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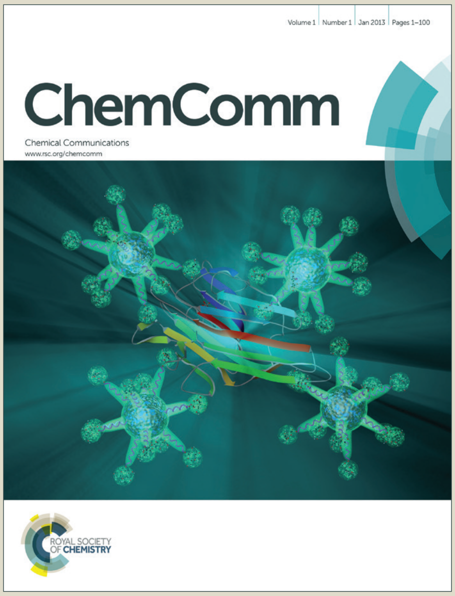

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# MOFs synthesized in ionothermal method coping with leaching problem of IL-polymer composite membrane

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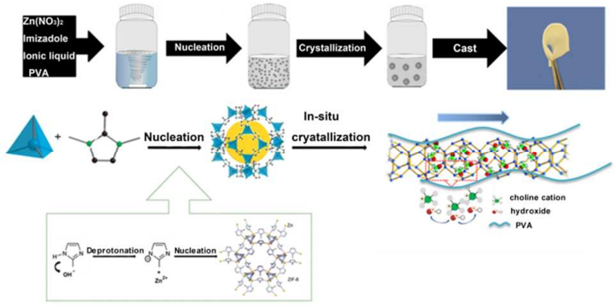
**The liquid nature of ionic liquids (ILs) limits their use in potential electrolytes due to the problem of leakage. Herein, we design a new strategy to immobilize ionic liquid by incorporating it with ZIF-8(ZIF= zeolitic imidazolate framework) by ionothermal method.**

Ionic liquids (IL) are room-temperature molten salts with negligible vapour pressure, owing to the properties of nonflammability, high thermal stability and wide liquid range.[1] They are considered as unconventional and green solvents, attracting much attention in the development of a range of emerging technologies, especially in batteries and fuel cells where their ion conductivities are exploited,[2] and a great of literature have been focused on the protic ionic liquid used in proton exchange fuel cells (PEFCs).[3] A major challenge towards economically viable fuel cells is ionic liquid leakage. [4] In the past few years, polymer nanocomposites by incorporation of nanometer sized filler materials,[5] such as inorganic particles (e.g., all kinds of silica,[6] polyhedral oligomeric silsesquioxanes (POSSs)),[7] have been widely used to reduce leaching of IL. However, ionic liquid still cannot be well preserved in these composite membranes while faced water flood.

In 2004, Cooper et al. reported a new method referred to as ionothermal synthesis, which was the use of an ionic liquid or a deep eutectic mixture as both the solvent and the structure directing agent (sometimes also known as templates) to prepare zeolites and other porous materials[8]. This realisation led to the attempts to prepare zeotype frameworks using ILs as both the solvent and the template provider at the same time.[9] In 2008, Bu et al. reported the use of ionic liquids for the preparation of a series of Metal–organic frameworks (MOFs), the ability of ionic liquids to serve as solvent/template was demonstrated both the cationic and anionic components were found to be located within cavities.[9b] However, for the applications of gas separation, the feature of ionothermal method and the lower thermal stability of MOFs compared with zeolites lead to several issues regarding the removal of ionic templates from the materials. Usually removing the IL cation is not possible without collapsing the structure.[10] On the other hand, this annoying fact actually inspired us to immobilize ILs in MOFs by ionothermal method while fabricating IL-polymer membranes.

Previously, ZIF-8 nanocrystals have been synthesized by ionothermal method; the applied ionic liquid is eutectic mixture of choline chloride and urea.[11] As ZIF-8 nanocrystals are very stable in alkaline environment,[12] we propose to design an alkaline anion polymer electrolyte containing ZIF-8 nanocrystals which are synthesized by ionothermal method. Ionic liquid in the ZIF-8 channels play role of hydroxide conducting. As for we aim to synthesize alkaline anion electrolyte, we replace the eutectic mixture by choline hydroxide.



**Scheme1** Illustration of the preparation of PVA-ZIF8i composite membranes.

In addition, the successful preparation of composite polymer electrolytes is critically affected by aggregation between inorganic nanocrystals and polymer during the composite membrane casting, which will limit the performance of composite membranes.[13] As literatures reported, the in situ crystallization process to fabricate nanocomposite membranes is a good way to solve those problems.[14] However, there is no report refers to in-situ crystallization to fabricate MOF-polymer membranes.

In the publications about ionothermal method, it has been noted that, while ionothermal synthesis takes place in a predominantly ionic environment, it does not preclude the presence of small, reactant quantities of molecular species, such as water.[15] These characteristics bring in situ crystallization process possible, as the polymer chosen in this experiment is poly (vinyl alcohol) (PVA) which is a water-soluble and alkaline-stable polymer[16], and also has been used to proton[17] and anion exchange membranes.[18] Moreover, water-soluble polymer has been reported to have a positive effect on dispersing of nanoparticles while in-situ synthesis.[19]

Thanks to various advantages of MOFs, ionothermal method and in-situ crystallization, herein, we proposed to fabricate a PVA- based alkaline anion composite membranes with alkaline-stable ZIF-8 nanocrystals as fillers by ionothermal method and in-situ crystallization. IL takes effect as template and remains in

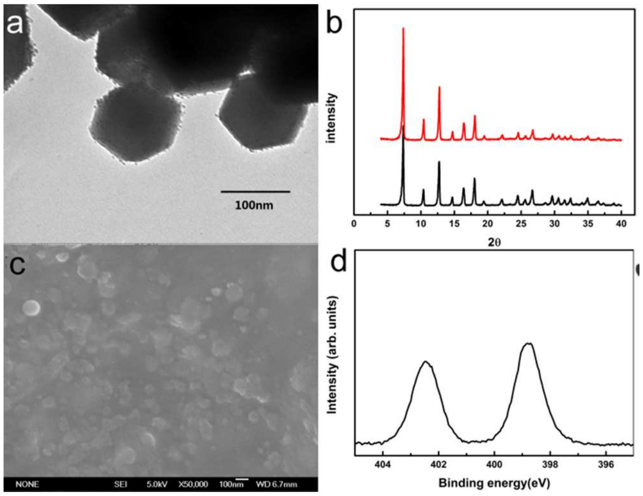


**Fig.1** (a) TEM image of fillers in PVA-ZIF8i-48 composite membrane. (b) XRD patterns of fillers in PVA-ZIF8i-48 composite membrane(red) and the simulated one from ZIF-8 crystal structure data excluding guest species (black); (c) SEM image of PVA-ZIF8i-48 composite membrane; (d) XPS patterns of the PVA-ZIF8i-48 composite membrane XPS signals of the core-level N 1s for PVA-ZIF8i-48 composite membrane.

the frameworks. Through this way, the membranes can hold ionic liquid with the protection of ZIF-8 nanocrystals.

Scheme 1 shows a schematic illustration of the process of preparing ZIF-8 crystals in ionic liquid (choline hydroxide) and fabricating composite membranes by in-situ crystallization method. The reactant (zinc nitrate and 2-methylimidazole) was firstly put into the ionic liquid; PVA polymer was added after the reactants were well dissolved but before ZIF-8 nanocrystals formed. Reactants dispersed in the form of ion uniformly as stirring. Then, hydroxide deprotonated imidazole and accelerated the formation of ZIF-8 nanoparticles.[20] Deprotonated imidazole assembled to $Zn^{2+}$ to form topological framework, while quaternary ammonium, which is traditional template agent, may help directing formation of ZIF-8 crystals. During the in-situ crystallization, ZIF-8 nanocrystals were dispersed uniformly in the PVA polymer matrix.

To prove the existence of ZIF-8 nanoparticles in composite membranes, we dissolved the composite membranes in boiling water to remove the polymer. The residue nanoparticles were tested by TEM tests. The typical morphology of ZIF-8 can be observed clearly in **Fig. 1a**, which shows that crystals have a typical hexagonal morphology. The PXRD patterns of residue nanoparticles are presented in **Fig. 1b**. Its FT-IR spectrum is shown in **Fig.S1†**. All the characteristic peaks of ZIF-8 nanocrystals are visible, indicating that the crystalline structure of ZIF-8 is synthesized by in-situ growth method successfully. These results indicated our in-situ crystallization method in this work was very effective to prepare homogeneous ZIF-8 and PVA composite membranes. The morphology of the composite membranes was observed using a SEM from the surface direction. The images are showed in **Fig. 1c**, where can be seen that the ZIF-8 nanocrystals distributed uniformly in PVA and show partial crystals from the polymer membranes surface. It may be explained that the ZIF nanocrystals had in-situ grew in PVA polymer which avoided the incompatibility behaviour among inorganic and organic materials.

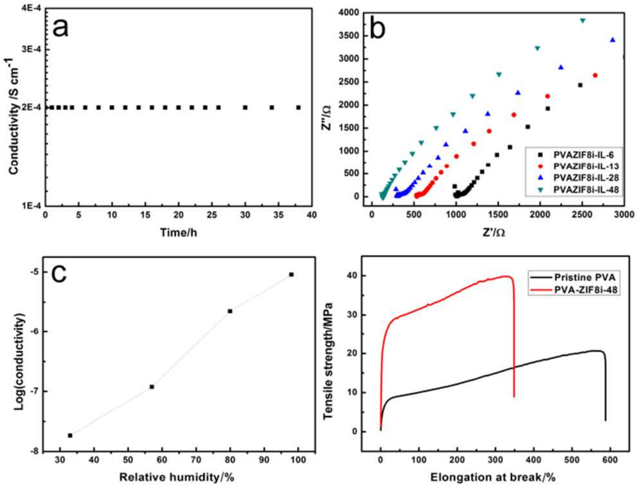


**Fig.2** (a) Conductivities of the PVA-ZIF8i-48 composite membrane immersed in water for different time; (b) Conductivities of the PVA-ZIF8i composite membranes indifferent content of ZIF-8 fillers; (c) Conductivities of the PVA- ZIF8i-48 composite membrane in different relative humidity (33%, 57%, 80% and 98%); (d) Tensile strength and elongation at break of the PVA-ZIF8i-48 composite membrane and pristine PVA membrane.

To confirm the presence of ionic liquid embedded in ZIF-8 matrix. Nitrogen gas adsorption measurements and XPS were carried out.**Fig.S2†** shows the $N_2$ adsorption and desorption isotherms of MOFs synthesized by an ionothermal method. The BET surface area of the as-synthesized ZIF-8 nanocrystals is 583 $m^2g^{-1}$, which is much lower than the values that were reported from those ZIF-8 samples without templates in channels prepared by traditional methods(>1000 $m^2$ $g^{-1}$).[21] The measured pore volume of ZIF-8 with templates in channels is also smaller than that of the former reported ones.[22] These results proved that the ionic liquid had been introduced into the matrix of ZIF-8 nanocrystals. **Fig. 1d** shows XPS spectra of the core-level N 1s of residue nanoparticles in the composite membrane. The characteristic binding energies according to the reference spectra of ionic liquid (choline hydroxide) were found. The ratio found for the two N1s peaks at 402.6 eV for ammonium and 399.1 eV for the nitrogen on imidazole of ZIF-8 nanoparticles, respectively, suggests the presence of choline hydroxide in the ZIF-8 matrix.

We assume that if the ionic liquid was embedded in the ZIF-8 fillers, the conductivity of composite membrane will not change. Then we investigated ionic liquid holding property of membranes by testing conductivity when they are soaked in water for a long time, which plotted in **Fig. 2a**. The ion conductivity for PVA-ZIF-8 composite membrane exhibited stable conductivity, which suggests that composing of ZIF-8 in the composite membranes have property in holding ionic liquid. The hydrophobic nature of ZIF-8, in addition to its template effect with ionic liquid, confines the IL within the membrane and minimizes leaching after immersion in water.

In order to prove it is the ionic liquid in the framework of ZIF-8 contributes to hydroxide conducting, another kind of composite membrane without ionic liquid in the framework has also been fabricated. The membrane was composed with ZIF-8 nanocrystals synthesized in methanol, and ionic liquid was blended into the membrane simultaneously. Besides, the content of these two components were the same with the as-synthesized membrane. We also tested the conductive stability when soaked in water. The data was shown in **Fig.S3†**. The results showed that as time went by, the conductivity decreased obviously and finally reached a stable conductivity which is three magnitudes lower than that of composite membrane synthesized in ionothermal method, which suggests that ionic liquid retained in the channels of ZIF-8 mainly plays role of conducting. The conductivity of this membrane with no ionic liquid in the matrix mainly contributes to ionic liquid attached to PVA by molecules interaction.

Generally, conducting property of materials is mainly influenced by temperature and the content of doped compound. **Fig. 2b** depicts the anion conductivities of the composite membranes with various contents of ZIF-8 nanocrystals at room temperature in water. It can be observed that varying the loading amounts of ZIF-8 nanocrystals from 6% (PVA-ZIF8i-6) to 48 wt. % (PVA-ZIF8i-48) results in an increase of conductivity of the composite membrane from $2 \times 10^{-5}$ S $cm^{-1}$ to $2.6 \times 10^{-4}$ S $cm^{-1}$. The stability of the composite membranes is superior to ionic liquid–based membranes composed with inorganic materials[3a]; the conductivity is higher than that of the former report about MOF-polymer electrolyte[17] and that of the hydroxide conducting MOF[18]. The ionic conductivity of PVA-ZIF8i composite membrane increases with relative humidity(RH), suggesting that the ability of adsorbing water molecules in composite membrane is strongly related to the ion-conducting, shown in **Fig. 2c**. We selected PVA-ZIF8i-48 to further study the effect of temperature. The conductivity of PVA-ZIF8i-48 is gradually increasing with an increase of temperature. A linear relationship between ln (σT) and $1000T^{-1}$ is demonstrated in **Fig.S4†**, which gives the corresponding activation energy of 0.38 eV. This Ea value is higher than that of hydrated $OH^{-}$ ions in liquid (less than 0.2 eV) and infers that there are some unfavourable features in the conducting pathways like low conductivity between ZIF-8 fillers and some obstruction in ZIF-8 channels.

The mechanical properties of the as-synthesized composite membrane are shown in **Fig. 2d**. Compared to the pristine PVA membrane, tensile strength of the composite membrane with the highest content of ZIF-8 was raised in more than 2 times. The elongation at break of this membrane is 350%, which means that the membrane shows high flexibility. These results show that ZIF-8 nanoparticles improved mechanical properties of PVA, which is beneficial for practical usage.

The mechanism for hydroxide conduction in these ionic liquid based systems and how the ionic liquid interacts with ZIF-8 matrix are at present unclear. Former literatures and some positive results about stable conductivity achieved by the PVA-ZIF-8 composite membranes give some confidence that ionic liquid was well embedded in the ZIF-8 matrix. Besides, molecules interaction between hydroxyl of PVA and hydrophilic group of choline leads some ionic liquid bond with PVA, which provides a conducting bridge between ZIF-8 fillers, improving the continuity of ZIF-8 conductive channels.

In summary, we have demonstrated a facile and novel method to fabricate an IL-polymer composite membrane with ZIF-8 fillers to retain the ionic liquid for alkaline anion electrolyte, which is the combination of ionothermal method aiming to introduce ionic liquid into ZIF-8 and in-situ crystallization leading ZIF-8 to dispersing in polymer matrix (PVA) uniformly. Ionic liquid was used as both solvent and template and retained in the framework of ZIF-8, which makes as-synthesized composite membranes with stable electrochemical property in hydroxide conducting, solving the conventional problem of ionic liquid leaching. This is the first time introducing MOF as conductors into composite alkaline anion membranes. This synthesis concept should have an impact on further investigations in the field of exchange membrane for fuel cells.

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## Notes and references

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