▌**Ionic Liquids** │*Hot Paper*│

A Metal–Organic Framework Impregnated with a Binary Ionic Liquid for Safe Proton Conduction above 100 °C

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Dedicated to Professor Thomas C. W. Mak on the occasion of his 80th birthday

Abstract: To develop proton-conducting materials under low-humidity conditions and at moderate working temperature still remains challenging for fuel-cell technology. Here, a new type of proton-conducting material, EIMS-HTFSA@MIL, which was prepared by impregnating the binary ionic liquid, EIMS-HTFSA (EIMS = 1-(1-ethyl-3-imidazolium)propane-3-sulfonate; HTFSA = N,N-bis(trifluoromethanesulfonyl)amide), into a mesoporous metal–organic framework, MIL-101 ([Cr$_3$F(H$_2$O)$_2$O(BDC)$_3$·nH$_2$O] ($n \approx 0.25$, BDC = 1,4-benzenedicarboxylate)) is reported. By taking advantage of the ionic-liquid properties, such as high thermal stability, non-volatility, non-flammability, and low corrosivity, EIMS-HTFSA@MIL shows potential application as a safe electrolyte in proton conduction above 100 °C.

Proton exchange membrane (PEM) fuel cells are acknowledged as one of the best candidates for the energy-supplier in next generation electric vehicles.[1] Among different types of fuel cells, anhydrous PEM fuel cells that operate at a moderate temperature (100–300 °C) would have ideal performance and lower cost, because expensive platinum catalysts may be replaced by abundant oxide-based catalysts, and the cumbersome water management system can be dramatically simplified.[2] The state-of-the-art proton conductive separators for PEM fuel cells, perfluorosulfonic polymers (e.g., Nafion®),[3] require a high degree of hydration to maintain their high conductivity, which limits their maximum working temperature to below the boiling point of water (i.e., 100 °C at 10^5 Pa).

During the past few decades, crystalline porous materials, such as metal–organic frameworks (MOFs)[4] and covalent organic frameworks (COFs),[5] have attracted significant scientific and technological attention due to their potential applications as separators, sensors, catalysts, and proton conductors.[5,6] An efficient strategy for achieving high conductivity above 100 °C is by loading anhydrous proton carriers, such as N-rich heterocycles (e.g., triazole,[7] imidazole,[8] and histamine[9]) or strong inorganic acids (H$_2$SO$_4$/H$_3$PO$_4$/CsHSO$_4$)[2b,10] into MOFs. However, those proton carriers either have relatively low sublimation temperatures that are detrimental to their long-term stability, or can only be applied to a few MOFs due to the poor acid-resistance of most MOFs. Moreover, special cautions are required when preparing and using these highly corrosive inorganic acids such as H$_2$SO$_4$/H$_3$PO$_4$ as proton carriers.

In comparison, ionic liquids (abbreviated as ILs) are promising candidate materials for safe electrolytes at moderate temperatures[11] due to their high thermal stability, non-volatility, non-flammability, and low corrosivity.[12] Incorporating ILs into MOFs to create a novel soft-media-in-hard-matrix material may overcome the viscosity drawback of ILs,[12c] and actually lower the cost of ILs through efficient dispersion over the large internal surface of MOFs. Moreover, ionic liquids even exhibit unusual and interesting anomalous phase behavior at low temperature (below 200 K) as they are incorporated into a porous MOF.[13] Rationally utilizing these advantages of ILs to serve as proton conductors at high temperature remains an underexplored topic, which is perhaps surprising as they are promising proton carriers at moderate temperature.

1-(1-Ethyl-3-imidazolium)propane-3-sulfonate (EIMS, pK_a ≈ 6.8) is a zwitterionic liquid, which has both a cation and anion that are tethered together and cannot migrate along potential gradients, and thus may favor proton conduction only.[14] Mixing EIMS with N,N-bis(trifluoromethanesulfonyl)-amide (HTFSA, pK_a ≈ 2),[15] forms a Brønsted acid–base buffer (Scheme 1a).[16] In this mixture, the protonated -SO$_3$H/HTFSA and unprotonated -SO$_3^-$/TFSA$^-$ matrix thus act as proton-source, and proton-defect sites, respectively, enabling H$^+$ hopping between the negatively charged sites (-SO$_3^-$/TFSA^{-1}) for efficient transport (Scheme 1b).

Inspired by this, we report the first study of such a novel binary ionic-liquid-impregnated MOF material, EIMS-HTFSA@-MIL, as a safe, anhydrous, solid-state electrolyte for effective

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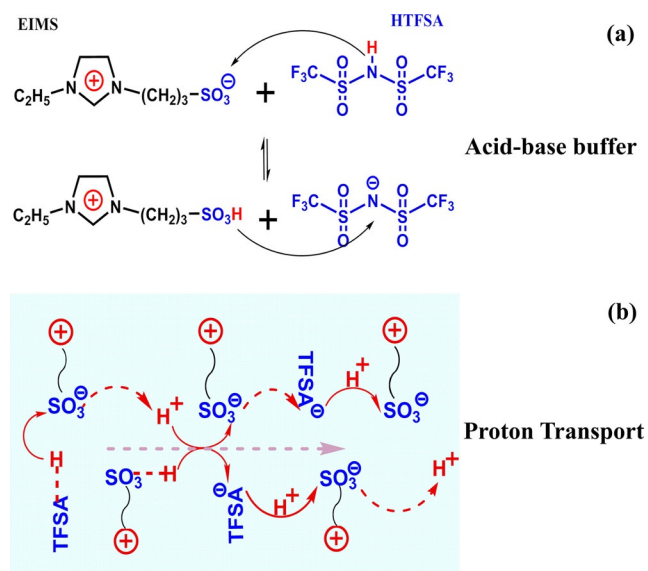
Scheme 1. a) Diagram of the binary ionic liquid EIMS-HTFSA and Brønsted acid–base buffer. b) Illustration of H⁺ hopping within the matrix of EIMS-HTFSA.
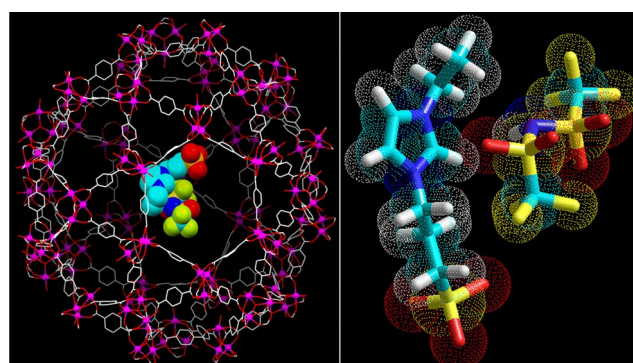

Figure 1. Model structure of EIMS-HTFSA@MIL including one EIMS-HTFSA pair, drawn using a CPK model (left), and a stick model of EIMS-HTFSA (right).

H⁺ conduction at moderate temperature (MIL-101 = $[Cr_3F(H_2O)_2O(BDC)_3 \cdot n\,H_2O]$ ($n \approx 0.25$, BDC = 1,4-benzenedicarboxylate)).[17] Because the EIMS-HTFSA binary exhibits high stability and low corrosivity (pH ≈ 2.8), the EIMS-HTFSA@MIL conductor can operate in air, and shows feasible environmentally friendly operation, and a favorable level of safety. Moreover, EIMS-HTFSA@MIL exhibits H⁺ conductivity of $2 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 140 °C, which is around six orders of magnitude higher than empty MIL-101 and is in the range of the most conductive MOF-based materials at this temperature.[7–10]

The binary ionic liquid EIMS-HTFSA, a mixture of EIMS and HTFSA in a molar ratio of 3:2 (Table S1 in the Supporting Information), is a colorless liquid at room temperature. Thermogravimetric analysis (TGA) carried out under dry air shows the onset decomposition temperature of the mixture is 308 °C (Figure S1a), being sufficiently stable in a moderate operating temperature range for use as an anhydrous electrolyte. MIL-101 is well known as a chemically and thermally stable MOF (up to 335 °C), featuring a mesoporous structure with two types of spherical cages (ø ≈ 2.9–3.4 nm) (see Supporting Information).[17] Its smallest pentagonal window (with a free opening of ≈ 1.2 nm) is large enough to smoothly impregnate HTSFA (van der Waals volume, $V_{vdW} = 147\,\text{Å}^3$)[18a] and EIMS ($V_{vdW} = 603\,\text{Å}^3$ with ≈ 7.73 Å across)[18b] into the cage (Figure 1). The calculated maximum number of pairs of EIMS-HTFSA accommodated within the large cage (≈ 20 600 Å³) and small cage (≈ 12 700 Å³) are 27 and 17, respectively.

EIMS-HTFSA@MIL materials were prepared through a heterogeneous mixing and grinding method, together with capillary action[13] (see Supporting Information). EIMS-HTFSA@MIL samples with varying amounts of EIMS-HTFSA impregnated were prepared, based on the pore volumes of 1.895 cm³ g⁻¹ of activated MIL-101 (Table S4 in the Supporting Information), and with the EIMS-HTFSA theoretically occupying 25, 50, and 100 % pore volumes of a MIL-101 sample. These are denoted as BIL25, BIL50 and BIL100, respectively (Table S2). BIL25–BIL100 samples are stable up to 320 °C in air (Figure S1 in the Supporting Information). The mass percent of Cr_2O_3 remaining after heating (above 620 °C) of BIL25–BIL100 agree well with their calculated values (Table S2). FT-IR and energy dispersive spectra of BIL25–BIL100 samples unambiguously confirmed the presence of EIMS-HTFSA (Figures S3 and S4). The broad band of C–H (phenyl) vibration centered at 1606 cm⁻¹ of MIL-101 becomes sharper after impregnation of EIMS-HTFSA, suggesting strong intermolecular contacts, such as H-bonding and Van der Waals interactions, occurred between the EIMS-HTFSA and MIL-101 framework. These interactions combined with capillary action may well account for the facile impregnation of EIMS-HTFSA into MIL-101 through heterogeneous mixing.

To further identify the loading of EIMS-HTFSA within the pores of MIL-101, N₂ sorption isotherms were measured (Figure 2a). N₂ uptake and the pore-size distributions (Figure S5 in the Supporting Information) decreased with increasing amount of EIMS-HTFSA. In contrast to the 100 % pore volume of MIL-101, the measured percent of the pore volumes of BIL25–BIL100 agree well with their theoretical values (Table S4), which suggests the ILs have been exactly impregnated into the pores of MIL-101. Additionally, scanning electron microscopy images show that the crystal morphology of BIL100 is similar to that of MIL-101 (Figure S4). These observations indicate that the EIMS-HTFSA is preferentially introduced into the pores rather than the outer surface of the MIL-101 nanoparticles.

Powder X-ray diffraction (PXRD) patterns of BIL25–BIL100 suggest that the framework of MIL-101 was maintained after EIMS-HTFSA incorporation (Figure 2b). The intensities of the peaks at low 2θ angles decreased as the amount of EIMS-HTFSA increased, whereas those at high 2θ angles increased accordingly. Such a phenomenon is attributed to the disordered distribution of impregnated molecules that would produce background diffraction and decrease the diffraction at low 2θ angles. This observation suggests the incorporation of EIMS-HTFSA inside the pores of MIL-101 as that commonly found and well elucidated in other MOF materials.[12,13] Variable temperature PXRD of BIL100 shows it was stable when heated
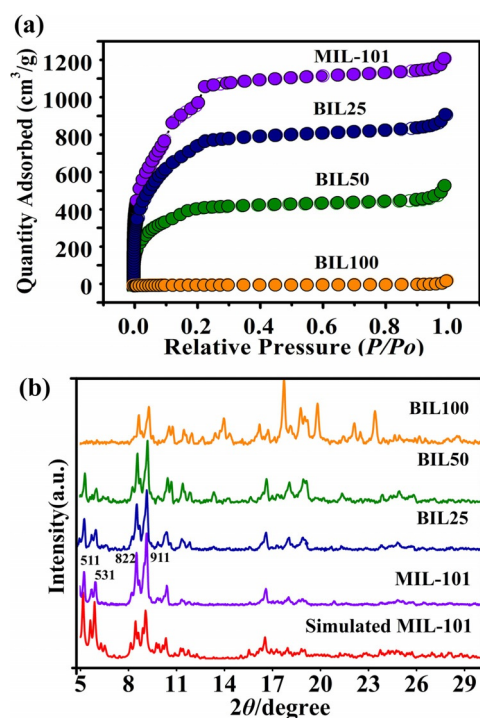
Figure 2. N_2 adsorption isotherms collected at 77 K (a) and PXRD patterns of MIL-101, BIL25, BIL50, and BIL100 at room temperature (b).

to 150 °C (Figure S6 in Supporting Information); above the 120 °C stability temperature desired for hydrogen fuel cells.[2]

The temperature-dependent conductivities of MIL-101 and BIL25–BIL100 were tested in an oven, using pressed powder pellets, through alternating current (AC) impedance analysis with a quasi-four-probe method. All samples were heated to 140 °C for 8 hours, and then the conductivity of each sample was recorded from 140 to 50 °C. (Shown for BIL100 in Figure 3a) At each temperature point, the measurements were performed repeatedly with an interval of half an hour until equilibrium was reached. The H^+ conductivities of all the samples show linear Arrhenius behavior, having increasing conductivities with temperature (Figure 3b). In comparison, other reported H^+ carriers incorporated within MOFs, such as imidazole, triazole, and histamine,[7,8] have drastic conductivity changes due to the phase transitions occurring at their respective melting points (Table S3). The linear variation of the conductivity of EIMS-HTFSA@MIL enables its conductivity to be smoothly controlled in a fuel cell.

Compared to other reported H^+ carriers impregnated into MOFs, EIMS-HTFSA also has superior safety and long-term stability at high temperature due to its high thermal stability, non-volatility, and low flammability hazard. As shown in Figure S1 and Table S3, TGA of EIMS-HTFSA shows its thermal stability up to 308 °C (even heating in air), being much higher than those reported heterocycle proton carriers (stable below 112 °C). EIMS-HTFSA@MIL materials also show good stability up
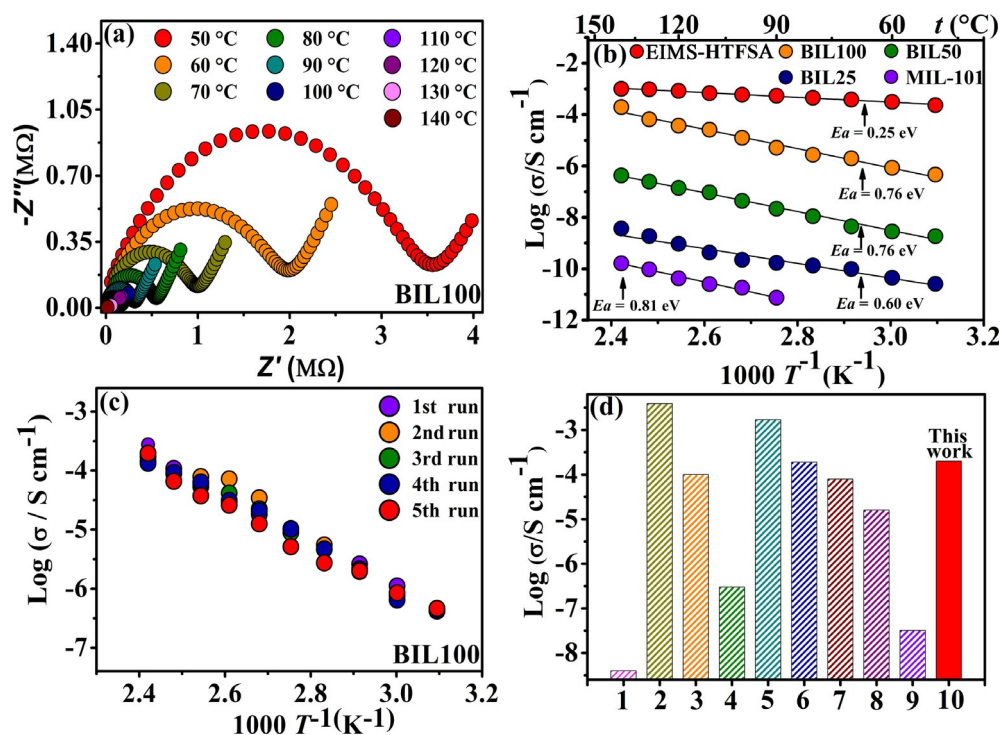

Figure 3. a) Nyquist plots of BIL100 from 50 to 140 °C. b) Temperature-dependent conductivities of MIL-101, BIL25–BIL100, and EIMS-HTSFA. c) Recycle test of the temperature-dependent conductivity of BIL100. d) Anhydrous H^+ conductivity of BIL100 and that of other representative MOFs at 140 °C (His@Zn-MOF-74 (**1**),[9b] CsHSO$_4$@MIL-101 (**2**),[10] {[(Me$_2$NH$_2$)$_3$(SO$_4$)]$_2$[Zn$_2$(ox)$_3$]}$_n$ (**3**),[2c] [Co$_2$Na(bptc)$_2$][Emim]$_3$ (**4**),[20a] His@[Al(OH)(1,4-ndc)]$_n$ (**5**),[9a] β-PCMOF$_2$(Tz)$_{0.3}$ (**6**),[7] [Zn(H$_2$PO$_4$)$_2$(TzH)]$_n$ (**7**),[2a] [Zn(H$_2$PO$_4$)$_2$(HPO$_4$)](H$_2$dmbim)$_2$ (**8**),[20b] [Zn(H$_2$PO$_4$)$_2$(HPO$_4$)](H$_2$dabco)$_2$ (**9**)[20b]) (bptc = 2,2′,4,4′-biphenyl tetracarboxylate, Emim = 1-ethyl-3-methyl imidazolium, 1,4-ndc = 1,4-naphthalenedicarboxylate, Tz = 1*H*-1,2,4-triazole, dmbim = 5,6-dimethylbenzimidazole, dabco = 1,4-diazabicyclo [2.2.2]octane).

to 320 °C, being thermally stable enough for a safe PEM working at moderate temperature. The flash point of imidazolium-based ionic liquids is as high as that of polyethylene ($\approx$ 433 °C), making EIMS-HTFSA a low flammability hazard.[12d] Comparatively, the heterocycle proton carriers normally have flash points close to 140 °C (Table S3). The measured impact sensitivity value of > 40 J and friction sensitivity of > 360 N for EIMS-HTFSA (see Supporting Information) also suggest its insensitivity towards impact and friction.[12e] In comparison to H_2SO_4 or H_3PO_4, the Brønsted acid–base buffer of EIMS-HTFSA is a weaker acid with a relatively high pH value of 2.83 (Table S1), which has much lower corrosivity. The unusual property of this binary liquid ion enables it to be applied to MOFs that have lower stability to strong acids, and to be less hazardous if leaked.[12b]

Bulk EIMS-HTFSA has a protonic conductivity as high as 1.17×10^{-3} S cm^{-1} at 140 °C, whereas the conductivity of the activated MIL-101 is slightly lower than 10^{-10} S cm^{-1} at 140 °C (Figure 3 b), the combination of which meets the protonic conducting, but electrically insulating requirement to be the separator in a fuel cell. BIL25–BIL100 show their conductivity increased with the increasing amount of EIMS-HTFSA in MIL-101. In comparison, the conductivity of BIL100 is six, five, and three orders of magnitude higher than that of MIL-101, BIL25, and BIL50 at 140 °C, respectively. These observations suggest that the H$^+$ conductivity of EIMS-HTFSA@MIL is strongly connected with the amount of EIMS-HTFSA in the MOF, which can be ascribed to a more continuous conduction pathway through the ILs within the pores of the MOF when they are saturated, similar to that of Li$^+$ conduction reported by Kitagawa.[13] The conductivity of BIL100 reaches 1.99×10^{-4} S cm^{-1} at 140 °C (Figure 3 b), which is comparable to the highest conductivity of reported anhydrous H$^+$ conductive MOFs at this temperature (Figure 3 d and Table S5). Moreover, BIL100 has good cyclability when repeatedly varying the temperature from 50 to 140 °C. After 5 cycles, Arrhenius plots follow a similar linear trend without marked deviation (Figure 3 c). These results indicate that there is no leaching, no phase transition, and no evaporation/sublimation of the ILs taking place during the heating.

The activation energy (E_a) of BIL25–BIL100, calculated by the Arrhenius equation, are 0.60, 0.76, and 0.76 eV, respectively. These values are higher than those of the typical hydrated proton conductors with H$^+$ transfer through a Grotthuss mechanism, such as Nafion ($E_a = 0.22$ eV)[3] and $HUO_2AsO_4 \cdot 4\,H_2O$ ($E_a = 0.32$ eV),[19] but are comparable to that of the anhydrous proton conductors, such as 0.66 eV for $[Zn(H_2PO_4)_2(HPO_4)] \cdot (H_2dmbim)_2$,[20b] and 0.90 eV for Im@{Al(μ_2-OH)(1,4-bdc)}$_n$ (dmbim = 5,6-dimethylbenzimidazole; 1,4-bdc = 1,4-benzenedicarboxylate).[8a] The rate-limiting step of the Grotthuss mechanism is the structural reorientation of the proton carrier after H$^+$ transfer, and thus the E_a would automatically be higher for a larger molecule. Therefore, the conduction mechanism of BIL25–BIL100 is a Grotthuss mechanism.

In summary, we demonstrated a binary ionic liquid as a new type of proton carrier which can be inserted into a MOF to generate a safe, anhydrous, solid-state electrolyte. This new material shows a high conductivity at 140 °C in air. The stability

and low corrosivity of the ionic liquid may enable it to be suitable for many other MOFs. This heterogeneous hybridization provides a facile method that would open up a way to achieve a library of new, stable, anhydrous PEM materials with high performance, environmentally friendly operation, and low hazard at moderate temperatures.

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