Supporting Information

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

Cong Liu, Sinan Feng, Zhuang Zhuang, Duo Qi, Guibin Li, Chengji Zhao*, Xuefeng Li and Hui Na*

Experimental Section

Materials

Zn $(NO_3)_2 \cdot 6H_2O$ (>98%, Sigma-Aldrich), 2-Methylimidazole (>99%, Acros Organics), Choline hydroxide (45% wt. % in water, TCI), Ethanol (Fischer Scientific), PVA (99% hydrolyzed, average Mw = 86,000–89,000, Sigma-Aldrich)

Synthesis of IL@ZIF-8 nanocrystals by an ionothermal method

Zinc nitrate (0.76g) and 2-methylimidazole (0.4g) were slowly added into choline hydroxide (10 ml) and stirred for about 12 hours at room temperature and keep still for a day. After centrifuging and overnight drying, IL@ZIF-8 nanocrystals were obtained.

Preparation of IL@ZIF-8/PVA/IL composite membranes

PVA was fully dissolved in water to make a 10% solution at 90◦C (10ml). Different amount of IL@ZIF-8 nanoparticle dispersion liquid (in water) was slowly added into PVA solution. This mix solution was stirred for about 4 hours at room temperature. After removing the air under vacuum, the solution was poured into glass plates, and water was evaporated at 60oC. When visually dry, the membrane was peeled off from the glass substrate and washed repeatedly with distilled water. A series of composite membranes were obtained and named IL@ZIF-8/PVA/IL-x (13, 29, and 41). The x was

the weight percentage ratio of the IL@ZIF-8 nanoparticles to the composite membrane.

Structure characterization

The crystalline structure of ZIF-8 nanocrystals was determined by the X-ray diffraction (XRD) measurements using a Siemens D5005 diffractometer with Cu-Kα radiation (λ=1.5418 Å).

The morphology of composite membranes was tested by field-emission scanning electron microscope (FE-SEM: JEOS JSM 6700F).

Thermogravimetric analysis (TGA)

TGA measurements were performed on a Perkin-Elmer TGA-2 thermogravimetric analyzer from 100 to 800 ^{o}C at a heating rate of 10 ^{o}C min^{-}1 under air atmosphere. Before the heating scan, all the samples were pre-dried under air at 100 ^{o}C for 10 min to remove the residual water. The TGA images of the membranes were shown in **Fig.S2**.

Hydroxide conductivity

AC impedance spectroscopy was performed to measure hydroxide conductivity of materials from 0.1 Hz to 100 kHz, 10 mV AC perturbation and 0.0V DC rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). (1). Composite membranes were cut into rectangle with a length of 5cm and a width of 1 cm. (2).ZIF-8 nanoparticles were prepared by pressing the materials at 40 KN cm^{-2} and shaped into pellets of 13mm in diameter and 500 μm thick; Silver glue was blushed on both sides of the pellet. The prepared device was waiting for further measurement. The hydroxide conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (1)$$

where σ is the conductivity, L is the distance between the electrodes used to measure the potential, R is membrane resistance and A is cross-sectional area of membrane.

Mechanical properties

Dynamic mechanical analysis (DMA) was performed on a TA Instrument (DMA Q800) in tension mode on films and the temperature was ramped at 5 °C/min at a frequency of 1 Hz from 20 °C up to 100 °C.

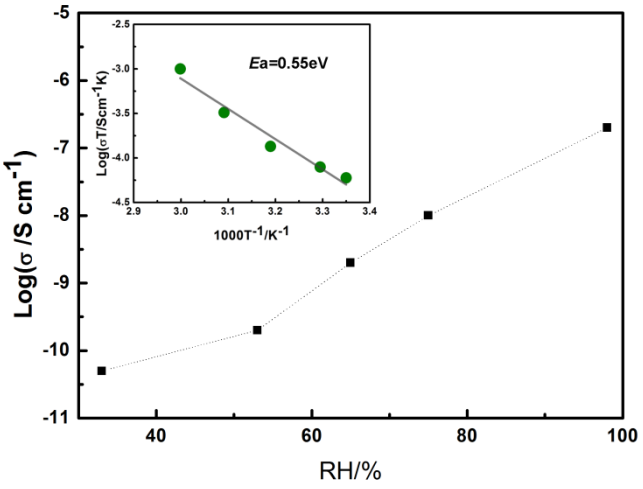

Fig.S1 (a) Conductivities of t IL@ZIF-8 nanopaticles in different relative humidity (33%, 53%, 65%, 75% and 98%); (b) Arrhenius-type plot of the conductivities of IL@ZIF-8 nanoparticles at various temperatures

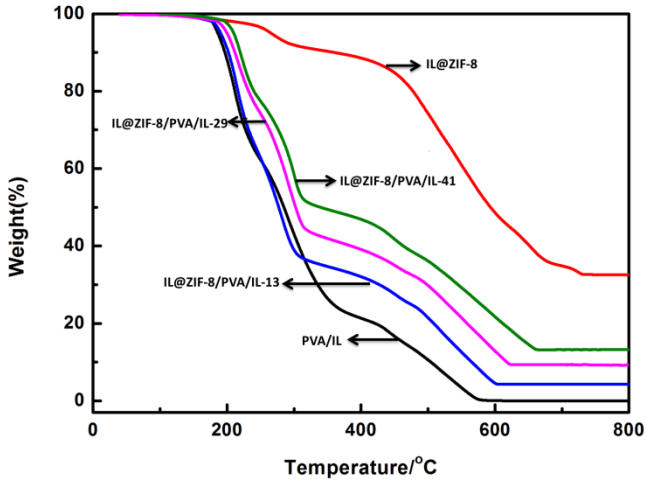

Fig.S2 TGA images of IL@ZIF-8/PVA/IL composite membranes, PVA/IL composite membranes and IL@ZIF-8 nanoparticles

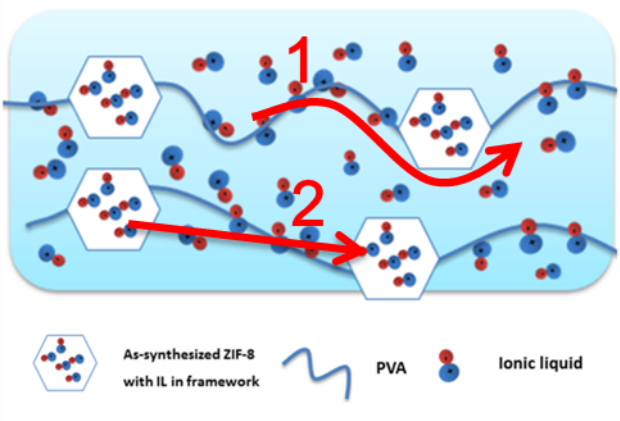

Fig .S3 Proposed conductive pass-ways

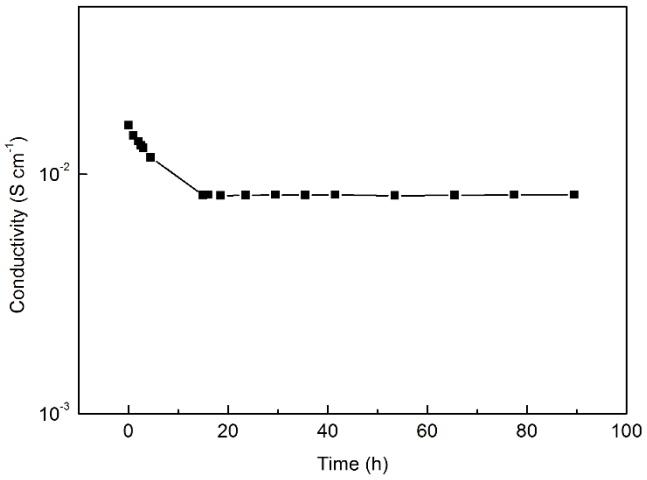

Fig.S4 Conductivities of IL@ZIF-8/PVA/IL-29 composite membrane after humidity testing (RH=80%, 60 °C) for different time

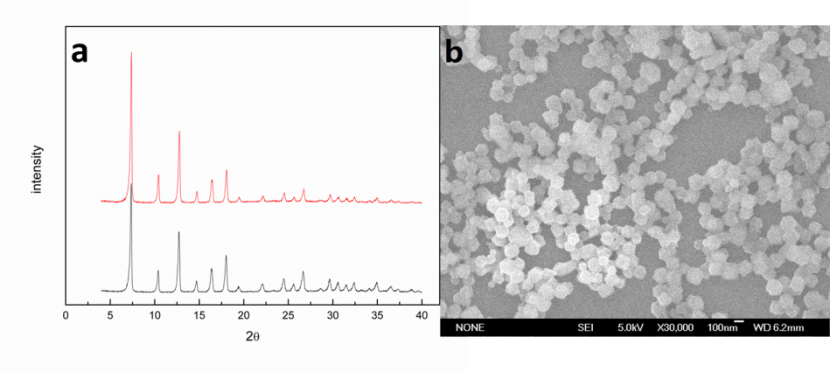

Fig .S5 (a) XRD patterns of the as-synthesized IL@ZIF-8 samples (black) and the simulated one from ZIF-8 crystal structure data excluding guest species (red) after humidity treatment for two days; (b) SEM image of the as-synthesized IL@ZIF-8 samples after humidity treatment for two days.

The filling content of ionic liquid in the composites membranes and its effects on conductivity.

The weight ratio of ionic liquid and PVA is 0.5:1. We prepared other composite membranes containing different amount of ionic liquid, its weight ratio with PVA is 0.25:1, 1:1 and 1.5:1. We name this series of membranes PVA/IL-x(x represents weight ratio of ionic liquid and PVA). The electrochemical performance of these membranes in different humidity level is shown in Table 1.

With the increasing of content of ionic liquid, the conductivities of these membranes are improved. The reason why we choose this ratio (0.5:1) is that we immerse composite membranes IL@ZIF-8/PVA with different amount nanofillers in ionic liquid to evaluate how much ionic liquid can the membrane absorb spontaneously, and found that the result is about 19~27% (wt.%), which is close to the ratio 0.5:1. We name this series of membranes IL@ZIF8/PVA/IL-6, IL@ZIF8/PVA/IL-13, IL@ZIF8/PVA/IL-28, and IL@ZIF8/PVA/IL-48. We believed that it is the ability the PVA and ZIF-8/PVA matrix can hold the ionic liquid. Considering the effects of mechanical properties and ionic liquid leaching, we finally choose to dope less ionic liquid.

Table S1 Conductivity of the composite membranes in different humidity level(S cm^{-1})

Membrane	RH=33% (25°C)	RH=98% (25°C)
PVA/IL-0.25	1×10^{-5}	0.00012
PVA/IL-0.5	0.000337	0.0034
PVA/IL-1	0.0011	0.0055
PVA/IL-1.5	0.0014	0.0074

Table S2 Water uptake, swelling ratio and mechanical properties of the composite membranes

Membrane	IL absorption (%)	Water uptake (%)	Swelling ratio (%)	Tensile strength (MPa)
PVA	0.27	38.1	14.7	15.1
IL@ZIF8/PVA/IL-6	0.25	37.2	14.4	20.4
IL@ZIF8/PVA/IL-13	0.22	36.4	11.9	24.2
IL@ZIF8/PVA/IL-28	0.21	35.7	10.8	28.5
IL@ZIF8/PVA/IL-48	0.19	31.2	8.7	39.8

Note: The water uptake was measured in 98%RH.