# Supporting Information for

# Protic Ionic Liquids: An Alternative Proton-conducting Electrolyte For High Temperature Proton Exchange Membrane Fuel Cells†

**Changchun Ke [a,b], Jin Li, [a,b] Xiaojin Li, *[a] Zhigang Shao*[a] and Baolian Yi [a]**

[a] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian, 116023, China. E-mail: xjli@dicp.ac.cn; zhgshao@dicp.ac.cn

[b] Graduate University of the Chinese Academy of Sciences, Beijing, 100039, China

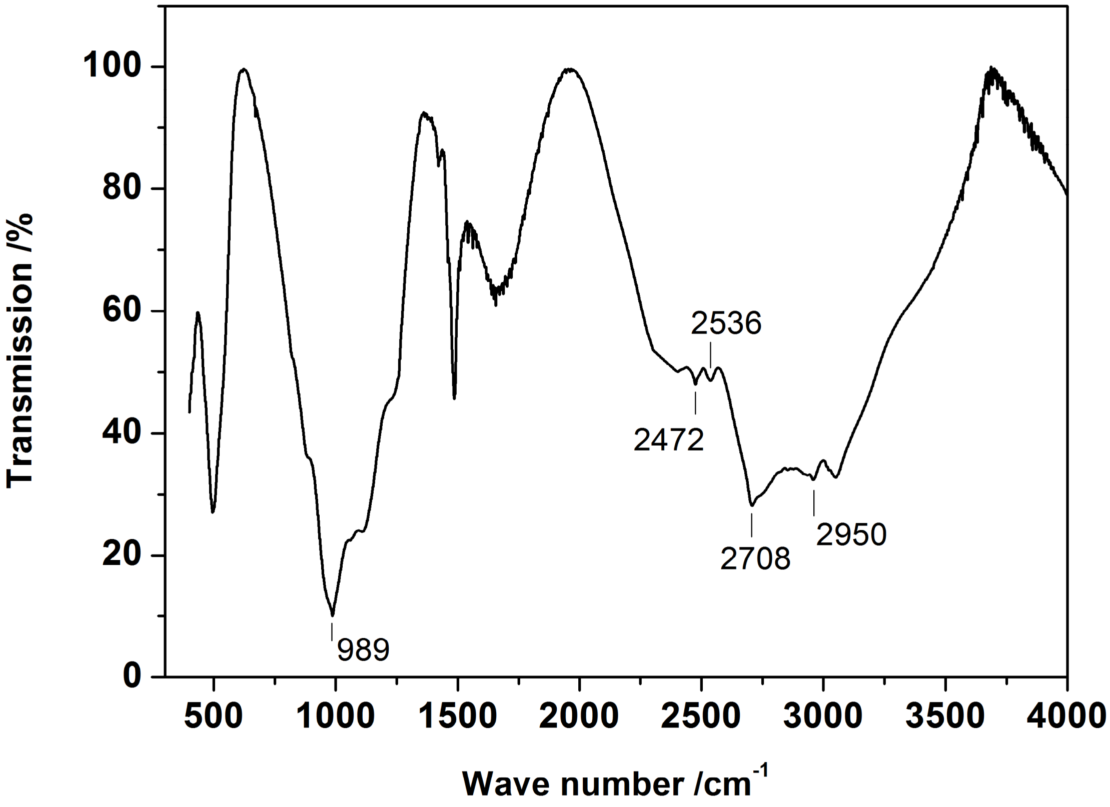
## *Experimental Procedure*

### Materials

The ionic liquid $[N_{111}].H_2PO_4$ is provided by Chinese Academy of Science, Lanzhou Institute of Chemical Physics, and prepared by a direct neutralization of $N(CH_3)_3$ and phosphoric acid, just as that 5 of the literature[1] describes. Nonwoven is provided by Shi-Long Tech Co. Ltd (Shanghai, China), the chemical constitution is polypropylene. The FT-IR and $^1$H NMR of the product $[N_{111}].H_2PO_4$ are shown in Fig. S1 and Fig. S2.

The absorption bands at 2950 cm$^{-1}$ is the stretch vibration of $CH_3$. The absorption bands at 989 cm$^{-1}$ is the stretch vibration of C-N. And the absorption bands at 2472 cm$^{-1}$ 2536 cm$^{-1}$ and 2708 cm$^{-1}$ are the 10 characteristic stretch vibration of $N^+$-H.

The H$^a$ peak is the hydrogen of methyl, with the chemical shift 2.68 ppm. The H$^b$ is the hydrogen of the $N^+$-H and O-H, all the hydrogen atoms here are active hydrogen, which form a delocalization, and lead to a same chemical shift.



15 **Fig. S1** FT-IR of the $[N_{111}].H_2PO_4$ used in our experiments

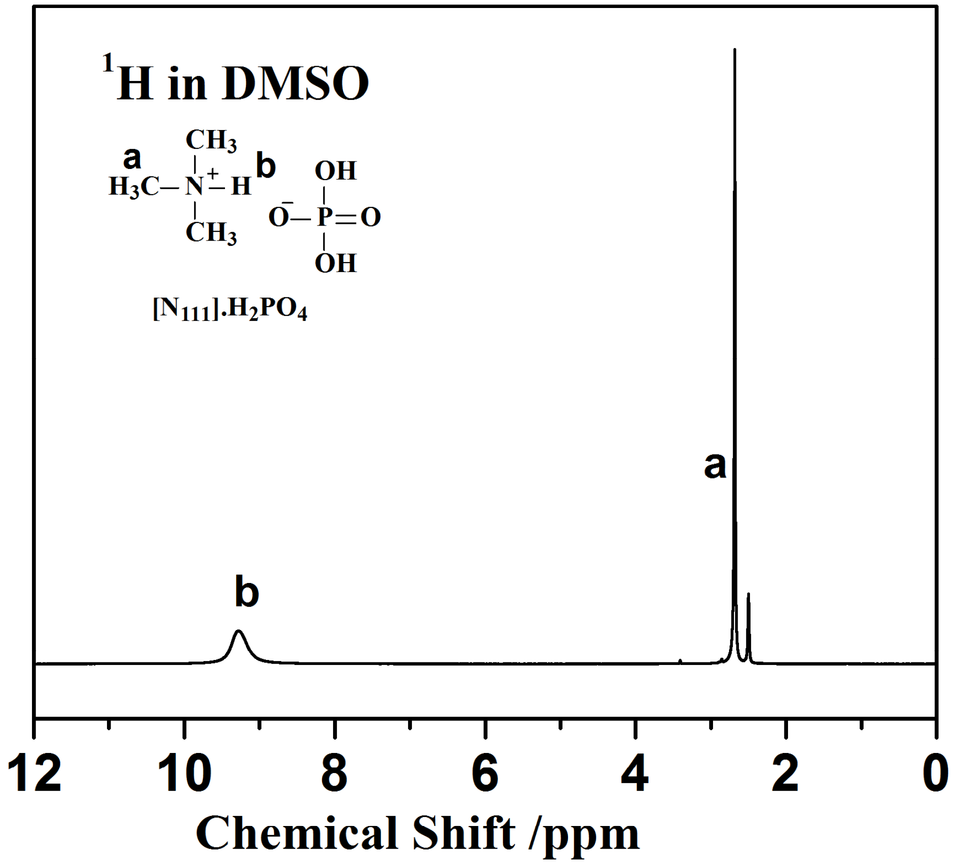


**Fig. S2** NMR the $[N_{111}].H_2PO_4$ used in our experiments

## Preparation of PP-NW/$[N_{111}].H_2PO_4$ hybrid membrane

The PP-NW/$[N_{111}].H_2PO_4$ composite membranes is prepared by a reciprocating rolling process. The ionic liquids are smeared to the surface of the PP nonwoven, and then the nonwoven is rolled with a rounded glass rod to make the ionic liquid permeate into the matrix of the nonwoven. The ionic liquid content ( $\Delta W\%$) in the obtained composite membrane can be calculated by the weight of the non-woven before ($W_b$) and after rolling ($W_a$).

$$\Delta W\% = \frac{W_a - W_b}{W_b} \times 100\% \tag{S1}$$

## Cyclic voltammetry scanning of Pt/C under the ionic liquids circumstance

The cyclic voltammetry (CV) measurements are carried out using a CHI730D electrochemical workstation produced by Shanghai Chen-Hua Instrument Co. Ltd in a three-electrode electrochemical system, as described in Reference.[2] A Platinum sheet electrode is used as counter electrode (CE), a saturated calomel electrode (SCE, 0.241 V Vs normal hydrogen electrode, NHE) is used as the reference electrode (RE), and a specified volume of 0.5 M $H_2SO_4$ solution was used as the electrolyte in the three-electrode electrolytic cell. The working electrodes (WE) are prepared by a glassy carbon rotating disk electrode method. Firstly, 5 mg Pt/C (40%, Johnson Matthey) was added into the mixture of Nafion solution (50 µL, 5wt %) and ethanol (4 mL). The mixture was dispersed by an ultrasonator for more than 30 min, until a homogeneous catalyst ink was obtained. Then, 10 µL of the ink was dripped on the glassy carbon rotating disk electrode drop by drop. During the dripping process, the glassy carbon rotating disk electrode was dried under an infrared lamp to form a thin catalyst film on the surface of the glassy carbon rotating disk electrode, drip the next drop until the former drop was dried on the surface of the electrode. Before the CV measurements, the electrode was activated by repeatedly voltage scanning from -0.241 V to 0.759 V (VS SCE) at a rate of 100 mV $s^{-1}$ in $H_2SO_4$ solution deaerated by high purified $N_2$. Then, the CV curves were recorded from -0.241 V to 0.759 V (Vs SCE) at a scanning rate of 50 mV $s^{-1}$. After the CV test, the electrode was immersed into certain ionic liquids for 5 min. Then the CV of the electrode infected with ionic liquids was recorded as the method described as previously mentioned.

In the practical $H_2/O_2$ proton exchange membrane fuel cell surroundings, $H_2O$ is inevitable, because $H_2O$ is the reaction product of the oxygen reduction reaction (ORR) of cathode. Generally, the electrochemical windows of the ionic liquids are much wide, usually wider than $H_2O$. So, if use the neat ionic liquids as electrolyte, the experimental results would be against the physical truth under the practical PEMFC. So, using water system electrolyte $H_2SO_4$ solution as electrolyte is more reasonable.

## FESEM

Micro-structure morphology of the polypropylene nonwoven (PP-NW) is observed by the Field Emission Scanning Electron Microscopy (FESEM). In this experiment, a S4800 (Hitachi, Japan) microscope is used. The testing parameters for each sample are attached to the corresponding result image.

## Single cell test

The gas diffusion electrode (GDE) was prepared first. In the preparation of GDE, carbon paper from Toray, 70 wt% Pt/C from Johnson Matthey, PTFE suspension and Nafion solution (DuPont, USA) were used. Both the loading of Pt/C catalyst on the anode and cathode was 0.4 mg Pt $cm^{-2}$. Then, two pieces of GDE with an effective area of 5 $cm^2$ were placed on two sides of a piece of membrane to fabricate MEA. The MEA was sandwiched into a single cell with stainless steel end plates and graphite groove flow fields as current collectors. The performance of the fuel cell was evaluated by polarization curves measurement at a temperature of 140 °C, with dry $H_2/O_2$ gases. The $H_2$ and $O_2$ were fed in co-flow orientation into the fuel cell. The inlet gases were controlled at a fixed rate of 30 ml $min^{-1}$.

## Open circuit potential decay acceleration test

The anode and cathode are supplied with $H_2$ and $O_2$ at a fixed rate of 30 ml $min^{-1}$, and the cell is kept at 140 °C and no back press. The variation of open circuit voltage (OCV) as time could be recorded by a PARSTAT 2273 (Princeton, USA) electrochemical station. The OCV is very stable during the testing.

## Reference

1 V. D. Noto, E. Negro, J. Y. Sanchez, C. Iojoiu, *J. Am. Chem. Soc.* **2010**, 132,2183-2195.
2 Z. M. Zhou, Z. G. Shao, X. P. Qin, X. G. Chen, Z. D. Wei, B. L. Yi, *Int. J. Hydrogen Energ.* **2010**, *35*, 1719–1726.