

Tuning of Nafion[®] by HKUST-1 as Coordination Network to Enhance Proton Conductivity for Fuel Cell Applications

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ABSTRACT

Metal-organic frameworks (MOFs) can be intentionally coordinated to achieve improved proton conductivity, making MOFs candidate materials for fuel cell application. Using the concept of a coordination network, the conductivity of Nafion[®] was tuned by the incorporation of HKUST-1 that provides an improved protonic channel depending on the water content. Increased ion exchange capacity, water uptake, proton conductivity, and thermal stability (as confirmed by thermogravimetric analysis) were achieved. The structure of HKUST-1 was confirmed via field emission scanning electron microscopy and X-ray diffraction, while the porosity and adsorption/desorption capacity were characterized by porosity analysis.

Keywords: PEMFC, coordination network, MOF, HKUST-1.

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1 INTRODUCTION

Metal-organic frameworks (MOFs) are a new class of exciting materials that have been explored for a wide variety of popular applications [1]. Apart from their conventional applications, MOFs may potentially be applied as proton conductors in fuel cells [2]. The factors that may lead to enhanced proton conductivity in a MOF include an increase in the number of charge carriers, greater motional entropy, lower activation energy, and a 3-dimensional conduction pathway.

HKUST-1 is a nanoporous crystalline material constructed from paddlewheel-coordinated (CuII)₂ nodes and 1,3,5-benzenetricarboxylate (BTC) linkers [3]. Although HKUST-1 is neutral, coordination of water molecules in the structure to CuII renders these molecules sufficiently acidic to contribute protons to acidic molecules in the pores, thereby enhancing the alternating current conductivity. Three methods (types *a*, *b*, *c*) have been suggested for the fundamental design of highly proton-conductive MOFs that contain proton carriers and conducting media inside the pores. In the type *a* approach, the proton carriers are introduced directly into the pores as counteranions; in the type *b* approach, acid groups are

positioned on the frameworks; and in the type *c* methodology, acidic molecules are incorporated into the voids [4].

Polymer-based electrolyte membranes utilize acidic groups as proton carriers and hydrogen-bonding networks as proton-conducting pathways to facilitate proton transport or transfer. Nafion[®] has been widely used as a solid electrolyte in proton exchange membrane fuel cells (PEMFCs). Nafion[®] consists of a perfluorinated polyethylene backbone grafted with side chains possessing terminal sulfonic acid groups. The acidic groups function as proton carriers, and this membrane has been the popular material of choice. However, Nafion[®] suffers from several limitations. Active humidification is necessary for adequate performance, which adds a layer of complexity, while the potential for physical degradation due to hydration/dehydration results in a loss of efficiency. In addition, there is an energy requirement for powering the humidifiers. To date, three methods have been used to fine-tune the proton conductivity of MOFs. The first involves modification of the acidity of the functional group. The second involves injecting proton conducting chemicals such as imidazole molecules and H₃PO₄ into the empty pores of insulating MOFs. The third is to control the quantity of the conducting media, which assists proton transport through the hydrogen bonding networks [4].

In this study, HKUST-1 is incorporated into the Nafion[®] polymer matrix as a filler and imbibed with H₃PO₄ to form composite membranes to achieve enhanced proton conductivity; the developed composite is very promising for fuel cell application.

2 EXPERIMENTAL

HKUST-1 was prepared by using a novel solvothermal method based on the reported procedures [5]. Nafion[®]/HKUST-1 composite membranes were prepared by the solution casting method [6]. Each of the prepared membranes was carefully and individually soaked in 100 mL of 50 wt% H₃PO₄ (85%; Duksan Pure Chemicals Co.) in a Teflon dish for 24 h at room temperature. At the end of the process, the membranes were placed on other Teflon dishes and dried in a vacuum oven for 24 h at 60 °C. The dried membranes were ready for further characterization. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

The morphology and molecular structure of the membranes were determined by field-emission scanning electron microscopy (FE-SEM) (Hitachi, JSM-6701F, JEOL) and powder X-ray diffraction (XRD; Bruker D2 PHASER, Germany). The water uptake and ion exchange capacity of the composite membranes was evaluated to explore their applicability for PEMFC. These characterizations were performed according to the method reported by Choi et al. [6]. The Fourier transform infrared (FTIR) spectra of the sulfonated membrane and MOF were acquired using a Perkin-Elmer (Spectrum GX & Autoimage) instrument. The proton conductivities of the acid doped HKUST-1/Nafion[®] composite membranes were measured between 0.1 kHz and 1 MHz using AC impedance spectroscopy (Versastat 3, Ametek).

3 RESULTS AND DISCUSSION

Evaluation of the crystallinity and morphology of HKUST-1 and the composite via FESEM (Figure 1(a)) demonstrated that the MOF had an octahedral crystalline structure with average diameter of 15–20 μm . The rough surface and nano-pores are evident in Figure 1(b). As shown in Figure 1(c) and (d) the MOF crystals were split into sub-micron rods and were well dispersed over the Nafion[®] membrane.

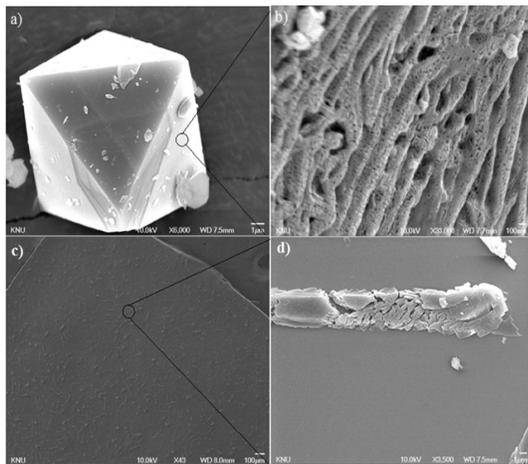


Figure 1. FESEM images of a) HKUST-1 crystal, b) nano-pore of HKUST-1, c) composite membrane, and d) sub-micron rods in the composite membrane.

These sub-micron rods have a length about 5–8 μm and an average diameter of 1–2 μm . In this study, the HKUST-1 MOF sub-micron rods are the dispersed phase and the Nafion[®] polymer is the continuous phase. The HKUST-1 sub-micron rods were well-mixed and homogeneously distributed in the Nafion[®] membrane, which may be highly beneficial for enhancing the proton conductivity of the composite membrane [7].

The phase purity of pristine HKUST-1 was confirmed via XRD measurement (Figure 2(b)) [8]. The XRD patterns of

Nafion[®] and the HKUST-1/Nafion[®] composite membrane [9] were also acquired. Because Nafion[®] is not crystalline, no peaks were observed in the XRD profile. The non-crystallinity of the HKUST-1/Nafion[®] composite membrane is also demonstrated by the absence of peaks in the XRD profile, indicative of segregation of the octahedral MOF crystals into sub-micron-rods in the Nafion[®] membrane.

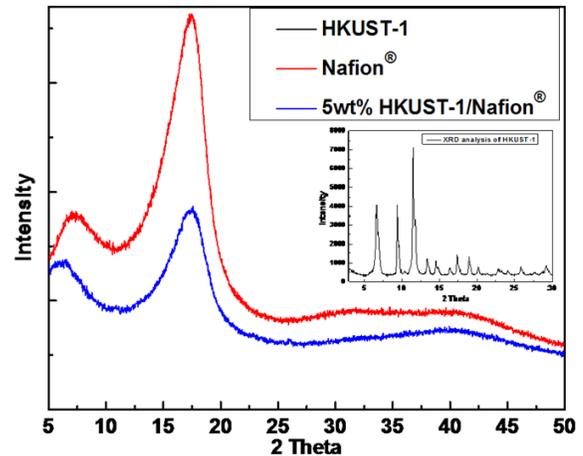


Figure 2. Powder XRD patterns of HKUST-1, Nafion[®], and composite membrane.

The thermogravimetric (TG) profiles of the MOF and the composite membranes are shown in Figure 3. TG analyses revealed an initial weight loss for all samples, which was attributed to water elimination, in a process that occurred in a single step and ended at temperatures ≥ 300 $^{\circ}\text{C}$. 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. Based on the TG curves, the HKUST-1/Nafion[®] composite membranes had greater thermal stability than Nafion[®] at the intended operation temperature, i.e., around 300 $^{\circ}\text{C}$, which suggests the prospective suitability of the composite for PEMFC application.

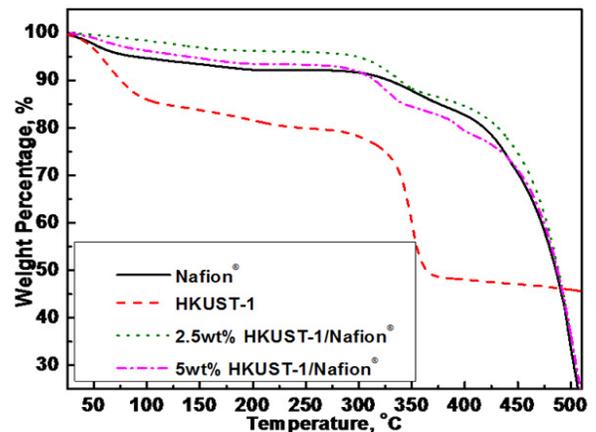


Figure 3. Thermogravimetric curves of Nafion[®], HKUST-1, and composite membranes.

FTIR analysis shows the characteristic peaks of HKUST-1 at 1645, 1613, 1551, and 1445 cm^{-1} , corresponding to the C=O symmetric and asymmetric and Ar-C=C absorptions, and a peak at 1369 assigned to C-O [10]. The FTIR spectrum of Nafion[®] shows -COC- symmetric stretching bands at 974, -SO₃- symmetric stretching vibrations bands at 1056 and asymmetric stretching of the -SO₃- groups at 1205 cm^{-1} . The double broadening, observed in the bending vibrations of the O-H deformation peak at 1728 cm^{-1} and the bands at 3455 cm^{-1} are indicative of intermolecular hydrogen bonding [11]. The spectrum of the composite was dominated by peaks associated with HKUST-1 in the region of 1100–1200 cm^{-1} , obscuring the peaks attributable to the -CO- and OH functional groups of Nafion[®]; this indicates interactions between the dispersed graphite oxide and the hydrate groups of the Nafion[®] polymer matrix.

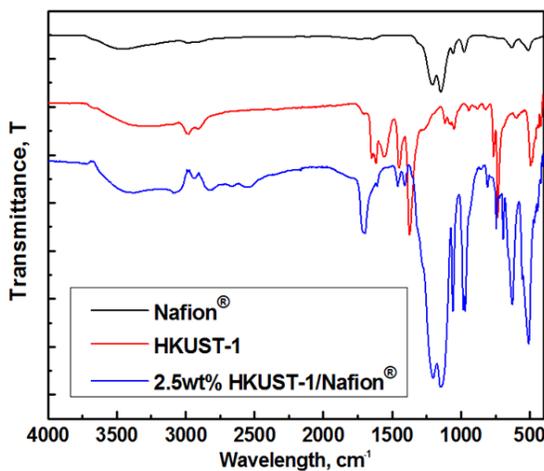


Figure 4. FTIR spectra of Nafion[®], HKUST-1, and composite membrane.

The water uptake capacity of polymeric membranes is an important factor that influences the effectiveness of a membrane under high temperature operation. However, excess water uptake can lead to dimensional changes in the membrane, which in turn result in impaired mechanical properties [12]. The presence of water molecules in Nafion[®] polymer membranes has a significant effect on the transport of protons and the hydrated structures formed around the negatively charged fixed ions in the acids such as sulfonic acid, phosphoric acid, or carboxylic acid groups. The water uptake of the HKUST-1/Nafion[®] composite membranes was lower than that of Nafion[®]; this occurs because of modification of Nafion[®] by the HKUST-1 sub-micron rods distributed in the membrane, which decreases the size of the pores that can generally accommodate water molecules. Based on the data in Figure 5, increasing the weight percentage of HKUST-1 in the Nafion[®] matrix decreases the water uptake value.

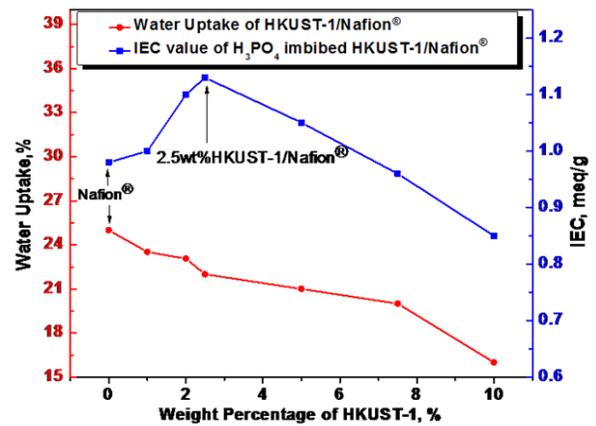


Figure 5. Water uptake and ion exchange capacity of Nafion[®], and H₃PO₄-doped HKUST-1/Nafion[®] composite membranes wrt weight percentage of MOF.

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. The variation of the IEC value of the acid-doped composite membranes with the weight percentage of the MOF is also depicted in Figure 5. The observed increase in the IEC of the doped composite membranes may be because PO₄³⁻ in the composite membrane can provide Brønsted acid sites that can be exchanged. The membrane, by virtue of its IEC and water uptake, regulates the water content at the membrane/electrode interface, which in turn influences the electrochemical characteristics [13]. An increase in the IEC values as the weight percentage of HKUST-1 incorporated into the membrane increased was apparent. The membrane containing 2.5 wt% HKUST-1 gave rise to the maximum IEC; it is likely that H₃PO₄ formed a better acid-MOF-polymer complex in the composite membrane.

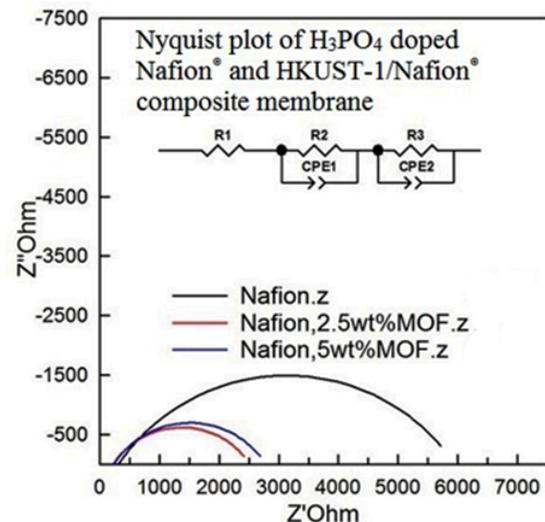


Figure 6. Nyquist impedance plot for Nafion[®] and H₃PO₄ doped HKUST-1/Nafion[®] composite membranes along their equivalent circuit.

Two-probe impedance analysis of the H₃PO₄ Nafion[®] and composite membranes was performed at room temperature to acquire the Nyquist plot according to the described method [13,14]. From Figure 6, it is apparent that the impedance of the composite membrane is less than that of Nafion[®]. The circuit used to determine the impedance analysis is also specified in the figure. The proton conductivities of the membranes were also determined and are as follows: (I) cast Nafion[®]: $1.1 \times 10^{-2} \text{ Scm}^{-1}$, (II) acid doped 2.5 wt% HKUST-1/Nafion[®] composite membrane: $1.8 \times 10^{-2} \text{ Scm}^{-1}$, and (III) acid doped 5 wt% HKUST-1/Nafion[®] composite membrane: $1.5 \times 10^{-2} \text{ Scm}^{-1}$ at 100% relative humidity (RH) and 298 K. Based on this data it can also be concluded that the increased proton conductivity of the composite membranes is due to the inclusion of PO₄⁻³ and as well as H⁺ ions as a result of doping the membranes with 50 wt% H₃PO₄ solution. Herein, 2.5 wt% HKUST-1/Nafion[®] was found to exhibit the best proton conductivity among the evaluated membranes and is also favorable due to the higher IEC values.

4 CONCLUSION

The H₃PO₄-doped HKUST-1/Nafion[®] composite membrane is demonstrated to be a promising material based on its proton conductivity. HKUST-1 has an average particle diameter of around 15–20 μm. The proton conductivity, IEC values, and the thermal stability of the 2.5 wt% HKUST-1/Nafion[®] composite membrane suggest that HKUST-1 may be a promising candidate as a proton conductive material in the polymer electrolyte fuel cell membrane due to its reasonable proton passageway, favorable surface area, and facile synthesis.

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REFERENCES

- [1] S. Goswami, A. Adhikary, H. S. Jena, S. Biswas and S. Konar, *Inorg. Chem.* 52, 12064, 2013.
- [2] J.G. Xu, T. Yamada, K. Otsubo, S. Sakaida and H. J. Kitagawa, *J. Am. Chem. Soc.* 134, 16524, 2012.
- [3] S. S. Y Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science* 283, 1148, 1999.
- [4] M. Sadakiyo, T. Yamada, K. Honda, H. Matsui and H. Kitagawa, *J. Am. Chem. Soc.* 136, 7701, 2014.
- [5] I. Ahmed, Z. Hasan, N. A. Khan and S. H. Jung, *Appl. Catal. B. Environ.* 129, 123, 2013.
- [6] M. D. A. Sayeed, K. Talukdar, H. J. Kim, A. I. Gopalan, Y. Park, Y. H. Kim, K. P. Lee and S. J. Choi, *J. Nanosci. Nanotechnol.* 14-12, 9329, 2014.
- [7] S. Zhang, H. Liu, C. Sun, P. Liu, L. Li, Z. Yang, X. Feng, F. Huo and X. Lu, *J. Mater. Chem. A* 3, 5294, 2015.
- [8] N. C. Jeong, B. Samantha, C. Y. Lee, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.* 134, 51, 2012.
- [9] H.-C. Kuan, C.-S. Wu, C.-Y. Chen, Z.-Z. Yu, A. Dasari and Y.-W. Mai, *Electrochem. Solid-State Lett.* 9 (2), 76, 2006.
- [10] D. Laura, O. Neil, H. Zhang and Bradshaw, *J. Mater. Chem.* 20, 5720, 2010.
- [11] R. Kumar, C. Xu and K. Scott, *RSC Adv.* 2, 8777, 2012.
- [12] S. Bose, T. Kuila, T. X. H. Nguyen, N.-H. Kim, K. T. Lau and J.-H. Lee, *Prog. Polym. Sci.* 36, 813, 2011.
- [13] K. Talukdar, H. J. Kim, Y. H. Kim, H. C. Lee and S. J. Choi, *Sci. Adv. Mater.* 6, 1, 2014.
- [14] S. Ma, A. Kuse, Z. Siroma and K. Yasuda, *Measuring conductivity of proton conductive membranes in the direction of thickness*, *Espec Technology Report No20*, 12, 2005