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Electronic Supplementary Information

The impact of imidazolium with steric hindrance on the dissociation of phosphoric acid and the performance of high-temperature proton exchange membranes

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4 figures (Fig. S1 to S4).

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Computational Section

Density functional theory (DFT) computations were employed to calculate interaction energy (E_{int}) and dissociation energy (E_{d}) using the DMol3 code in Materials Studio program.

Based on the optimized structure, the E_{d}s of PA in different chemical enviorments were calculated by the following formula:

$$E_{int} = \sum E_{ion} - E_{total} \quad (1)$$

Where E_{total} and E_{ion} represent the total energy of the system and the energy of each ion in the system, respectively. The energy of H^+ is -6.28 kcal/mol.[S1]

The E_{int}s between different structure units and PA molecule were calculated by the following formula:

$$E_{int} = E_{total} - \sum E_{component} \quad (2)$$

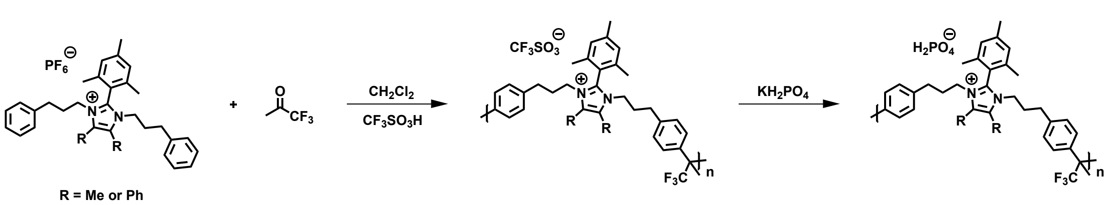
Where E_{total} and $E_{\mathrm{component}}$ represent the total energy of the system and the energy of each component in the system, respectively.

Experimental Section

Synthesis of P-Im and ion exchange

The synthesis of imidazolium monomer Im [PF_6] can be found in Ref [S2,3]. Im [PF_6] (5 mmol), 1,1,1-trifluoroacetone (0.6723 g, 6 mmol), and dichloromethane (CH_2Cl_2) (5 mL) were added to a 50 mL one-neck round bottom flask at 0 °C. Trifluoromethanesulfonic acid (CF_3SO_3H) (5 mL) was then added as the catalyst. The reaction mixture was allowed to react and its viscosity increased gradually. After reacting for 12 h, the solution was poured into ethanol and stirred overnight. The polymer was filtered by vacuum filtration, rinsed with deionized water, and dried in vacuum overnight.

P-Im [CF_3SO_3] was immersed in 1 M KH_2PO_4 aqueous solution and heated at 50 °C for 12 h to exchange the counterion from $CF_3SO_3^-$ to $H_2PO_4^-$. After that, the target polymer P-Im [H_2PO_4] was obtained.



Scheme S1. Synthetic pathway of P-Im [H_2PO_4].

Procedure of membrane casting

The membranes were prepared by solution casting. The blend polymer was dissolved in DMSO at a 5 % wt/v concentration. Then the obtained solution was filtered through a sand core funnel and cast onto a flat plate of glass, heated in an oven at 80 °C for 12 h and dried in vacuum at 120 °C for 12h, after that a transparent homogeneous membrane was prepared. The membrane was immersed in PA at 120 °C for 24 h and PA doped membrane was obtained.

Characterization and measurements

The X-ray diffraction (XRD) measurements were taken on a Rigaku MiniFlex 600 (Cu K_α radiation, λ = 1.5405 Å) at a scanning rate of 10° min^{-1} (2θ from 3° to 45°). UV-vis absorption spectra were performed on a SHIMADZU 1800 SPC spectrophotometer (wavelength from 255 to 500 nm). Tensile stress-strain behaviors of membranes were measured with an Instron-1121 mechanical testing instrument at a crosshead speed of 5 mm min^{-1}. Thermogravimetric analysis (TGA) was measured with a PerkinElmer TGA-2 thermogravimetric analyzer at a temperature range of room temperature to 800 °C with a heating rate of 10 °C min^{-1} under continuous N_2 flow. Differential scanning calorimetry (DSC) analysis was tested using a PerkinElmer DSC-7 at a temperature range of -45 °C to 200 °C with a heating rate of 10 °C min^{-1}.

The PA uptake (PU) and swelling ratio (SR) were measured via recording the weight and volume change before and after HT-PEMs membranes immersed into PA (85 wt%) at 120 °C for 24 h and dried in a vacuum oven at 80 °C for 12 h. The PU and SR were calculated as following formulas:

$$PA\,uptake\,(\%) = \frac{W_d - W_u}{W_u} \times 100\% \quad (3)$$

$$Swelling\ ratio\ (\%) = \frac{V_d - V_u}{V_u} \times 100\% \quad (4)$$

where W_d and V_d are the weight and volume of the PA doped HT-PEMs, respectively; and W_u and V_u are the weight and volume of the PA undoped HT-PEMs, respectively.

ADL defined as the mole number of PA molecules per mole of polymer repeat unit was calculated according to formula (5).

$$ADL = \frac{(W_d - W_u)/M_{PA}}{W_u/M_{polymer}} \quad (5)$$

In-plate proton conductivity (σ, S cm^{-1}) of HT-PEMs membranes was measured using a two-point probe method with alternating current impedance on an electrochemical workstation (BioLogic VSP) under controlled temperature. The frequency ranged from 10 Hz to 100 kHz. And at each temperature, the system was equilibrated for at least 1 h before measuring the resistance value. Conductivity was calculated using following formula:

$$\sigma = \frac{D}{RA} \quad (6)$$

where σ is proton conductivity (S cm^{-1}), D is the distance between two adjacent probes (cm), R is the measured resistance value corresponding to the real Z′ Nyquist plot and A is the cross-sectional area of the membrane (cm^2).

The calculated proton conductivity values at different temperatures were fitted to the Arrhenius formula shown below to obtain the activation energy (E_a) of the proton conduction process:

$$ln\sigma = -\frac{E_a}{kT} + ln\sigma_0 \quad (7)$$

where σ is proton conductivity, σ_0 is the pre-exponential factor, T is the absolute temperature in kelvin, E_a is the activation energy and k is the Boltzmann constant.

PA retention could be obtained by fuel cell environmental simulation. The PA doped membranes were placed in a thermoshygrostat at 80 °C and 40% relative humidity (RH). After a certain period of time, the membranes were taken out and dried. Then, the remaining weight was recorded. PA retention was calculated as below:

$$PA\, retention\,(\%) = \frac{W_{after}}{W_{before}} \times 100\% \qquad (8)$$

where W_{before} and W_{after} represent the weight of the PA doped membranes before and after the PA leaching process.

Oxidative stability of HT-PEMs were tested by immersing the membranes into Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm Fe^{2+}) at 80 °C.

To evaluate the performance of blend membranes, the membrane electrode assemblies (MEAs) with OPBI&P-PhIm-10%/PA and OPBI/PA membranes were then assembled in a single cell fixture with an active area of 9.0 cm^2 (3.0 cm × 3.0 cm) for high-temperature proton exchange membrane fuel cells (HT-PEMFCs) test, respectively. Catalyst layer compositions: anode/cathode: 60% Pt/C (Pt loading: 0.8 mg cm^{-2}; 80 wt%), PIM-P ionomer (20 wt%). Electrochemical characterization was initiated by running polarization and power density curves, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and in-situ durability. Polarization and power density curves were measured using a fuel cell test station (Dongfang Electric Corporation Limited) with no humidification or backpressure. The single cell was operated at 160 °C and 200 °C with dry H_2 at 200 sccm and O_2 at 400 sccm fed into anode and cathode, respectively. Prior to the test, the cell was active at a constant voltage of 0.6 V for at least 1 h until the current stable. And then, the polarization curves were recorded. LSV and EIS of HT-PEMFCs was measured by a Biologic electrochemical workstation (Biologic VSP, France). LSV was conducted from 0.1 V to 0.8 V with a sweep rate of 100 mV s^{-1} at 160 °C after cell stabilization about 30 min and with H_2 at 200 sccm and N_2 at 400 sccm fed into anode and cathode, respectively. In situ EIS analysis was performed by sweeping frequency from 100 Hz to 1 MHz at 160 °C. In-situ durability of H_2/O_2 HT-PEMFCs based on OPBI&P-PhIm-10% and OPBI membranea were test under a constant current density of 200 mA cm^{-2} at 160 °C.

Supplementary Results

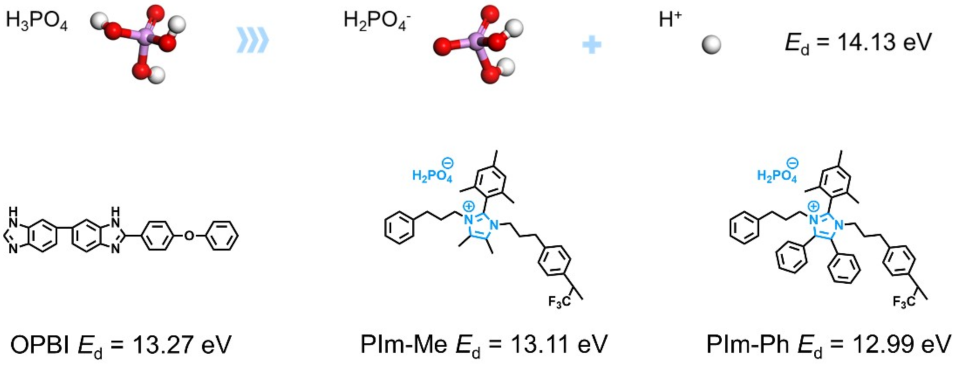
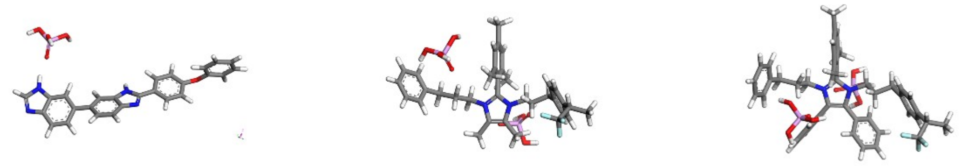


Fig. S1 The dissociation energies (E_ds) of PA molecule and PA exposed to different chemical environments.



OPBI E_{int} = -16.26 kJ/mol PIm-Me E_{int} = -23.82 kJ/mol PIm-Ph E_{int} = -31.84 kJ/mol

Fig. S2 The interaction energies (E_{int}s) between PA molecule and different polymer structure unit.

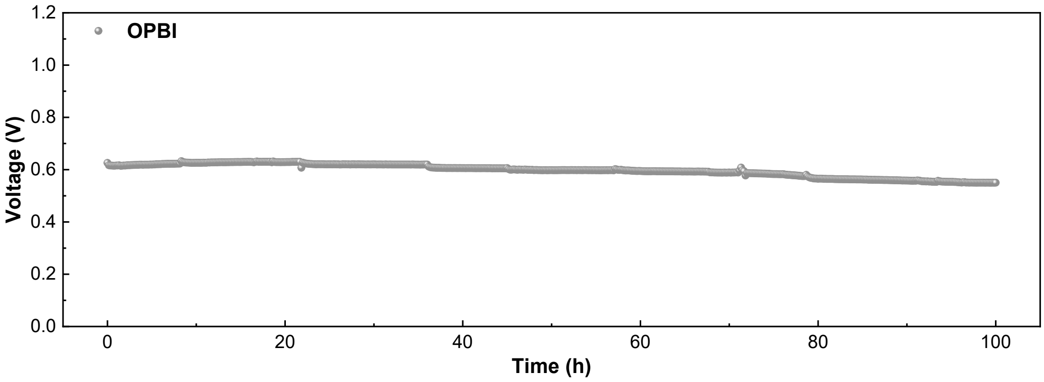


Fig. S3 In-situ durability of HT-PEMFC equipped with OPBI/PA PEM tested under a constant current density of 200 mA cm^{-2} at 160 °C.

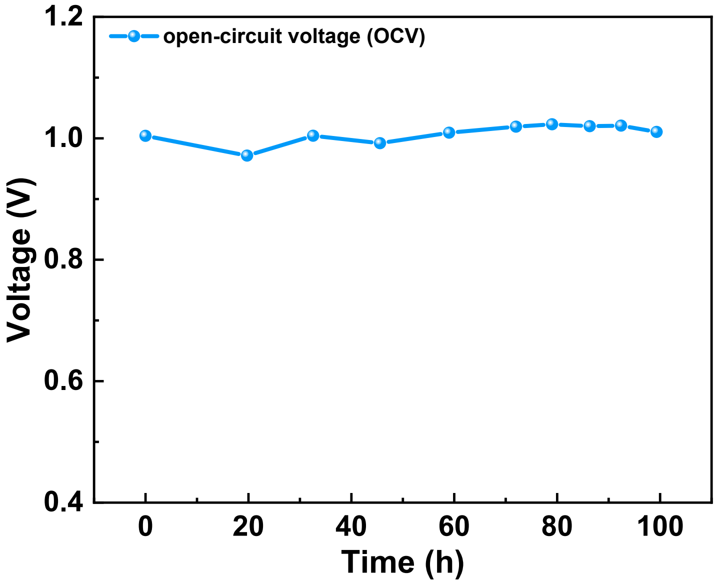


Fig. S4 Open-circuit voltage of HT-PEMFC equipped with OPBI&P-PhIm-10% membrane during the long-term stability test.

References

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