

# Zn(II)-based metal-organic framework/Nafion<sup>®</sup> composite membrane with high proton conductivity for fuel cell applications

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## ABSTRACT

Intentional coordination of Metal-organic frameworks (MOFs) with a conductive polymer was targeted to improve the proton conductivity and propose a better candidate material for fuel cell applications. Employing the concept of coordination networks, the conductivity of Nafion<sup>®</sup> was amplified by fabricating a composite of it with an inexpensive and highly proton-conductive three-dimensional MOF, namely,  $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$  (**1**, Me = methyl, ox = oxalate). Along with slightly higher thermal stability, increased ion exchange capacity and lower water uptake were observed, and the addition of 1 wt% of MOF **1** to Nafion<sup>®</sup> was found to be maximally efficient. The physico-chemical characteristics of MOF and membranes were also studied. This study may offer a cost-effective and facile fabrication technique for a variety of proton exchange membranes with characteristic proton-conducting properties for fuel cell applications.

**Keywords:** PEMFC, coordination network, MOF, proton Conductivity, Nafion

## 1. INTRODUCTION

Metal-organic frameworks (MOFs) are newly emerging inorganic-organic hybrid porous coordination polymers (PCPs) that are being explored for their unique applications, such as storage and selective separation of gases [1, 2], catalysis [3], drug delivery [4], magnetism [5], photoluminescence [6], and proton conduction [7]. As proton conductors, MOFs are showing progress owing to their highly ordered crystallinity, well-designed and tailorable pores, post-synthetic functionalization [8], and dynamic behavior. The viability of proton-conducting MOFs (PCMOFs) for fuel cell applications can be enhanced through the fabrication of a composite with polymer-based electrolyte membranes. In general, polymer-based electrolyte membranes such as proton exchange membranes (PEMs) use acidic groups as proton transporters and hydrogen-bonding networks as passageways for proton conduction to assist proton transfer. Nafion<sup>®</sup>, the most widely used PEM to date, consists of a hydrophobic perfluorinated polyethylene backbone grafted with hydrophilic terminal sulfonic acid groups as side chains. Nafion<sup>®</sup> utilizes these sulfonic acid groups as proton carriers only under humid conditions. Consequently, as a low-temperature PEM, Nafion<sup>®</sup> suffers from several shortcomings,

such as requirement of high humidification for better performance and related water management, catalyst poisoning by carbon monoxide, poor heat management, reduced diffusion rate, and associated technological costs [9]. Therefore, several studies have reported the introduction of inorganic or composite solids, a common practice to tackle those limitations of polymer membranes. A new approach to incorporate PCMOFs into the Nafion<sup>®</sup> matrix, as reported in our previous paper [10], showed excellent promise for proton conductivity improvement.  $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$  (**1**, Me = methyl, ox = oxalate) is an oxalate-based three-dimensional (3D) PCMOF with a nanoporous crystalline structure. MOF **1** consists of an anionic framework of  $[\text{Zn}_2(\text{ox})_3]^{2-}_n$  and a cationic supramolecular net of  $[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]^+_n$  that interpenetrate each other. Compound **1** features facile synthesis from inexpensive starting materials and high proton conductivity in both humid and anhydrous conditions [11]. In this study, we focused on integrating MOF **1** crystals as fillers into the Nafion<sup>®</sup> matrix to produce composite membranes for enhanced proton conductivity under ambient conditions and intended to explore the improvement of other characteristics such as thermal stability, water uptake, and ion exchange capacity (IEC) for application in proton exchange membrane fuel cells (PEMFCs).

## 2. EXPERIMENTAL

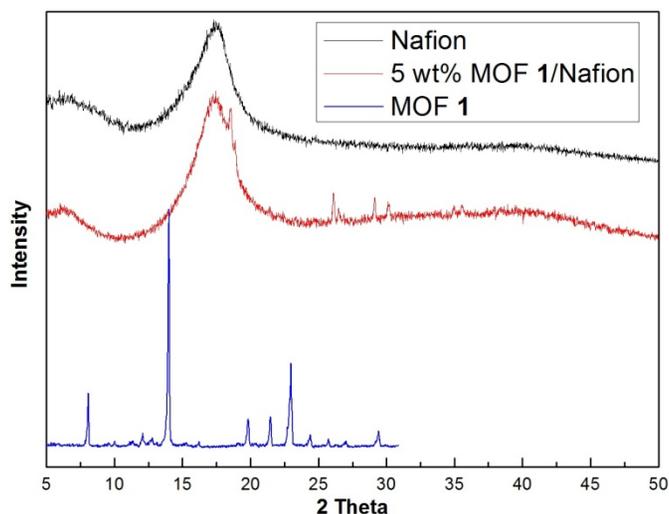
A solution of 5% Nafion<sup>®</sup> (D521, DuPont South Korea) contains Nafion<sup>®</sup> polymer (maximum 5.4 wt. %) that is stabilized in a mixture of water and 1-propanol. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

MOF **1** was synthesized by using a novel solvothermal method based on reported procedures [11]. MOF **1**/Nafion<sup>®</sup> composite membranes were prepared using the solution casting method [10]. The molecular structures and morphologies of the membranes were confirmed by powder X-ray diffraction (XRD; Bruker D2 PHASER, Germany) and field-emission scanning electron microscopy (FE-SEM) (Hitachi, JSM-6701F, JEOL), respectively. The water uptake and IEC of the composite membranes were measured according to the procedure reported by Sayeed et al. [12]. The Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer (Spectrum GX & Autoimage) instrument. Thermogravimetric analysis (TGA, TGA-2050, TA Instruments) was performed under a nitrogen atmosphere

from RT to 700 °C at a heating rate of 10 °C min<sup>-1</sup>. The proton conductivities of the MOF 1/Nafion<sup>®</sup> composite and Nafion<sup>®</sup> membranes were determined between 0.1 kHz and 1 MHz using alternating current (AC) impedance spectroscopy (VersaSTAT 3, Ametek).

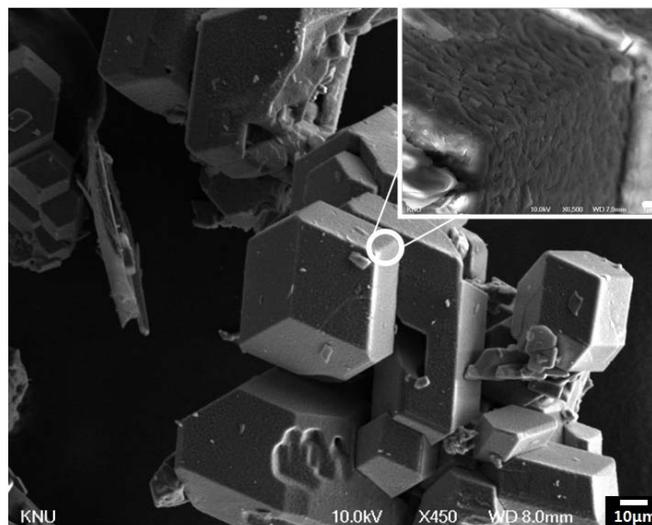
### 3. RESULTS AND DISCUSSION

The phase purity of pristine MOF 1 was established via powder X-ray diffraction (PXRD) measurement (Figure 1). For effective proton conduction, an extended hydrogen-bonded network is crucial. Single-crystal X-ray data revealed extensive 3D hydrogen bonding between the dimethylammonium cations and sulfate anions of MOF 1 [11]. In addition, the highly crystalline structure of MOF 1 was confirmed through the sharp peaks in its XRD profile. A highly crystalline structure is also necessary for efficient proton conduction. The XRD patterns of the Nafion<sup>®</sup> membrane [13] and the MOF 1/Nafion<sup>®</sup> composite membrane were also obtained. Because Nafion<sup>®</sup> is not crystalline, no peaks appeared in the XRD profile. The noncrystallinity of the MOF 1/Nafion<sup>®</sup> composite membrane was also confirmed by the absence of peaks in the XRD patterns, which is indicative of segregation of the MOF 1 crystals in the Nafion<sup>®</sup> matrix.



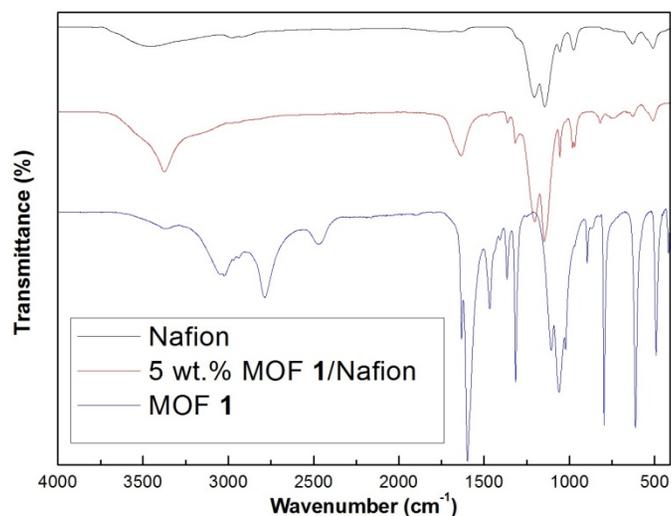
**Fig. 1** Powder X-ray diffraction (PXRD) patterns of MOF 1, Nafion<sup>®</sup>, MOF 1/Nafion<sup>®</sup> composite membranes

FE-SEM analysis was used to evaluate the crystallinity and morphology of MOF 1. The FE-SEM image (Figure 2) shows that MOF 1 has a cubic shape with an average crystal size of 0.001 mm<sup>3</sup> [11]. A rough surface and nanopores (inset image of Figure 2) are also evident and may provide the 3D proton transfer pathways. In the MOF 1/Nafion<sup>®</sup> composite membrane, MOF 1 is the dispersed phase and the Nafion<sup>®</sup> polymer is the continuous phase. MOF 1 crystals were well blended and homogeneously distributed in the Nafion<sup>®</sup> matrix, and this may be highly favorable for improving the proton conductivity of the MOF 1/Nafion<sup>®</sup> composite membrane.



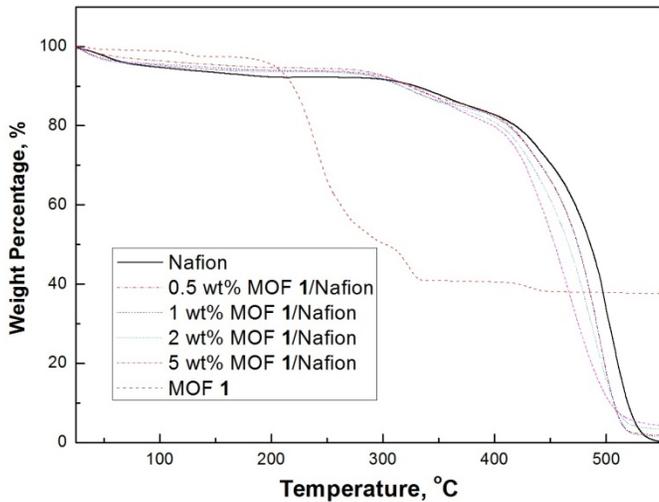
**Fig. 2** FE-SEM images of MOF 1 crystals (inset image: nanopores on the surface of MOF 1 crystal)

The spectra of all membranes exhibited characteristic bands at 804 (–CF<sub>2</sub>–CF<sub>2</sub> stretch), 982 (C–O–C), 1147 (symmetric stretching of –CF<sub>2</sub> groups), 2900 (CH<sub>2</sub>O), and 2988 cm<sup>-1</sup> (CHF) [14]. The peaks observed at 1056 and 1202 cm<sup>-1</sup> can be attributed to the symmetric and asymmetric stretching vibrations of SO<sub>3</sub><sup>-</sup> groups, respectively. The double broadening, observed at 1728 cm<sup>-1</sup>, was due to the bending vibrations of the O–H bonds, and the bands at 3455 cm<sup>-1</sup> are indicative of intermolecular hydrogen bonding. The spectrum of the composite was dominated by peaks associated with MOF 1 in the 1100–1200 cm<sup>-1</sup> region, which obscured the peaks attributable to the –CO– and OH functional groups of Nafion<sup>®</sup> [15]; this indicates interactions between the dispersed MOF 1 and the hydrate groups of the Nafion<sup>®</sup> polymer matrix.



**Fig. 3** FTIR spectra of Nafion<sup>®</sup> and MOF 1/Nafion<sup>®</sup> composite membranes

The thermogravimetric (TG) profiles of MOF 1 and the composite membranes are presented in Figure 3. MOF 1 is stable upto 180 °C, and no phase transition occurs under this temperature [11]. TG analyses revealed an initial weight loss for all membrane samples, which was attributed to water elimination, in a process that occurred in a single step and ended at temperatures above 300 °C. Since the samples were dried before the analyses, the water that was eliminated was likely to have been rapidly adsorbed during sample handling because of the hygroscopic nature of the MOF and membranes. According to the TG curves, the MOF 1/Nafion®

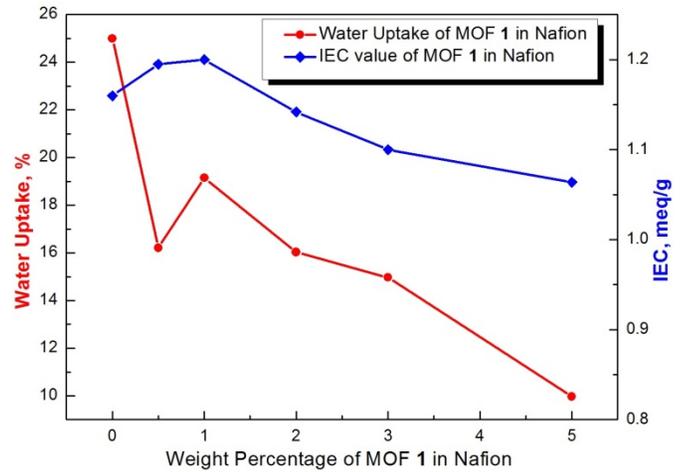


**Fig. 4** Thermogravimetric curves of and MOF 1, Nafion®, MOF 1/Nafion® composite membranes

composite membranes had greater thermal stability than Nafion® at the desired operation temperature, i.e., around 300 °C, which suggests the potential suitability of the composite for PEMFC applications.

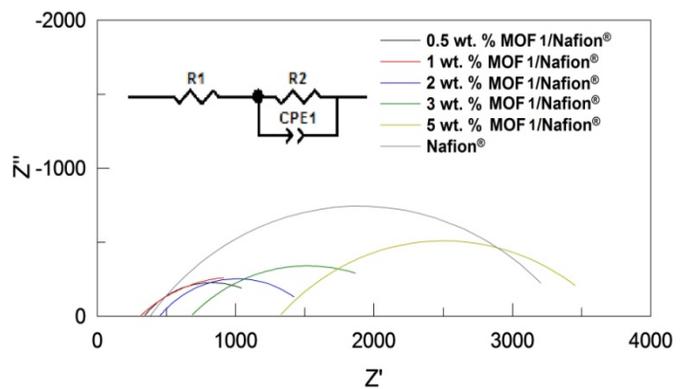
The water uptake capacity of a polymeric membrane is an important factor that influences its effectiveness during elevated temperature operation (i.e., above RT). However, excess water uptake can lead to dimensional changes in the membrane, which in turn result in impaired mechanical properties [16]. The presence of water molecules in Nafion® polymer membranes has a significant effect on the transport of protons and the hydrated structures that form around the negatively charged fixed ions in the acids [9]. The water uptake of the MOF 1/Nafion® composite membranes was lower than that of Nafion®; this was because of the modification of Nafion® by the MOF 1 crystals distributed in the membrane, which decreases the size of the pores that can generally accommodate water molecules. According to the data in Figure 5, increasing the weight percentage of MOF 1 in the Nafion® matrix decreases the water uptake value.

The IEC provides an indication of the amount of acid groups present in a polymer matrix; these groups are responsible for the conduction of protons, and thus, the IEC provides an indirect and reliable approximation of the proton conductivity.



**Fig. 5** Water uptake and ion exchange capacity of Nafion® and MOF 1/Nafion® composite membranes

The IEC values of the MOF 1/Nafion® composite membranes are shown in Figure 5. A possible reason for the increased IEC of the MOF 1/Nafion® composite membranes is that the SO<sub>3</sub><sup>-</sup> groups of the Nafion® matrix can provide Brønsted acid sites that can be exchanged and, additionally, the hydrophilic (Me<sub>2</sub>NH<sub>2</sub>)<sup>+</sup> cations of MOF 1 in the composite membrane provide easily dissociable protons [17] under humidified conditions. The membrane, by virtue of its IEC and water uptake, regulates the water content at the membrane/electrode interface, which in turn influences electrochemical characteristics. From Figure 5, we can also ascertain that IEC values initially rise with increasing weight percentage of MOF 1 in the membrane. The highest IEC was shown by the membrane containing 1 wt% MOF 1, in which a better MOF-polymer complex formed through the composite membrane to facilitate proton conduction. Further increasing the weight percentage of MOF 1 in the membrane caused reductions in the IEC values.



**Fig. 6** Nyquist impedance plots of Nafion® and MOF 1/Nafion® composite membranes along their equivalent circuits

We performed two probe impedance analyses on the Nafion® and composite membranes at RT (298K) and 100% RH to acquire Nyquist plots. Figure 6 shows that the impedance of the composite membrane is lower than that of

Nafion<sup>®</sup>. The circuit used to determine the impedance is also shown in Figure 6. The proton conductivities of the membranes were determined using reported procedures [10].

**Table 1** Proton conductivity data of cast Nafion<sup>®</sup> and MOF 1/Nafion<sup>®</sup> composite membranes

Membrane	H <sup>+</sup> Conductivity, Scm <sup>-1</sup>
Cast Nafion <sup>®</sup>	1.1×10 <sup>-2</sup>
0.5 wt% MOF 1/Nafion <sup>®</sup>	1.2×10 <sup>-2</sup>
1 wt% MOF 1/Nafion <sup>®</sup>	1.3×10 <sup>-2</sup>
2 wt% MOF 1/Nafion <sup>®</sup>	9×10 <sup>-3</sup>
3 wt% MOF 1/Nafion <sup>®</sup>	6×10 <sup>-3</sup>
5 wt% MOF 1/Nafion <sup>®</sup>	3×10 <sup>-3</sup>

From the data in Table 1, we can conclude that the increased proton conductivity of the composite membranes is due to the inclusion of MOF 1. MOF 1 itself showed high water-assisted proton conductivity (4.2×10<sup>-2</sup>S cm<sup>-1</sup> at 98% RH) and fair proton conductivity (1×10<sup>-4</sup>S cm<sup>-1</sup> at 150 °C) under anhydrous conditions. The main reason for this is the proton-conducting passageway created by its supramolecular net of acid-base pair units under both types of conditions. The coexistence of crystallinity, extent of hydrogen bonding, presence of three-dimensionally ordered arrangements of high-boiling proton carriers, and higher carrier concentrations [11] are responsible as well for the increased proton conductivity. Under humidified conditions, the lattice water of MOF 1 serves as a mediator between neighboring carboxylic groups and thereby assists the Nafion<sup>®</sup> matrix for efficient proton conduction in the MOF 1/Nafion<sup>®</sup> composite membrane. The proton conductivity data (Table 1) are consistent with previously shown IEC data (Figure 5). In this study, 1 wt% MOF 1/Nafion<sup>®</sup> membrane showed best proton conductivity among all other membranes owing to its higher IEC and water uptake values.

#### 4. CONCLUSION

In summary, we have discussed the improvement of proton conductivity under ambient conditions by introducing an oxalate-bridged 3D MOF,  $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$  (**1**), into a Nafion<sup>®</sup> membrane. A high proton conductivity of 1.3×10<sup>-2</sup>Scm<sup>-1</sup> was found at 100% RH with the 1 wt% MOF 1/Nafion<sup>®</sup> composite membrane. Thus, in this work, we demonstrated that the MOF 1/Nafion<sup>®</sup> composite membrane can be a promising candidate as a PEM based on its improved proton conductivity, IEC with lower water uptake values, and slightly higher thermal stability compared to those of Nafion<sup>®</sup>. Furthermore, facile fabrication of the composite and the inexpensive starting-materials for MOF 1 synthesis increase the potential of the composite to be used as a PEM for fuel cell applications.

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