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# Boosting the proton conduction using protonated imidazole for advanced ion conducting membrane

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## ABSTRACT

Fine-tuning the nanochannels of ion conducting membrane is the key to achieving high performance electrochemical devices. Here, we describe an effective way to enhance the membrane performance using heterocyclic imidazole compound as an additive for Nafion. The hygroscopic nature of the imidazole offered sufficient amount of water molecules to the nanochannel of Nafion, affording wider and continuous nanochannel configuration, as characterized by small angle X-ray scattering (SAXS). Moreover, proton conduction was boosted by the hydrogen bonding interaction between the water molecules and two nitrogen atoms on imidazole ring. The developed membrane showed improved proton conductivity up to 23% and 50% under high and low humidity condition, respectively, compared to pristine Nafion. Additionally, the membrane exhibited excellent stability under harsh condition. Finally, we implemented the developed membrane in fuel cell application and the cell showed enhanced power density without performance degradation, compared to that employing pristine Nafion membrane.

## 1. Introduction

Ion conducting membranes have been widely applied to energy devices such as fuel cell, redox flow battery (RFB), reverse electrodialysis (RED), and desalination. Materials used for the ion conducting membrane include protogenic polymers [1–3], porous frameworks [4,5], and miscellaneous materials [6,7]. Among them, membranes employing protogenic polymers – proton exchange membranes (PEMs) – have gained much interest due to their physicochemical stability and ease of synthesis. There have been much efforts to increase the ion conducting performance of PEM via various methods such as doping ionic liquid [8], patterning membrane by lithography [9], and employing precisely ordered sulfonic acid groups [10]. One of the easiest methods employed for this purpose is to expand the nanochannels of the PEM, which leads to enhanced proton conductivity. For instance, the size of nanochannels can be expanded via controlling the degree of sulfonation on the surface of membrane; however, membrane swelling problem is inevitable for highly sulfonated polymers [11,12]. Similarly, attaching long side chain to the polymer backbone [13,14] or employing block copolymer [15,16] have also been known to induce efficient hydrophilic-hydrophobic

phase separation, affording expansion of the nanochannels as well as enhanced membrane performance. While the above mentioned methods showed effectively enlarged nanochannels, they require complex, time-consuming synthetic process, increasing the overall cost of processing.

In this regard, composite membrane, in which nanoscale additives are dispersed in the polymer matrix, could be a simple alternative. Typically, hygroscopic fillers such as SiO<sub>2</sub> [17,18] and TiO<sub>2</sub> [19] were used as nanoscale additives to improve water retention capacity of the membrane. Graphene oxide (GO) functionalized with sulfonic acid [20, 21] and carbon nanotube (CNT) [22,23] also offered improvement of membrane performance and mechanical strength to the membrane. Notably, the composite membranes using imidazole-functionalized nanoparticles showed considerable potential [24–29]. These studies reported that the additional hydrogen bond could be formed between nitrogen atom of added imidazole and water molecules in the nanochannel, affording increment in proton conduction. However, despite the presence of two nitrogen atoms in imidazole ring, only one nitrogen atom could contribute to the hydrogen bond in these studies, due to the formation of covalent bond between nanoparticle and the other nitrogen

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