

Synthesis and characterization of polydopamine-modified MOFs for polymer electrolyte membranes

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The operational efficiency of batteries, supercapacitors, and fuel cells depends on the delicate balance among ionic conductivity, mechanical robustness, and ion crossover resistance. Proton-conductive membranes are widely used to enhance the performance of these systems. Nafion is a widely used commercial proton-exchange membrane. However, its widespread use is constrained by its high cost and other performance limitations. In this study, novel electrospun sulfonated poly(phenylene sulfone) (sPPSU) composite membranes loaded with metal-organic frameworks were synthesized and characterized. Four types of zirconium-based metal-organic frameworks (MOF-801, MOF-808, MIL-140, and UiO-66) were surface-modified with polydopamine (PDA) and incorporated into an sPPSU matrix. This PDA functionalization improved the dispersion of the MOF particles within the polymer matrix and created additional proton-conducting pathways throughout the membrane structure. The membranes were characterized in terms of morphology using scanning electron microscopy (SEM), electrochemical properties using impedance spectroscopy, and mechanical properties according to the ASTM D882 standard. The experimental results revealed that the UiO-66-P membrane exhibited the highest proton conductivity (16.6 mS/cm). Notably, the ion-exchange capacity of MOF-801-P was 9.75 meq/g, exceeding the 7.35 meq/g of commercial Nafion 212. Additionally, the mechanical strengths of the MIL-140-P and UiO-66-P membranes reached levels comparable to the 22.24 MPa benchmark of Nafion 212. These findings demonstrate that PDA-modified Zr-MOF/sPPSU electrospun membranes are promising candidates for next-generation proton-exchange membrane applications.

Keywords: sulfonated poly(phenylene sulfone), metal-organic framework, proton-exchange membrane, electrospinning, polydopamine, electrochemical energy storage

INTRODUCTION

Proton exchange membranes are considered key elements of advanced electrochemical systems because they allow selective ion transport and act as an important physical barrier between the electrodes. Perfluorinated membranes (e.g., Nafion) are commonly used, but their use is often limited by high manufacturing costs and certain performance limitations under demanding operating conditions. To address these challenges, metal-organic frameworks (MOFs) have emerged as promising functional fillers for advanced membrane applications. Unlike traditional inorganic fillers, MOFs have unique internal nanochannels that allow efficient proton conduction through interconnected pathways and restrict the transport of larger species via size-exclusion mechanisms [1]. The high tunability of the pore size and chemical functionality enables the rational design of membranes with optimized ion selectivity and enhanced proton conductivity [2].

Zirconium-based metal-organic frameworks, particularly the MIL-140 family, are emerging materials for electrochemical energy storage applications owing to their high coordination numbers and binding energies, resulting in good chemical stability under corrosive acidic conditions [3]. Zr-based frameworks of the MIL-140 family represent a special class of materials with high hydrolytic stability and densely packed structures. Within this family, MIL-140A is especially characterized by its very restricted triangular apertures, generally smaller than 4 Å, which is a significant advantage for ion-sieving applications. The restricted pore dimensions may favor selective proton transport while hindering the crossover of larger ionic species, which is advantageous for membrane selectivity [4].

Sulfonated poly(phenylene sulfone) (sPPSU) has been employed as a promising matrix for proton-exchange membrane applications owing to its excellent chemical stability and strong mechanical

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properties. The inherent resistance of the polymer to corrosive acidic environments imparts durability during electrochemical cycling, and the tunable sulfonation degree provides a versatile means to control proton transport characteristics. These features position sPPSU as a reliable and cost-effective alternative to conventional perfluorinated membranes for electrochemical energy storage applications. In this study, the surfaces of MOF-801, MOF-808, MIL-140, and UiO-66 architectures were modified with polydopamine to improve their integration and compatibility with the polymer matrix. The modified frameworks were incorporated into sPPSU via electrospinning to prepare composite membranes. Finally, the resulting membranes were systematically characterized in terms of proton conductivity, ion-exchange capacity, and mechanical performance to evaluate their potential for advanced energy-storage systems.

EXPERIMENTAL

MIL 140 preparation

MIL-140 was synthesized by dissolving ZrCl_4 and terephthalic acid (H_2BDC) in 30 mL of DMF and transferring the mixture into a PTFE-lined stainless-steel autoclave. The reaction was carried out under hydrothermal conditions at 220 °C for 15 h; this elevated temperature is essential for obtaining the thermodynamically stable MIL-140 phase in pure form [5, 6]. After completion, the product was separated by vacuum filtration, washed with methanol, and dried at 60–80 °C.

MOF-808 preparation

MOF-808 was synthesized by homogeneously mixing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (4.85 g) and H_3BTC (1.05 g) in a DMF/formic acid solvent system (45 mL, 1:1 ratio) and storing the mixture under hydrothermal conditions at 130 °C for 48 hours [7]. After completion, the product was separated by centrifugation and sequentially washed with DMF, deionized water, and acetone. For pore activation, the samples were subjected to thermal treatment at 150 °C for 24 h under vacuum [8].

UiO-66 preparation

UiO-66 was synthesized by dissolving ZrCl_4 (2.7 mmol) and HCl as a modulator in 25 mL DMF, followed by the addition of terephthalic acid and 50 mL DMF to obtain a homogeneous suspension. The mixture was maintained at 120 °C for 24 h in a hydrothermal reactor [9]. The resulting precipitate was separated by vacuum filtration, washed three times with DMF, stirred in ethanol for 24 h, and dried at 40 °C [9].

MOF-801 preparation

MOF-801 was synthesized by dissolving $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and fumaric acid in a DMF/formic acid solvent system and transferring the mixture to a stainless-steel autoclave. The reaction was carried out under hydrothermal conditions at 130 °C for 6 h [10, 11]. The resulting white precipitate was separated by centrifugation, washed sequentially with DMF and methanol, and thermally activated at 150 °C for 24 h under vacuum [10].

PDA modification

In this study, four different zirconium-based MOFs (MOF-801, MOF-808, MIL-140, and UiO-66) were modified with PDA for the fabrication of electrospun membranes. The polydopamine (PDA) coating process improves the dispersion of MOF particles within the polymer matrix by forming a hydrophilic and highly adhesive layer on their surfaces. It also enhances the ionic conductivity of the system by creating additional proton transport pathways [12]. The literature frequently emphasizes that PDA directly facilitates proton transfer through acid-base pairs formed via the hydroxyl (–OH) and amine/imine (–NH₂/–NH–) functional groups in its chemical structure [13].

In the experimental process, 0.200 g of each MOF type was weighed, dispersed in a Tris-HCl buffer solution, and transferred to a dopamine hydrochloride solution. As a result of the coating process, which was carried out at room temperature under magnetic stirring for 24 h, a homogeneous PDA layer was formed on the surface of the MOF particles via spontaneous oxidative polymerization of dopamine [12]. After the reaction was complete, the resulting modified MOF particles were centrifuged, washed with distilled water, dried, and transferred to a solution suitable for electrospinning.

Membrane preparation

In the initial phase, 20 different formulations were tested, and it was determined that the most suitable solution for the electrospinning process was a formulation containing 30% sPPSU, 20–30% acetone, and the remainder as NMP. PDA-modified MOF particles were added at a loading of 3 wt% relative to the mass of sPPSU in the membrane formulation. The solution was stirred for 24 h at 35 °C. Once the appropriate viscosity was achieved, fiber production was performed using an electrospinning device with a voltage of 20 kV, a needle-collector distance of 15 cm, and a flow rate of 0.015 mL/min.

Membrane characterization

Commercial Nafion 212 was used as the reference membrane and characterized under the same experimental conditions for comparison.

Water uptake refers to the increase in membrane mass after water absorption. The membranes were immersed in water for 24 h, and water uptake was calculated from the difference between the wet and dry membrane masses.

$$WU (\%) = \left(\frac{M_{Wet} - M_{Dry}}{M_{Dry}} \right) \times 100 \quad (1)$$

The empirical porosity of the membranes was determined using 1 cm × 1 cm samples based on their masses before and after water immersion and the densities of water and sPPSU [14].

The membranes were immersed in 1 M H₂SO₄ solution for 24 h before impedance measurements [15, 16]. The proton conductivity (σ) was calculated from the electrical resistance (R) obtained from the impedance measurements using the following equation:

$$\sigma = \left(\frac{l}{R \times S} \right) \quad (2)$$

where l is the membrane thickness (cm), R is the electrical resistance (Ω), and S is the membrane surface area (cm²).

The ion exchange capacity (IEC) represents the milliequivalent amount of –SO₃H groups per gram of polymer and is the primary parameter that determines the proton transport performance [10]. The IEC was determined using NaOH back-titration [17].

$$IEC (meq/g) = \left(\frac{C_{NaOH} \times V_{NaOH}}{M_d} \right) \quad (3)$$

Here, C_{NaOH} represents the molarity of the sodium hydroxide (NaOH) solution used in titration, V_{NaOH} represents the volume of NaOH used, and M_d refers to the mass of the dry membrane sample used in the analysis.

For long-term use, the mechanical performance of polymer-based materials, specifically their strength, flexibility, and dimensional stability, must be assessed. Tensile tests were conducted in compliance with the ASTM D882 standard using an ANKARIN universal tensile testing machine. Commercial Nafion 212 was also tested under the same conditions and exhibited a tensile strength of 22.24 MPa. The electrospun reinforcement of sPPSU membranes has been reported to provide higher hydrolytic and mechanical stability than that of cast membranes [14, 18].

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the synthesized MOF particles. SEM micrographs are critical for understanding the morphology of the synthesized MOFs and their crystal structures, which directly impact their electrochemical performance. The well-defined polyhedral and nanocrystalline geometries of MOF-801 and UiO-66, with homogeneous particle distributions, may favor the formation of effective proton-transport pathways [19].

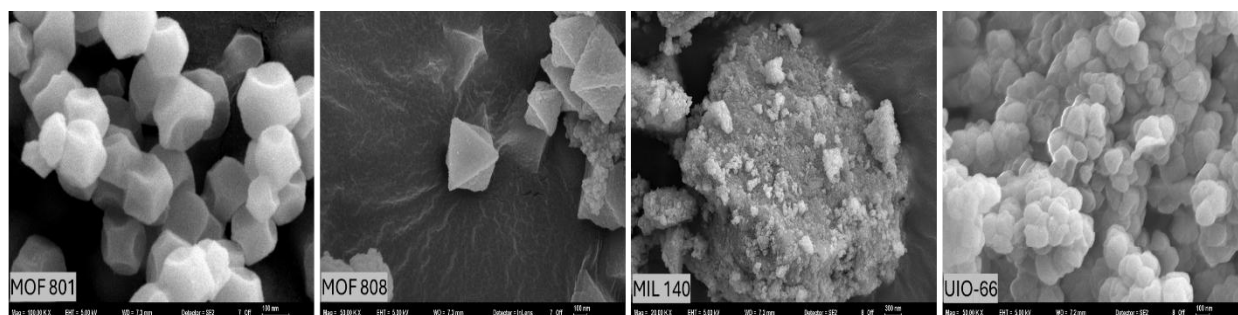


Figure 1. SEM images of synthesized Zr-based MOF particles: (a) MOF-801, (b) MOF-808, (c) MIL-140, and (d) UiO-66.

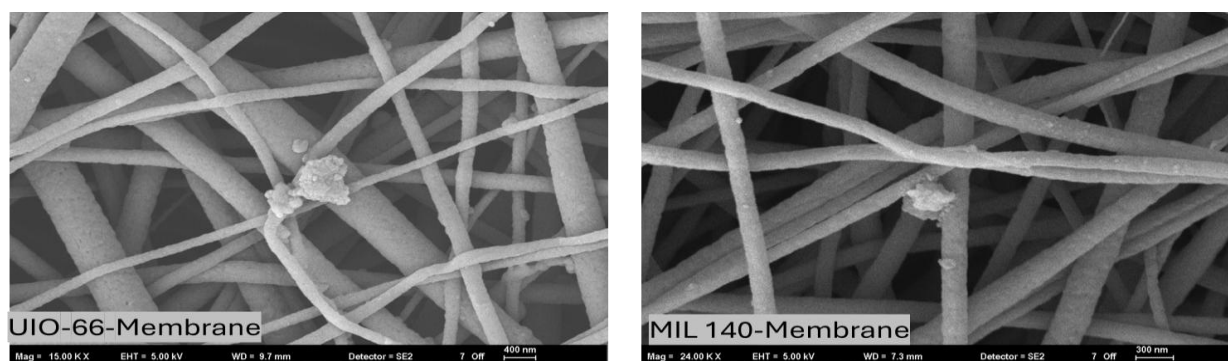


Figure 2. SEM images of electrospun sPPSU composite membranes containing 3 wt% (a) UiO-66-P and (b) MIL-140-P nanofillers.

In contrast, MOF-808 exhibits characteristic large octahedral crystals with sharp surfaces, indicating high crystallinity, and MIL-140 shows a more agglomerated and compact morphology, which may restrict the accessibility of the ion-exchange sites [20]. These morphological differences were directly correlated with the measured ion exchange capacity and proton conductivity.

The SEM images of the UiO-66- and MIL-140-doped membranes at a 3 wt% loading (Figure 2) reveal a highly porous and interconnected nanofiber network structure, indicating successful fiber formation by electrospinning. Continuous and randomly oriented nanofibers provide a high surface area-to-volume ratio, which is critical for optimizing proton conductivity [21]. Although the MOF nanoparticles were incorporated into the polymer matrix, the occasional “bead-on-string” formations suggest some local heterogeneity in the fiber morphology at a 3 wt% MOF loading. The incorporation of MOF particles into the fiber structure may contribute to the IEC and proton transport behavior by providing additional ion-exchange sites and interfacial transport pathways.

The hydrophilic functional groups of PDA may contribute to the water-retention behavior of the composite membranes. At the same time, PDA coating may partially restrict MOF pore accessibility, which could influence membrane porosity and ion transport. In the MOF-808-P membrane, the relatively low proton conductivity may be associated with restricted ion-transport pathways, despite the potential contribution of PDA to interfacial adhesion and water retention. Previous studies have reported that the catechol and amine groups of PDA can form hydrogen-bonding interactions with acidic groups and water molecules in the polymer matrix, which may facilitate the continuity of proton-transport pathways.

These results indicate that porosity and water uptake do not vary proportionally across the investigated membranes. This suggests that

hydrophilicity is jointly governed by surface chemistry and physical pore volume [22]. Optimized water retention values facilitate the hydrogen bond networks required for the Grotthuss mechanism, whereas excessive water retention can lead to dimensional instability and negatively impact ion selectivity.

Table 2 presents the electrochemical properties of the MOF-doped membranes. The electrochemical performance of the synthesized MOF-based membranes was evaluated in terms of proton conductivity and ion exchange capacity (IEC).

UiO-66-P exhibited the highest proton conductivity among the investigated composite membranes, at 16.6 mS/cm, followed closely by MOF-801-P (15.6 mS/cm). These values suggest that the pore structure and functionalization of the UiO-66 and MOF-801 frameworks facilitate efficient proton transport, likely via a well-connected hydrogen bonding network.

In contrast, MIL-140-P showed the lowest conductivity (2.9 mS/cm), which may be attributed to its specific crystal packing and the lower density of active proton-conducting sites within its channels. While all investigated composite membranes showed lower proton conductivity than commercial Nafion 212 (26.9 mS/cm), UiO-66-P and MOF-801-P demonstrated promising potential as alternative proton-conducting membrane materials.

MOF-801-P reached the highest IEC value of 9.75 meq/g, exceeding that of Nafion 212 (7.35 meq/g). This indicates a high density of exchangeable proton sites in the MOF-801-P composite membrane. Interestingly, although UiO-66-P has a lower IEC (5.26 meq/g) than MOF-801-P, it exhibits slightly higher proton conductivity. This suggests that proton transport in UiO-66-P may be facilitated by more effective transport pathways rather than by IEC alone. MIL-140-P showed a different trend, exhibiting a higher IEC (6.04 meq/g) than UiO-66-P and MOF-808-P, while showing the lowest proton conductivity. These

results indicate that a high IEC alone does not necessarily lead to high proton conductivity; membrane morphology and the effectiveness of proton-transport pathways also play important roles.

Table 1. Physical properties of membranes

Membrane	Thickness (μm)	Porosity (%)	Water uptake (%)
MOF-808 - P	65	29.44	32.35
MOF-801 - P	62	63.23	133.33
MIL-140 - P	59	67.36	160.00
UiO-66 - P	83	70.25	183.02

Table 2. Electrochemical properties of the membranes

Membrane	Proton conductivity (mS/cm)	IEC (meq/g)
MOF-801-P	15.6	9.75
MOF-808-P	4.7	4.96
MIL-140-P	2.9	6.04
UiO-66-P	16.6	5.26
Nafion 212	26.9	7.35

Table 3 presents the mechanical characteristics of the fabricated membrane. Overall, the P-series membranes exhibited the most balanced mechanical performance, approaching the reference value of Nafion 212 (22.24 MPa).

Table 3. Mechanical properties of the membranes

Membrane	Stress (MPa)	Strain (-)
MOF-801-P	8.5	0.028
MOF-808-P	13.6	0.050
MIL-140-P	21.86	0.11
UiO-66-P	20.91	0.16

In particular, the mechanical strengths of MIL-140A-P (21.86 MPa) and UiO-66-P (20.91 MPa) were only 2–7% lower than that of Nafion 212, suggesting a beneficial contribution of polydopamine modification to the mechanical performance of the composite membranes.

PDA establishes hydrogen bonds, π – π interactions, and acid-base interactions simultaneously with both the MOF crystal surface and the $-\text{SO}_3\text{H}$, $-\text{C}-\text{O}-\text{C}$, and aromatic ring groups in the polymer matrix (sPPSU) via the catechol and amine functional groups on its surface [23]. This multimodal bonding mechanism prevents the agglomeration of MOF particles, homogenizes stress transmission at the fiber-matrix interface, and maintains fiber continuity [23]. The regular and smooth fiber morphology exhibited by the P series in the SEM analysis also confirmed this structural integration. From a technical standpoint, these results suggest that PDA modification improves interfacial compatibility between the inorganic

fillers and the polymer phase, which may contribute to more effective stress transfer. This suggests that the commonly reported trade-off between ion-exchange capacity and mechanical strength may be mitigated by the molecular bridging effect of polydopamine [23].

CONCLUSION

In this study, PDA-coated composite membranes were prepared *via* electrospinning and characterized in detail. Four different Zr-based MOFs (MOF-801, MOF-808, MIL-140, and UiO-66) were doped into a sPPSU polymer matrix for electrochemical energy storage applications. SEM analyses indicated good integration of the PDA-modified MOF particles within the polymer matrix while maintaining the continuity of the fibrous morphology.

The porosity and water uptake differed for the different types of MOF, and the highest values were found in the samples UiO-66-P (70.25% porosity, 183.02% water uptake) and MIL-140-P (67.36% porosity, 160.00% water uptake). The results indicated that porosity and water uptake did not vary proportionally across the investigated membranes. Surface chemistry is as important as the physical pore volume in determining hydrophilic properties.

Among all MOF series, UiO-66-P exhibited the highest proton conductivity (16.6 mS/cm). MOF-801-P exhibited an IEC value of 9.75 meq/g, which was higher than that of the commercial reference membrane Nafion 212 (7.35 meq/g). However, MIL-140-P had the lowest proton conductivity in the series (2.9 mS/cm) despite a relatively high IEC value (6.04 meq/g), highlighting that IEC alone is not a sufficient metric for performance. These results indicate that IEC alone is not sufficient to determine proton-conducting performance and that membrane morphology and the effectiveness of proton-transport pathways also play important roles. Mechanical tests revealed that the PDA coating enhanced the fiber matrix fit *via* a multimode bonding mechanism (hydrogen bonding, π – π interaction, and acid-base pairs) at the polymer-MOF interface. MIL-140-P (21.86 MPa) and UiO-66-P (20.91 MPa) exhibited only 2–7% lower mechanical strength than Nafion 212 (22.24 MPa), showing that PDA modification may help mitigate the "conductivity-mechanical strength" trade-off of electrospun membranes.

In general, MOF selection and PDA modification strategies are the decisive factors for membrane performance. Among the investigated membranes, UiO-66-P and MOF-801-P showed the most balanced overall performance in terms of proton conductivity and IEC. The results suggest that Zr-

based MOF/sPPSU electrospun composite membranes can be a functional and cost-effective alternative to Nafion in electrochemical energy storage applications, particularly when combined with PDA surface modification. Future studies should further investigate the individual contributions of MOF structure and PDA modification, as well as the effects of different crosslinking strategies on membrane performance.

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