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## COMMUNICATION

# Towards basic ionic liquid-based hybrid membrane as hydroxide-conducting electrolyte under low humidity conditions

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**We have developed basic ionic liquid-based hybrid membranes with ionic liquid modified zeolitic imidazolate frameworks (ZIFs) as fillers, aiming to enhance the electrochemical and physical properties of the membrane.**

10 Ionic liquids (ILs) are room-temperature molten salts with negligible vapor pressure. Owing to the properties of nonflammability, high thermal stability and wide liquid range, ionic liquids are considered as unconventional and green solvents. During the past few decades, IL-polymer composites have 15 attracted much attention in the development of a range of emerging technologies[1-5], especially in batteries and fuel cells where their ionic conductivity is exploited. Immobilizing ILs within polymeric materials gives access to the fabrication of all-solid-state devices, disentangling the exudation of IL during the 20 practical applications. Recently, several protic ionic liquids have been incorporated into proton exchange membrane (PEM) acting as the ionic conductor under anhydrous condition[6-11], which benefits for the simplification of fuel cell system However, proton exchange membrane fuel cells (PEMFCs) have exhibited some 25 disadvantages including slow carbon monoxide poisoning of expensive Pt and Pt-based electro-catalysts at low temperatures[12]. To overcome the drawbacks, anion exchange membrane fuel cells (AEMFCs)[13] allow the application of non-precious metal electro-catalysts such as silver catalysts and perovskite-type oxides[14, 15]. 30 Conventional alkaline anion exchange membranes (AAEMs) exhibit proper electrochemical performance under fully humidified conditions. Unfortunately, AEMFCs operating at low temperature and high humidity require additional water management systems, including a pressurized humidity system. 35 Therefore, medium-temperature and low-humidity AEMFC systems have extensive potential in practical applications, particularly in the field of transportation. Herein, we aimed to fabricate basic ionic liquid-based hybrid membranes as AAEMs, because ionic liquid as hydroxide conductor could maintain 40 sufficient ion conductivity under low humidity condition.

Moreover, good mechanical property and dimensional stability is essential for IL-based polymer electrolytes. Polymer nanocomposites by incorporation of nanometer sized filler materials, such as inorganic particles, layered silicates, natural 45 fibers, carbon-based nanomaterials, polyhedral oligomeric silsesquioxanes (POSSs) etc[16-21], have been reported to own improved mechanical, thermal, gas barrier, and chemical resistance properties. This strategy has also been used to improve the physical and chemical properties of polymer electrolytes. 50 Furthermore, in order to maintain the ionic conductivity of the composite membranes, the inorganic fillers are usually modified with ionic molecular agents or groups. For example, POSSs[18]

functionalized with sulfonic acid groups have been used as nano-fillers to improve Nafion 117 membranes' mechanical strength 55 and conductivities, by providing extra charge carriers as well as constructing the ionic cluster microstructure. Therefore, we proposed to blend nanometer-sized fillers into the AAEMs in order to enhance the mechanical properties of basic ionic liquid-based composite membranes. To further improve the 60 electrochemistry properties of hybrid membranes, these filler materials should be better modified with hydroxide conducting agents. Ionothermal method is a perfect way to synthesize porous materials with IL modified, because IL can be held in the framework as template[22]. Previously, we succeeded synthesizing 65 alkaline-stable ZIF-8 nanoparticles in choline hydroxide by an ionothermal method, and found that the ionic liquid can be stably presented in the ZIF-8 channels[23]. The synthesized product denoted as IL@ZIF-8 is a good candidate for the fillers of IL-based polymer membrane due to its thermal and chemical 70 stability as well as high hydroxide conductivity.

Herein, we designed to fabricate IL@ZIF-8/PVA/IL composite membranes as anion conducting electrolyte in low relative humidity (RH=33%). The hydrophilic IL (choline hydroxide) provides conducting medium and enhances water-absorbing 75 ability of the membrane for operating in low humidity. PVA polymer has been widely used in AAEM and ionic liquid-based electrolyte, which as well is hydrophilic[24-26]. IL@ZIF-8 nanofillers are introduced to reinforced the mechanical property of PVA/IL membrane, at the same time itself can enhance the ion 80 conductivity of the membrane by providing extra charge carriers and forming smooth hydrophobic/hydrophilic interface with PVA-IL gel for IL conducting.

The phase purity of as-prepared ZIF-8 nanocrystals was verified by powder XRD analysis. As depicted in **Fig. 1**, compared to the 85 simulated one from the former reports[27], the similarity in XRD patterns indicated that ZIF-8 nanocrystals were synthesized successfully. The scanning electron microscope (SEM) image of as-synthesized nanocrystals showed the hexagonal faceted crystals of ZIF-8, a typical SOD (sodalite) zeolite-type structure, 90 and the average size of as-synthesized particles is about 300 nm.

The morphology of the composite membranes was observed by SEM. **Fig. 2** shows the SEM images of these hybrid membranes captured in both surface and cross-sectional directions. From the surface section, nanofillers are closely packed in all of the three 95 composite membranes, and this tendency is enhanced with the increasing amounts of the nanofillers. In the cross-sectional direction, it can be clearly seen that, as the contents of ZIF-8
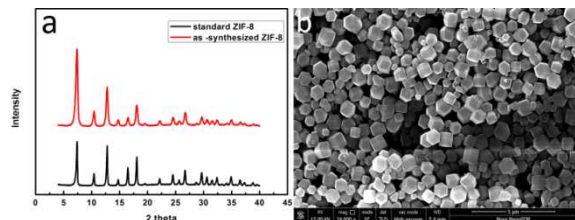
**Fig.1** (a) XRD patterns of as-synthesized ZIF-8 nanocrystals (red) and the simulated one from ZIF-8 crystal structure data excluding guest species (black); (c) SEM image of as-synthesized ZIF-8 nanocrystals
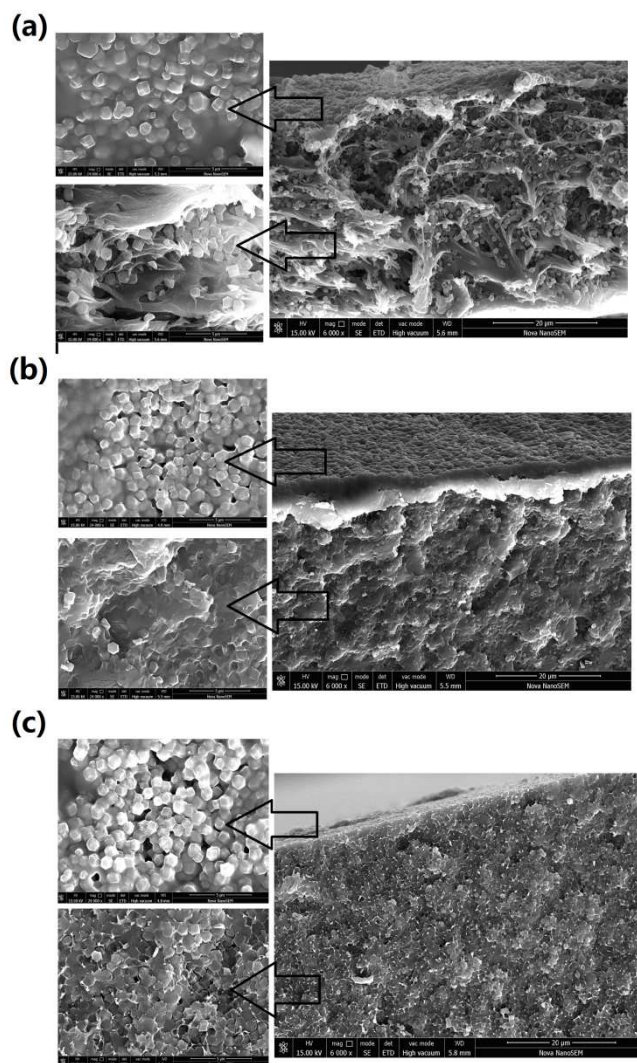


**Fig.2** SEM images of as-synthesized IL@ZIF-8/IL/PVA composites membrane with different IL@ZIF-8 addition :(a)13%;(b)29%;(c)41%

nanocrystals increasing, the fillers tend to be homogenously
10 embedded in the composite membranes. When the content reached up to 29%, there was no agglomerate of the inorganic fillers observed, comparing with IL@ZIF-8/PVA/IL-13 composite membrane. It is plausible to say that such homogenously distribution of hydrophobic fillers lead
15 hydrophilic PVA polymer to form continuous networks, enhancing the conductivities of hybrid membranes though constructing microphase-separated regions in the system.
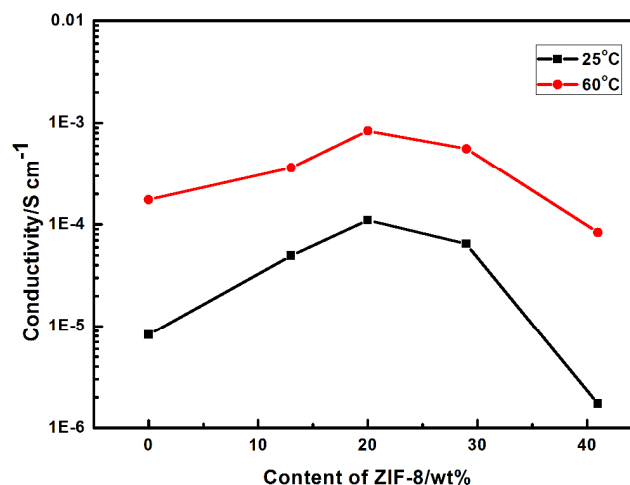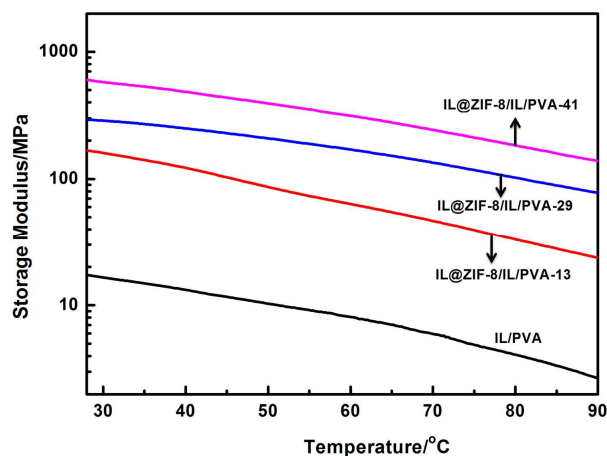


**Fig.3** Conductivities of IL@ZIF-8/IL/PVA composite membrane
20 with different IL@ZIF-8 fillers content at 25 $^o$C and 60 $^o$C in 33% RH.

When the amount of IL@ZIF-8 increased to 43%, the nanofillers are closely packed that the space between the IL@ZIF-8 nanofillers is extremely narrow, resulting in unsmooth polymer
25 channels in the composite matrix.

To evaluate the property of IL@ZIF-8 nanofillers on the ionic conductivity, we performed ac impedance measurements using compacted pellets of the powder sample. The ionic conductivities of IL@ZIF-8 nanoparticles and pristine ZIF-8 nanoparticles
30 synthesized in methanol were determined to be $4\times10^{-7}$ S cm$^{-1}$ and $4 \times 10^{-12}$ S cm$^{-1}$ (according to the literature[27]), respectively(25 $^o$C, ~98%RH). Considering that the identical framework structure of as-synthesized IL@ZIF-8 and pure ZIF-8, the observed enhancement in the ionic conductivity of 5 orders of
35 magnitude can be attributed to the included ionic liquid, which means that the electrochemical property of ZIF-8 nanoparticles has been reinforced by introducing ionic liquid in the framework. The ionic conductivity of IL@ZIF-8 nanoparticles increases with the increasing of RH (**Fig.S1**), suggesting that the conductivity is
40 not enhanced by the diffusion of choline anion but by the diffusion of hydrogen-bonding species of OH$^-$ ions. Therefore, we think that the structure of the adsorbed water molecules in IL@ZIF-8 is strongly related to the ion-conducting pathways. Besides, the hydrophilicity of ZIF-8 nanocrystals has been
45 enhanced after modification by IL. Overall, with incorporation of ionic liquid, the conductivity of ZIF-8 has been improved by providing more hydroxide carriers and the reinforcement of hydrophilicity benefits for the uniform distribution of nanofillers. The conductivities of the composite membranes with different
50 content of IL@ZIF-8 nanoparticles (0%, 13%, 20%, 29% and 41%) were tested in low humidity (RH = 33%) at different temperature (25 $^o$C and 60 $^o$C), which are shown in **Fig. 3**. Without the addition of IL@ZIF-8 nanofillers, the conductivity of genuine IL/PVA composite membrane is $2\times 10^{-6}$ S cm$^{-1}$ at room
55 temperature. As the amount of IL@ZIF-8 fillers increasing, the conductivities were elevated from $4.95 \times 10^{-6}$ S cm$^{-1}$ to ~~6.45×10$^{-5}$~~ $1.1\times10^{-4}$ S cm$^{-1}$ and then reduced to $1.73 \times 10^{-6}$ S cm$^{-1}$. As the temperature was elevated from room temperature to 60$^o$C,

**Fig.4** DMA images of IL@ZIF-8/IL/PVA composite membranes and IL/PVA composite membrane

the hydroxide conductivities of the hybrid membranes have been improved to a large extent. For instance, the conductivity of IL@ZIF-8/IL/PVA-41 composite membrane increased as much as two orders of magnitude. At 60 $^o$C, the same trend of conductivity with the amount of IL@ZIF-8 fillers occurred. ~~The hydroxide conductivity followed in the order of IL@ ZIF-8/IL/PVA-29, IL@ZIF-8/IL/PVA-13, IL/PVA and IL@ ZIF-8/IL/PVA-41.~~The hydroxide conductivity firstly increased to $9.8\times10^{-4}$ S cm$^{-1}$ and then decreased to $8.4\times10^{-5}$ S cm$^{-1}$. This phenomenon could be explained by the structure-property relationship. The SEM images revealed that the distribution of ZIF-8 nanoparticles tend to be more uniform as the content of IL@ZIF-8 nanofillers increased from 13% to 41%. The blank portion between the hydrophobic nanoparticles was filled with hydrophilic PVA/IL gel electrolyte constructing the primary ionic transporting channels because the ionic liquids in the PVA/IL gel play the role of ion transport medium. As the amount of IL@ZIF-8 nanoparticles ~~increased from 13% to 29%~~ was smaller, the ionic transporting channels were not blocked by hydrophobic ZIF-8 framework and still regular and smooth. The ionic liquids located in the IL@ZIF-8 channels were connected with each other as the content of ZIF-8 increased. The secondary ionic channels were then formed to enhance the hydroxide conductivity. However, as the content of nanofillers was further increased ~~from 29% to 41%~~, these ZIF-8 nanoparticles were too densely arranged. The primary ionic transporting channels formed by PVA/IL gel were blocked by the aggregated ZIF-8 frameworks. In addition, the obvious defect on the membrane will affect hydroxide conducting. In spite of more IL@ZIF-8, the ionic conductivity of the hybrid membrane is reduced. It can be seen from the result that the conductivity of IL@ZIF-8/IL/PVA is even lower than that of pure ionic liquid doped composite membrane IL/PVA, proving that excess inorganic nanofillers will weaken the electrochemical property of the composite membranes.

Typically, the performance of the IL-based membranes could be affected by a progressive release of ionic liquid component during operation in the fuel cells. In this work, it is expected that the incorporation of IL@ZIF-8 nanofillers could enhance the IL retention ability of the membrane. The model was confirmed by determining the conductivities of IL@ZIF-8/IL/PVA-29 after exposure to a harsh condition which is 80% relative humidity and

60 $^o$C. As shown in **Fig.S3**, the conductivity of the membrane at first dropped a little, and then maintained stable conductivity after four days testing. In addition, XRD and SEM (**Fig.S4**) confirmed the structural integrity of ZIF-8 retained after humidity treatment. These results confirmed that the ionic liquid-holding ability of IL@ZIF-8/PVA/IL composite membrane, which can be contributed to the hydrophobic property of ZIF-8 nanoparticles.

Another problem encountered in the ionic liquid-based polymer membrane is the enormous loss in mechanical properties, due to the mobility and the solvent nature of ionic liquid acting as a plasticizer. It would largely affect the ionic liquid-based polymer electrolyte's practical application in fuel cell or other energy devices. To solve this problem, we introduced ZIF-8 nanoparticles into ionic liquid-based polymer membranes and exploited whether it will enhance the mechanical properties. **Fig.4** showed the changes of the dynamic mechanical properties of the composite membranes. As can be seen from the curves, as more IL@ZIF-8 nanoparticles were added into PVA/IL membrane, the storage modulus tend to increase. Compared to PVA/IL composite membrane, the storage modulus of IL@ZIF-8/IL/PVA composite membrane increased about 40 times. As the temperature increases, storage modulus of the composite membranes decreased. The higher amount of IL@ZIF-8 particles added, the storage modulus decreased more gradually and gentle. Therefore, ZIF-8 nanoparticles can largely improve the mechanical properties of the ionic liquid-based polymer membrane.

In summary, we have demonstrated a novel basic ionic liquid-based composite membrane with IL@ZIF-8 nanoparticles as fillers for alkaline anion exchange electrolyte. The introduction of IL@ZIF-8 nanofillers reinforced the electrochemical and mechanical properties of the composite membranes due to the construction of hydrophobic-hydrophilic distribution and inorganic instinct property, respectively. Moreover, the prepared composite membranes have shown good conductivity in low humidity, which is meaningful for practice usage for fuel cell devices.

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### Notes and references

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