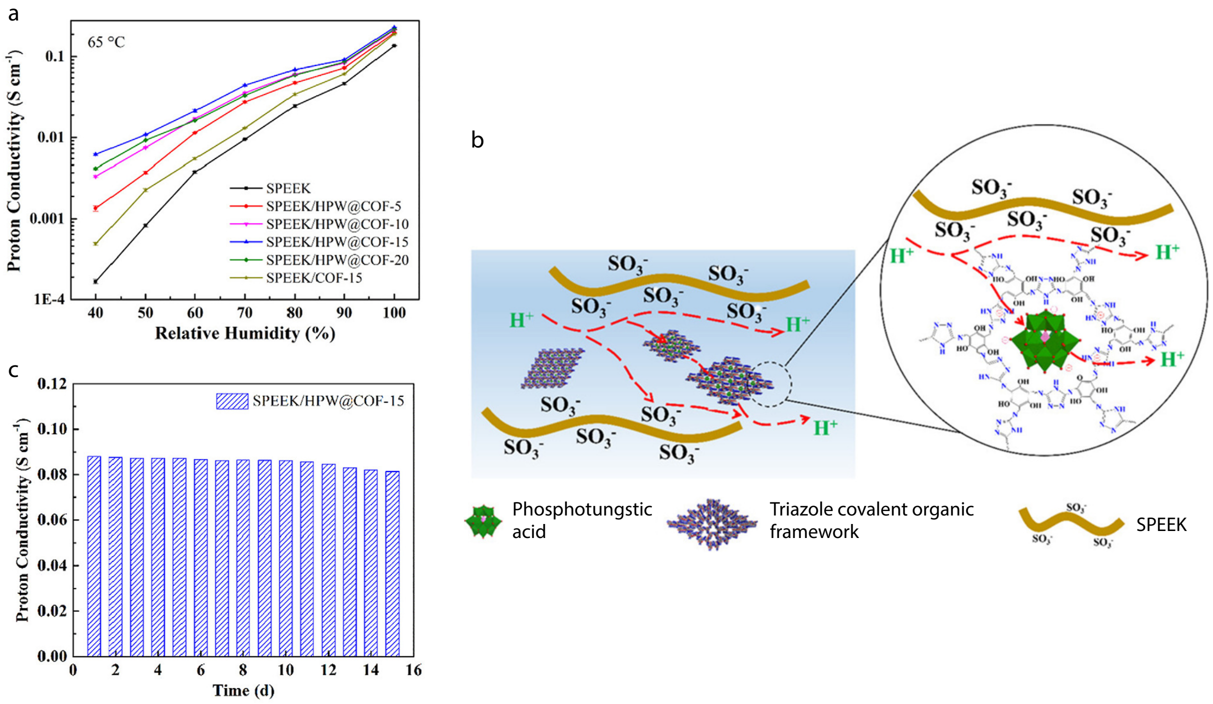

**Fig. 9** (a) Humidity-dependent proton conductivities of SPEEK and SPEEK/HPW@COF membranes; (b) Scheme of the proton conducting mechanism; (c) Long-term stability test for proton conductivity of SPEEK/HPW@COF-15 at 30 °C; (Reproduced with permission from Ref. [57]; Copyright (2020), Elsevier).

sources,[61] (iii) cathode flooding is mitigated,[62] and (iv) the cooling system is simplified due to an expanded temperature difference between the coolant outlet and ambient temperature. However, the proton-conducting performance of commercial PEMs deteriorates drastically under elevated operating temperatures (particularly above 100 °C), primarily due to their strong dependence on water molecules to mediate proton transport.[48,49] In the absence of water at the operating temperatures of HT-PEMFCs, phosphoric acid replaces water as the medium that maintains stable proton conductivity. At present, phosphoric acid-doped PBI is among the most established polymer membranes for HT-PEMFCs.[63−65] Proton transport in phosphoric acid-doped membranes is largely governed by the acid content. Increasing the phosphoric acid loading enhances proton conductivity, but beyond an optimal level the membrane plasticizes and its overall performance deteriorates. Consequently, the development of new, high-performance anhydrous proton-conducting materials remains essential to advance HT-PEMFC technology.

In 1995, Savinel[66] proposed that phosphoric acid-impregnated PBI could serve as an electrolyte for HT-PEMs. PA-doped PBI has emerged as a promising candidate because it combines appreciable proton conductivity, favorable mechanical performance, outstanding chemical and thermal stability. As an aromatic heterocyclic polymer, PBI's rigid aromatic backbone confers excellent thermal stability (glass transition temperature >430 °C), strong chemical resistance and high mechanical strength. However, due to PBI's inherently low proton conductivity ($10^{-12}$ S·cm$^{-1}$), phosphoric acid doping is required to enhance its proton conduction capacity. During doping, PBI membranes uptake substantial quantities of PA; their proton conductivity at high doping levels can approach that of fully hydrated perfluorosulfonic acid membranes at elevated temperature. Crucially, proton conduction in PA-doped PBI is markedly less sensitive to relative humidity than in hydrated polymer electrolytes. However, excessive PA loading causes a pronounced plasticizing effect that severely degrades mechanical integrity and induces large membrane swelling. Moreover, substantial PA loss can occur during fuel-cell operation, compromising long-term durability. COFs have been proposed as a means to enhance the compromised dimensional and mechanical stability of PBI-based PEMs, particularly under high acid doping levels, due to their ordered and rigid channel structures, as well as their functionalized sites.

Jiang's group[67] introduced a novel strategy that combines *in situ* synthesized sulfonated COF (SCOF) with PBI to tackle significant challenges associated with PA-doped PBI membranes. These challenges include degradation of mechanical properties, loss of PA, and inadequate proton conduction at low humidity levels. In this study, the interaction between sulfonic acid groups and imidazole groups serves as ionic crosslinkers, significantly enhancing mechanical and dimensional stability. Additionally, the high density of sulfonic acid groups and the ordered channel structure of the SCOF impart increased proton conductivity to the composite membranes, even at low PA doping levels. The results indicated that the PA-PBI/SCOF-10 composite membranes achieved a proton conductivity of 542.1 mS·cm$^{-1}$ at 80 °C and100% RH, alongside a mechanical strength of 64.0 MPa (PA uptake: 67.47%), which is 2.4 times that of the pristine PBI membrane. As relative humidity decreases, the PBI/SCOF-10 exhibit a low-

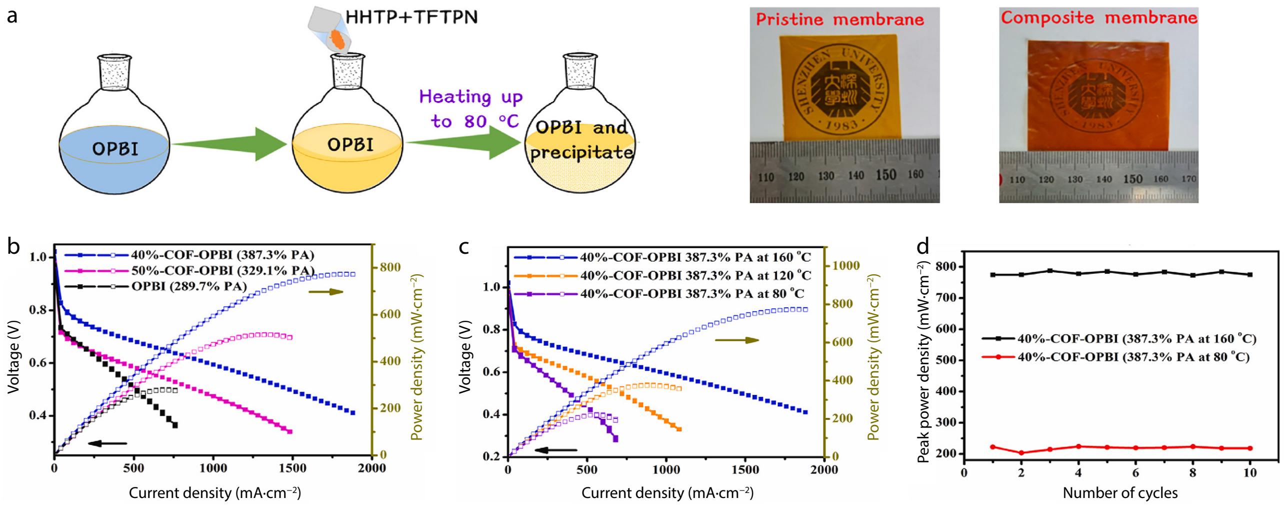

**Fig. 10** (a) Preparation of *in situ* composite membranes and photographs of pristine OPBI membrane and *in situ* composite membrane. Fuel cell performance of (b) PA-doped PBI membranes at 160 °C; (c) 40%-COF-OPBI under different temperature; (d) Cycles stability for 40%-COF-OPBI at 80 and 160 °C. (Reproduced with permission from Ref. [68]; Copyright (2022), Elsevier).

er proton conductivity of 134.1 mS·cm$^{-1}$ at 50% RH and 30 °C. In terms of application validation, the composite membrane achieves a cathode pressure of 0.33 MPa in electrochemical hydrogen compression (EHC), which is three times greater than that of the pristine PBI membrane. Additionally, it attains a peak power density of 227.2 mW·cm$^{-2}$ in a PEMFC at 160 °C without humidification, representing a 119% compared to the pristine PBI membrane. This study presents a novel approach that combines high proton conductivity with excellent mechanical stability, facilitating the practical use of COFs-based composite membranes in electrochemical devices, including high-temperature PEMFCs and EHC.

To enhance the high-temperature proton conductivity of PA-doped PBI, Peng *et al.*[68] designed composite membranes by *in situ* formation of uniformly dispersed, rigid COF sheets within a pliable OPBI matrix. Using tetrafluoroterephthalonitrile and hexahydroxytriphenylene as monomers, they synthesized lamellar COFs directly in the PBI phase to yield a 50 μm-thick membrane (Fig. 10a). The resultant hybrid-a flexible PBI substrate reinforced by rigid COF lamellae-substantially improved dimensional stability and mechanical strength even at high phosphoric acid uptake (387.3 wt%). Among the series, the 40%-COF-OPBI membrane achieved the best comprehensive properties, with an outstanding tensile strength tensile strength (12.1 MPa). Moreover, the rigid COF lamellae established continuous, efficient proton-transport pathways, producing a notable proton conductivity of 177.7 mS·cm$^{-1}$ and enhanced fuel-cell performance, delivering a peak power density of power density (774.7 mW·cm$^{-2}$) in unhumidified $H_2/O_2$ fuel cell tests at 160 °C (Figs. 10b–10d).

In recent years, most reported COFs have exhibited high proton conductivity only under hydrated conditions and at temperatures below 100 °C.[43] Moreover, the majority of COFs reported as proton conductors have been synthesized *via* esterification or Schiff base reactions. Because both —COO— and —C=N— linkages possess limited chemical stability due to the dynamic reversibility inherent to those reactions, such COFs tend to show poor long-term stability. In 2019, Babu *et al.* [42] reported a benzimidazole-linked covalent organic framework (PBI-COF) exhibiting a highly ordered crystalline structure. The imidazole moieties, whose single-atom sites possess lone-pair electrons, establish hydrogen-bonding networks with protons (H$^+$) from $H_2O$; this interaction facilitates rapid proton transport. Remarkably, the undoped PBI-COF shows an intrinsic proton conductivity $3.2\times10^{-2}$ S·cm$^{-1}$ at 95 °C and 95% RH. Compared with COFs built use —COO— or —C=N— linkages, the cyclic benzimidazole architecture of PBI-COF furnishes substantially improved chemical stability in acidic media. When impregnated with $H_3PO_4$, the COF-PBI composite membrane preserves the high proton conductivity typical of $H_3PO_4$@PBI, while mitigating the critical issue of phosphoric acid leakage; this improvement derives from the material's three-dimensional porous network with well-defined channels.

Ren *et al.*[69] prepared PBI-COF by condensing of 3,5-benzenetricarboxylic acid and 1,2,4,5-benzenetetramine tetrahydrochloride in poly(phosphoric acid). The resulting framework combines high porosity with ordered channels that spatially confine $H_3PO_4$ molecules and thereby suppress leakage (Fig. 11a). Mechanical grinding of the PBI-COF powder with $H_3PO_4$ produced $H_3PO_4$@PBI-COF composites with a maximum acid loading of 83 wt%. The covalently linked benzimidazole units within the PBI-COF also limit water-induced swelling, making these materials attractive candidates for high-performance proton conductors above 100 °C. Proton conductivity measurements demonstrate an extraordinary enhancement of 6–8 orders of magnitude relative to the pristine PBI-COF, with conductivities of $1.55\times10^{-2}$ S·cm$^{-1}$ at 30 °C, $1.01\times10^{-1}$ S·cm$^{-1}$ at 100 °C, and $1.57\times10^{-1}$ S·cm$^{-1}$ at 160 °C, values that exceed those of most high-performance proton-conductive COFs (Fig. 11b). Although the material exhibits high conductivity at raised temperatures, its fuel-cell performance has only been demonstrated under low-humidity, moderate-temperature conditions (50 °C, 23% RH), calling into question its high-performance under practical HT-PEMFC. In a membrane configuration, a 270 μm $H_3PO_4$@PBI mem-

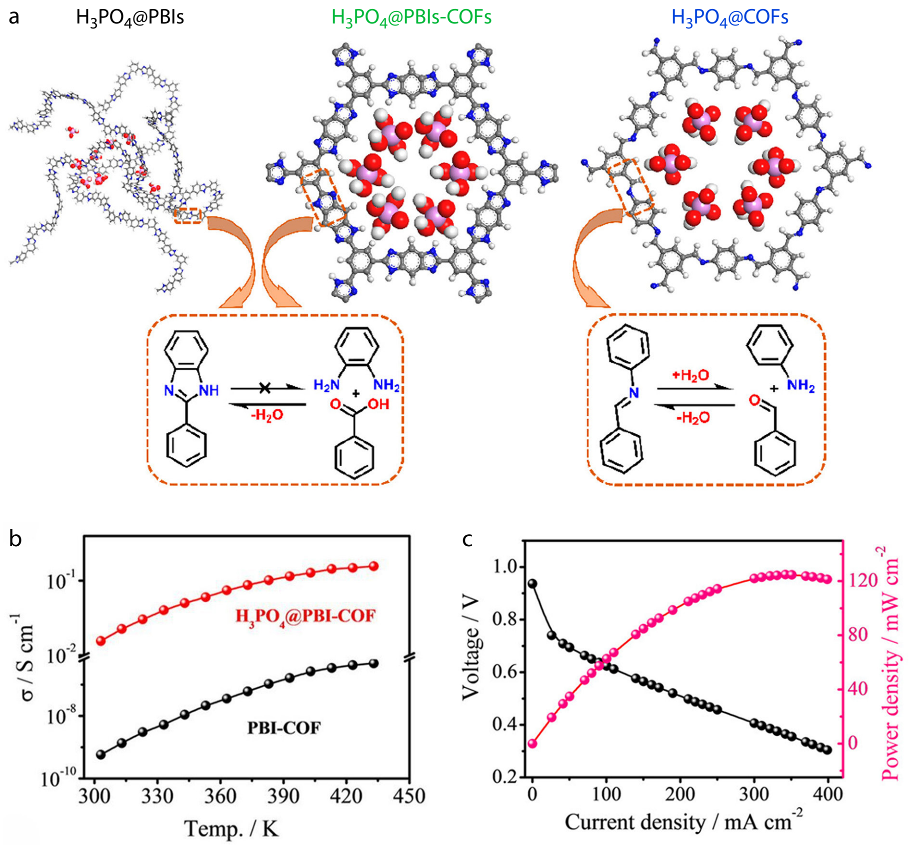

**Fig. 11** (a) Schematic illustration of PBI-COFs integrating the advantages of both PBIs and COFs for $H_3PO_4$ impregnation; (b) Temperature-dependent proton conductivity and (c) current-voltage polarization and power density of PBI-COF and $H_3PO_4$@PBI-COF. (Reproduced with permission from Ref. [69]; Copyright (2022), American Chemical Society).

brane containing 4 wt% PTFE binder exhibited an OCV of 0.936 V and a peak power density of 125 mW·cm$^{-2}$, figures that approach the performance of Nafion-based PEMFCs (Fig. 11c). Nevertheless, further work is required to address remaining challenges for real-world applications, particularly long-term stability and operation under typical PEMFC humidity and temperature regimes.

PBI-COF exhibits considerable promise for proton conduction at elevated temperatures. Its powdery form, however, compels blending with binders to produce composite membranes; this requirement markedly diminishes performance and constrains practical application. Consequently, the necessity for binders may also severely curtail their effectiveness in MEA devices operating at high temperature. Xu *et al*.[70] introduced an acidification and gelation strategy to create self-standing COF-modified gel membranes (PPA@PBI-COF) using an *in situ* method. The membrane was synthesized through a one-pot approach, employing alkaline polybenzimidazole-linked COF (PBI-COF) as the gelling agent and poly(phosphoric acid) (PPA) as both the solvent and proton source. The resulting gel membranes exhibit a uniform color, a flat and smooth surface, and good flexibility. This is attributed to the dynamic hydrogen-bonding interactions between PPA molecules and PBI-COF monolayers. In contrast to linear PBI (denoted as PBI-L), PPA@PBI-L remained in a liquid state with increased polymerization time, whereas PPA@PBI-COF developed into a stable gel PPA@PBI-L remained liquid state, while PPA@PBI-COF formed a stable gel. PBI-COF not only establishes a stable gel network with PPA through acid-base interactions, *π-π* stacking between COF monolayers, but also acts as "proton traps" to capture part of the protons from PPA, creating proton vacancies within the gel system and facilitating efficient proton transport pathways. (Fig. 12a). Performance tests indicate that the gel membrane possesses remarkable high-temperature stability, exhibiting no significant weight loss below 300 °C, alongside low gas permeability. Its anhydrous proton conductivity increases markedly with temperature, reaching 1.68×10$^{-1}$ S·cm$^{-1}$ at 180 °C, thereby surpassing most reported COF-modified materials. Furthermore, the gel membrane demonstrates excellent proton conduction stability (Fig. 12b). The MEA test conducted under anhydrous conditions with this membrane, achieves a maximum power density of 150 mW·cm$^{-2}$ at 180 °C. Moreover, the OCV of the MEA shows no significant attenuation after continuous operation for 24 h at 160 °C, demonstrating good long-term stability (Fig. 12c).

The findings demonstrate that incorporating COFs into polymer matrices substantially improves the mechanical integrity of composite membranes. In addition to reinforcing the polymer, COFs introduce proton-conducting sites and, through their porous architecture-characterized by high specific surface area and ordered channels-establish continuous pathways for proton transport. Recently, Jiang's group[71,72] introduced the first systematic investigation into the effects

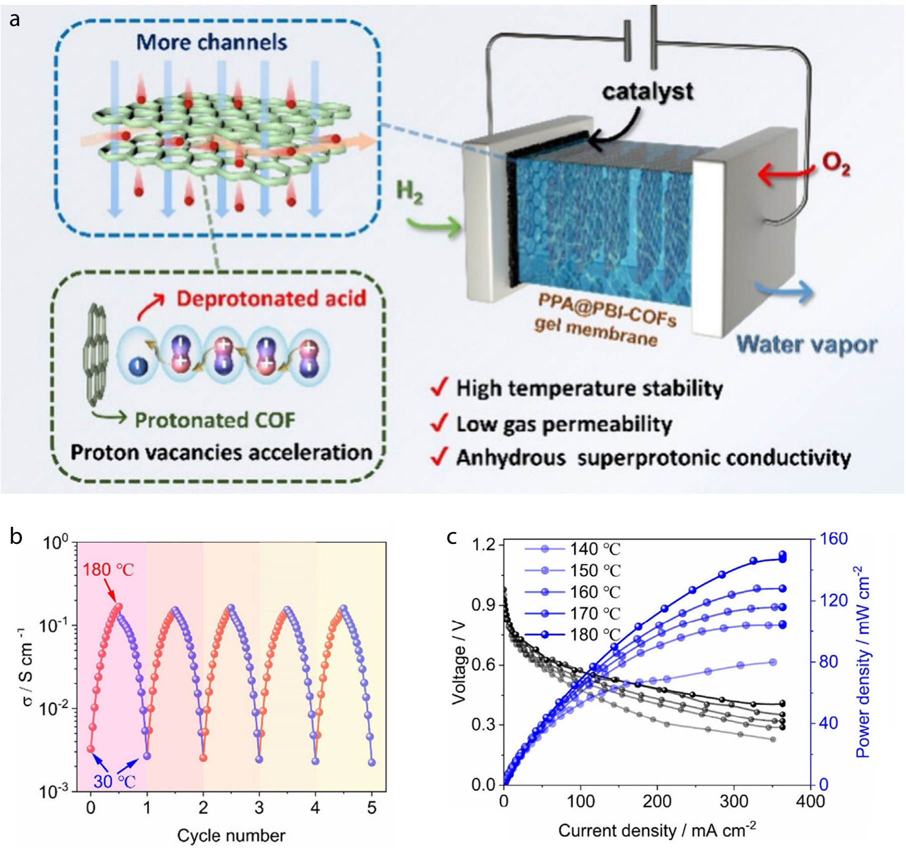

**Fig. 12** (a) Schematic diagram of the mechanism of proton vacancies accelerating proton conduction; (b) Temperature cycling-dependent anhydrous proton conductivity of PPA@PBI-COF; (c) Current-voltage polarization and power density plots of MEA fabricated by PPA@PBI-COF from 140 °C to 180 °C. (Reproduced with permission from Ref. [70]; Copyright (2025), American Chemical Society).

of pore environment—specifically pore volume, pore size, and topology—on proton conduction within a series of designed COFs. The study meticulously examines hexagonal COFs with progressively tuned pore sizes from micropores to mesopores, revealing that increasing pore volume exponentially enhances proton conductivity by up to 1150-fold and that pore size linearly regulates the activation energy barrier, with a distinct threshold (about 2.1 nm) separating fast-hopping from sluggish vehicle mechanisms. This foundational research is significantly expanded by a parallel exploration of diverse pore topologies-trigonal, tetragonal, hexagonal, and Kagome-demonstrating that the geometry of the nanochannels dictates an exponential acceleration of proton mobility, hierarchical as hexagon > Kagome > tetragon > trigon. By integrating these findings, the research establishes a comprehensive structure-property relationship, conclusively showing that a well-developed, continuous hydrogen-bonding network of phosphoric acid, stabilized by multipoint interactions with the pore walls, is crucial for achieving exceptional and stable anhydrous proton conduction. This systematic approach provides transformative, general guidelines for the molecular design of porous materials for advanced ion-conduction applications. Together, these attributes constitute an effective approach to the fabrication of HT-PEMFCs. Notably, *in situ* synthesis of COFs within the polymer matrix promotes uniform dispersion and strong interfacial bonding, thereby avoiding the defects commonly associated with conventional physical blending. By mitigating interfacial discontinuities, this strategy reconciles the often-competing demands of mechanical robustness and proton conductivity, yielding high-performance membranes for HT-PEMFCs. Current evidence suggests that targeted functionalization and deliberate pore-structure design of COFs is central to further performance gains. The synergistic interplay between functional groups and porous architecture points to promising directions for the development of multifunctional composite membranes. Future work should therefore focus on optimizing the identity and density of functional groups (*e.g.*, phosphonic acid moieties) and tuning pore sizes to improve proton-conduction selectivity. Complementary studies are also required to assess long-term durability under realistic fuel-cell operating conditions and to examine the behavior of COF-based composites at elevated temperatures and low humidities, thereby broadening their practical applicability.

## 5 CONCLUSIONS AND OUTLOOK

In recent years, substantial efforts have focused on developing proton-conducting COF-modified membranes. This review provides an overview of the relevant content from three dimensions. From the preparation standpoint, two widely employed strategies are discussed to achieve uniform dispersion and robust interfacial bonding within composite membranes. Regarding mechanism synergy, COFs facilitate continuous proton transport pathways, offering a promising approach for designing high-performance composite PEMs, particularly under harsh conditions, due to their abundant proton sites and highly porous structures with ordered channels. Incorporating COFs into polymer matrices effectively improves water retention while maintaining low swelling ratios (lowest at 9.4%), simultaneously enhancing mechanical properties (with tensile strength reaching up to 130 MPa) and endowing the composite PEM with outstanding thermal stability (up to 390 °C) as illustrated in Table 1. In terms of PEMFC performance, COF-modified composite membranes demonstrate substantial improvements in both proton conductivity and MEA performance. For Nafion-based composite PEMs fabricated by *in situ* blending with sulfonic acid-functionalized COFs, a significant improvement in power density is achieved in PEMFCs, underscoring the efficiency of COFs in promoting proton transport under low-temperature and high-humidity conditions (80 °C, 100% RH). Rational selection of COF species and doping concentration plays a critical role in optimizing overall membrane performance (Fig. 13a). On the other hand, for PBI-based composite PEMs, fuel cell performance under high-temperature conditions (160 °C) is strongly influenced by COF loading content. Specifically, higher COF mass ratio in composite PEMs leads to greater maximum power density, as presented in Fig 13(b).

The design and preparation of COF-modified composite PEMs have become a vibrant research field, yet it remains in its infancy. Several challenges still exist that need to be addressed. (i) The rigid porous structure of COFs exhibits which can lead to weak interfacial bonding and poor compatibility between the two phases. In this case, *in situ* growth, interfacial polymerization, or covalent grafting are adopted to enhance two-phase interfacial compatibility, and simultaneously improve the membrane's mechanical strength, dimensional stability, and long-term durability. (ii) Although the ordered channels of COFs are expected to provide oriented pro-

**Table 1** Mass ratio, water-related properties (affecting proton conductivity), mechanically properties, proton conductivity and MEA performance of COF-modified multifunctional membranes.

| COF-modified multifunctional membranes | Mass ratio of COFs to polymer | Water-related properties (affecting proton conductivity) | | Mechanical properties | | Proton conductivity (mS·cm$^{-1}$) | MEA performance ($H_2/O_2$ fuel cell application) | |
|---|---|---|---|---|---|---|---|---|
| | | Water uptake (%) | Swelling ratio (%) | Thermal Stability (°C) | Tensile strength (MPa) | | Open circuit voltage (V) | Max power density (mW·cm$^{-2}$) |
| Nafion-SCONs-0.6[35] | 0.6 wt% | 28.7±1.3 (30 °C) | 17.4 (30 °C) | – | | 265 (80°C, 100% RH) | – | 118.2 |
| Nafion-$H_3PO_4$@SNW-15[34] | 15 wt% | 26.4 (25 °C)<br>49.4 (80 °C) | 26.8 (80 °C)<br>15.1 (25 °C) | – | – | 137 (30 °C, 100%RH)<br>60.4 (80 °C, 51.4% RH) | – | 277 |
| Nafion/Z-COF-10[51] | 10 wt% | 31.1 (30 °C)<br>38.1 (80 °C) | 5.6 (30 °C)<br>9.4 (80 °C) | – | | 220 (80 °C, 100% RH) | 0.932 | 170 (80 °C, 100% RH) |
| ZUT-COF-$SO_3H$-Nafion[52] | 10 wt% | 21.57 | 9.39 | 390 | – | 133.8 (80 °C, 80% RH) | 0.97986 | 304.056 (80 °C) |
| Am-COF-3-$SO_3H$/Nafion[36] | 25 wt% | 27.54 (25 °C) | – | 200 | – | – | – | 1870 (105 °C, 80% RH)<br>2170 (80 °C, 100% RH) |
| SPEEK/TpPa-$SO_3H$-5[53] | 5 wt% | 19.34 (30 °C)<br>31.31 (60 °C) | 19.57 (30 °C)<br>31.69 (60 °C) | 240 | 74.5 | 346 (80 °C, 100% RH) | 1.01 | 86.54 (60 °C) |
| SPEEK/HPW@COF-15[57] | 15 wt% | – | – | – | 75 | 280 (75 °C, 100% RH) | – | – |
| PBI/SCOF-10 (PA-doped)[67] | 10 wt% | – | 35.27 | 200 | 130.1 | 542.1 (80 °C, 100% RH)<br>134.2 (30 °C, 50% RH) | 0.859 | 227.2 (160 °C) |
| PBI/SNW-1 (PA-doped)[73] | 30 wt% | – | 72.5 | 300 | 4 | 114 (160 °C) | – | 590 (160 °C) |
| 40%-COF-OPBI (PA-doped)[68] | 40 wt% | – | 167.4 | – | 12.2 | 177.7 (160 °C) | – | 774.7 (160 °C) |

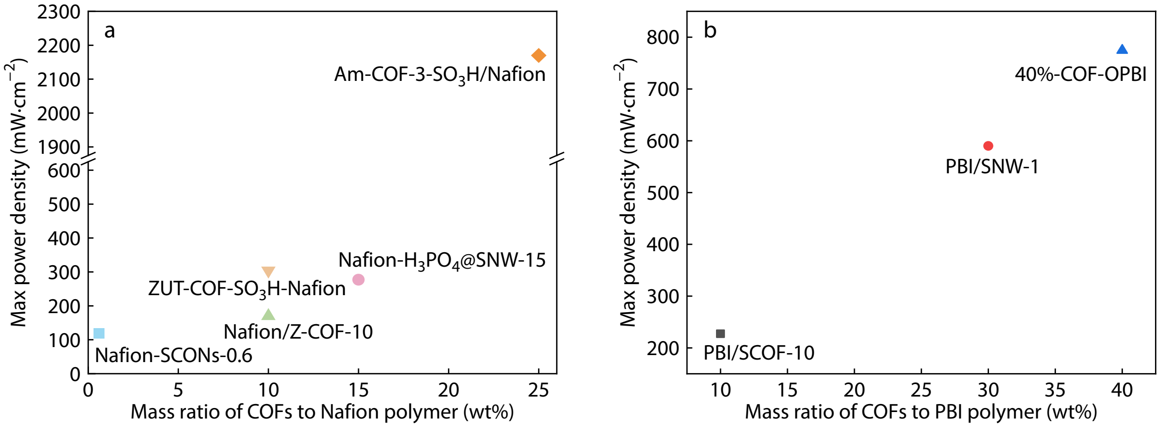

**Fig. 13** Single fuel cell performance of (a) Nafion-based composite membranes with different COF loadings; (b) PBI-based composite membranes with different COF loadings.

ton transport pathways, their pore sizes, functional groups, and distributions must be precisely tailored. (iii) Currently, the proton conduction pathways within COF structures, polymer matrices, and their interfacial regions remain ambiguous. Therefore, *in situ* characterization techniques and theoretical calculations are urgently required. (v) Under the acidic, oxidative, and humid operating conditions of fuel cells, chemical degradation tends to occur at the COF–polymer interface. Some covalent linkages (*e.g.*, imine bonds) are unstable under strong acidic or oxidative environments, which may cause the collapse of pore structures or the leaching of functional groups. Therefore, cycling tests are usually conducted to evaluate the long-term durability of composite membranes in practical fuel cell applications. (vi) The synthesis of COF is usually complicated and requires strict conditions, and the cost of large-scale preparation for high-quality COFs is relatively high. In this case, high-throughput computing and machine learning are expected to accelerate the material design process. Meanwhile, continuous preparation processes (*e.g.*, roll-to-roll coating) could help to reduce the overall cost, with the ultimate goal of meeting the urgent demand for next-generation high-performance PEMs in the clean energy technology field. In summary, future progress will focus on breakthroughs in material structures, fabrication techniques, and functional performance, which drives the transition from laboratory research to practical industrial applications.

## BIOGRAPHIES

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## Conflict of Interests

The authors declare no interest conflict.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52473220 and 52503276), the Key Research and Development Program of Shaanxi Province (No. 2025CY-YBXM-444), the Science and Technology Project of Yanchang Petroleum (Group) Co., Ltd. (No. YCSY2026-YYJC-B-28), the Fundamental Research Funds for the Central Universities and the "Young Talent Support Plan" of Xi'an Jiaotong university.

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## Graphical Abstract

### Covalent Organic Frameworks Modified Composite Proton Exchange Membranes towards Advanced Fuel Cells

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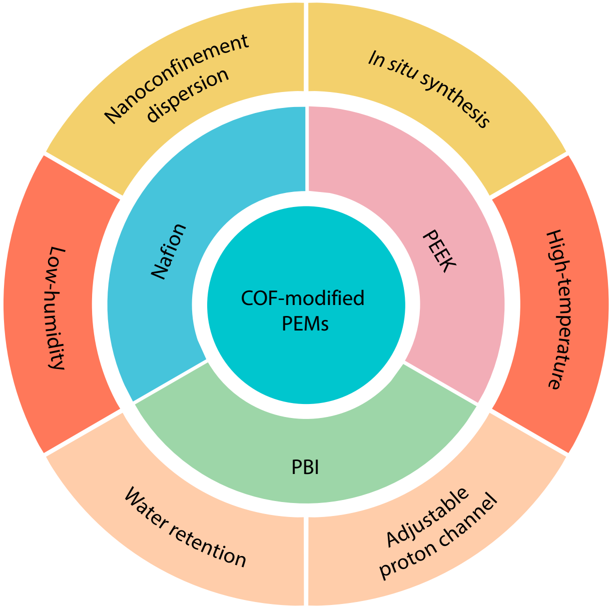
This review summarizes the synthetic strategies of covalent organic framework (COF)-modified proton exchange membrane (PEM) based on Nafion, SPEEK, and PBI for low-humidity and high-temperature applications, and clarifies COF-enhanced proton conduction mechanisms *via* water retention and adjustable proton channels.



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