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Electronic Supplementary Information

Nonhumidified High Temperature H_2/Cl_2 Fuel Cells Using Protic Ionic Liquids

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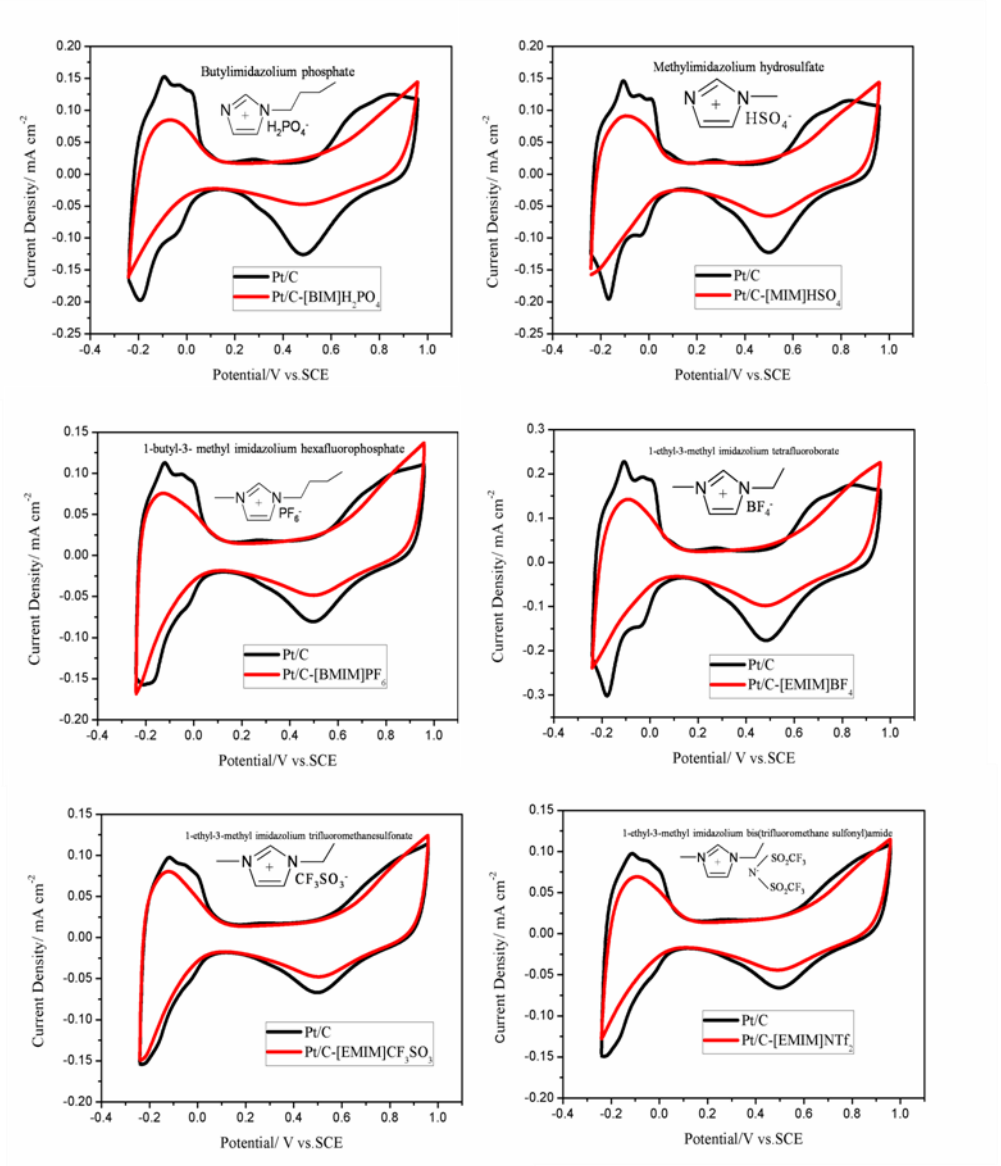
Result section

Table S1 Basic characteristics of PES/SPEEK NF substrate *

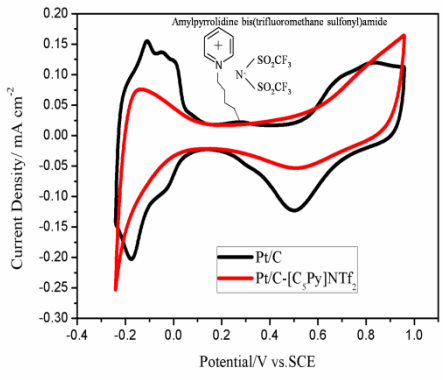
Substrate	SPEEK Content (wt.%)	Thickness (μm)	Mean Pore Size (nm)	Porosity (%)	Minimum bubble-point pressure (MPa)
PES/SPEEK NF Membrane	2	~75	2.69	81.00	0.80

*The PES/SPEEK NF membranes were prepared as reported in the reference [S1].

(a) Imidazole based ionic liquids



(b) Pyridine based ionic liquids



(c) Amine based ionic liquids

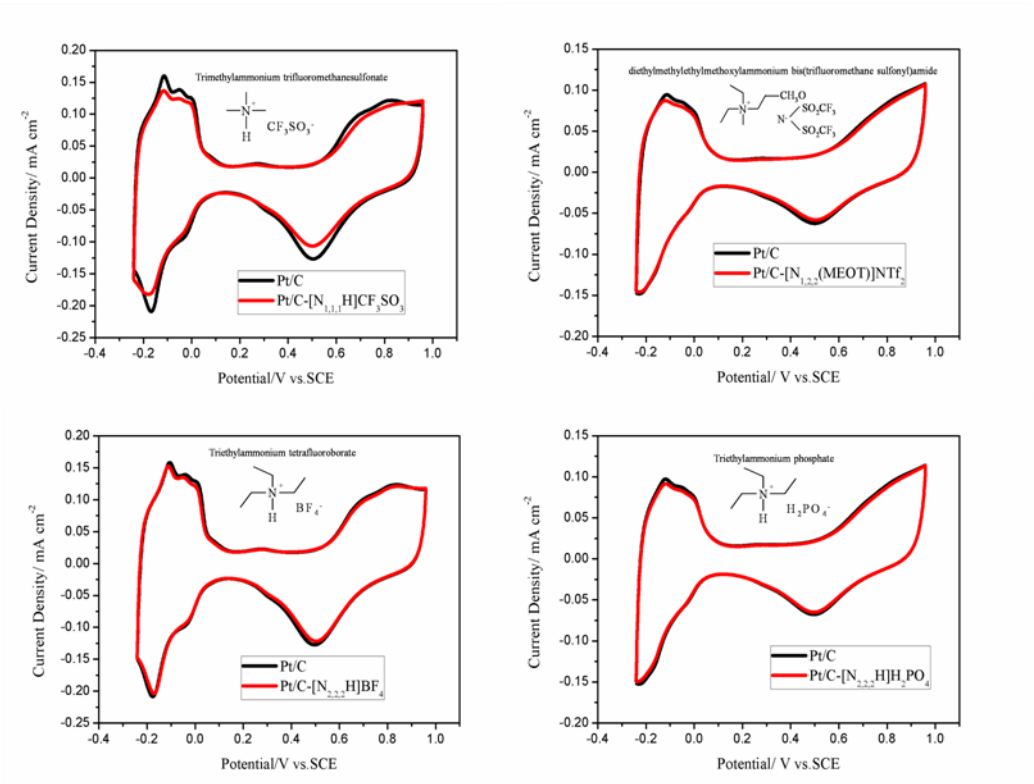


Figure S1 CV curves of blank Pt/C electrodes and Pt/C electrodes dyed with different types of ionic liquids.

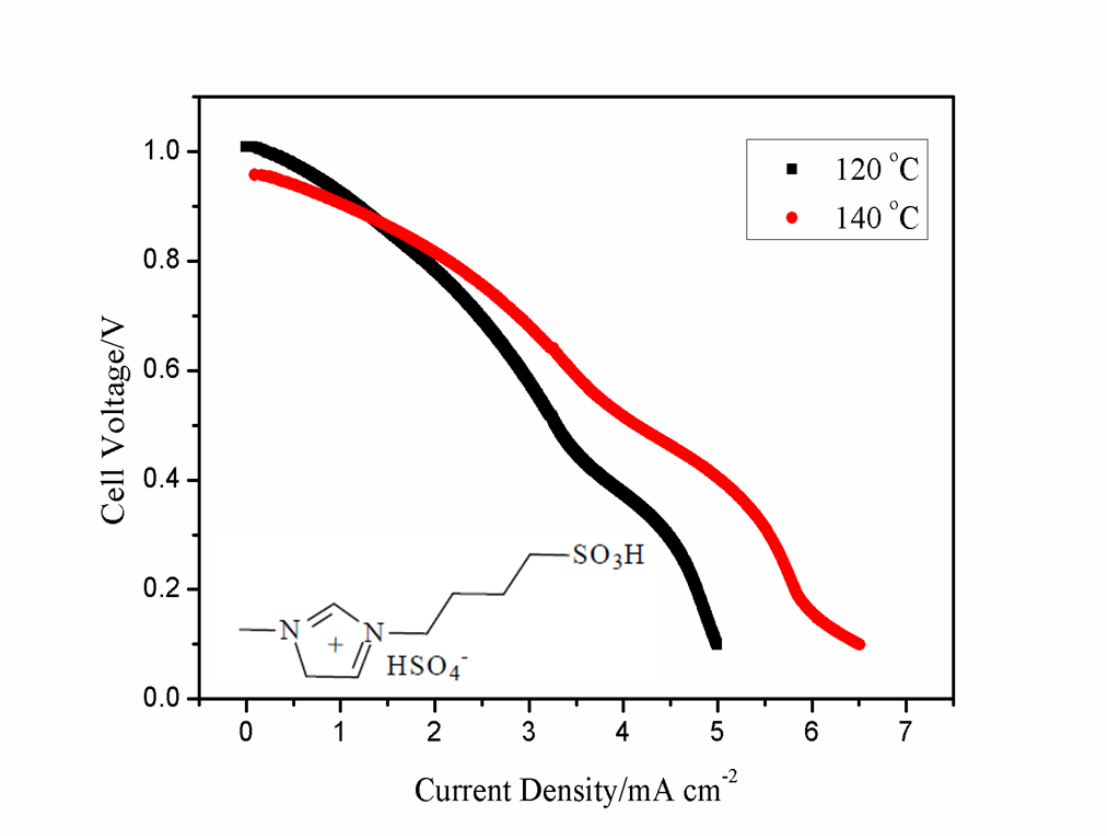


Figure S2 Single-cell H_2/Cl_2 fuel cell performance of NF/[BMIMHSO$_3$]HSO$_4$ hybrid membrane operated at different temperature.

Experimental section

Section S1 Materials

The ionic liquid $[N_{1,1,1}H]H_2PO_4$ is provided by Lanzhou Institute of Chemical Physics, Chinese Academy of Science. The FT-IR and NMR of the IL are shown in the reference [S2]. The thermal property of the IL is shown in the Figure 1 in the main document.

Section S2 Electrochemical Polarization

Cyclic voltammetry (CV) was conducted at room temperature (20 ± 1 °C) for both ILs, using an electrochemical workstation (CHI600C, Shanghai Chen-Hua Instrument Co. Ltd, China) in a three-electrode test cell. A saturated calomel electrode (SCE, 0.2415 V with respect to NHE reference electrode) was used as the reference electrode, whilst the counter electrode was a platinum sheet. All potentials in this work were reported versus the SCE reference electrode. The working electrodes were prepared by a glassy carbon rotating disk electrode (RDE) method. Firstly, 5 mg Pt/C catalyst (70%, Johnson Matthey) was ultrasonically suspended in 1 ml isopropyl alcohol and 50 μL Nafion® solution (5 wt.%, Du Pont) for about 30 min to obtain the catalyst ink, then 5 μL of the catalyst ink was spread onto the surface of RDE and dried at room temperature. Before the CV measurements, the electrode was activated by repeatedly voltage scanning form -0.241 V to 0.759 V at rate of 100 mV s^{-1} in 0.5 M H2SO4 solution deaerated by N_2 gas. Then, the CV curves were recorded from -0.241 V to 0.759 V at rate of 50 mV s^{-1}. After the test, the electrode was immersed into ionic liquid for 10 min. Then the CV of the electrode infected with ionic liquid was measured as the method described as previously mentioned above.

Section S2 Membrane characterizations

The IL content ($\Delta W\%$) in the prepared composite membrane can be calculated by the weight of the NF membrane before (W_b) and after immersing (W_a).

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

Microstructure morphologies of the NF substrate membrane and the NF/IL hybrid membrane were observed by the Scanning Electron Microscopy (SEM, JEOL JSM-6700F). The samples were firstly immersed into liquid nitrogen for a few minutes, then broken and deposited into a copper. All samples were coated with gold under vacuum before test.

The thermal stability of sample was evaluated by thermal gravitational analysis (TGA, STA449F3, NETZSCH, Germany). The samples were weighed and placed in crucible and then heated from 40 to 650 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under air atmosphere.

Section S3 Ion conductivity

The ionic conductivity of NF/IL membrane was measured at different temperature by 2-probe AC method in a frequency range from 10^6 to 100 Hz at a voltage amplitude of 20 mV using Sl 1260 Impedance/Gain-phase analyzer (Solartron). The samples were sandwiched between two smooth stainless disk electrodes (4.153 cm^2) in a cylindrical PTFE holder. The conductivity of the IL was measured by the conductivity meter (DSA-11, Shanghai LEI-CI Co. Ltd, China).

Section S4 Fabrication of membrane electrode assembly (MEA) and a single-cell test

A membrane electrode assembly (MEA) was fabricated by sandwiching a composite membrane between two gas diffusion electrodes (GDL, Sunrise Power Co. Ltd., China; 70 wt.% Pt on Vulcan XC-72, 0.4 mg cm^{-2}) without hot-pressed. The MEA was test in a single-cell with an active area of 5 cm^2 at ambient pressure. The fuel cell polarization curves were determined at different temperature by using PARSTAT® 2273 (Princeton, USA). Anhydrous H_2 and Cl_2 gases were supplied to the fuel cell at gas flow rate of 20 ml min^{-1} and 30 ml min^{-1} without any humidification at ambient pressure.

The permeation current density was measured by applying a positive voltage (0.25 V vs. NHE) at the cathode (while flushing it with nitrogen) in order to oxidize the hydrogen that permeated.

References

[S1] S. Liu, L. Zhou, P.J. Wang, L.S. Zhang, Z.G. Shao and B.L. Yi, *J. Mater. Chem.*, 2012, **22**, 20512.

[S2] C.C. Ke, J. Li, X.J. Li, Z.G. Shao and B.L. Yi, *ACS Advances*, 2012, **2**, 8953.