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Imparting High Proton Conductivity to a Metal–Organic Framework Material by Controlled Acid Impregnation

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Supporting Information

ABSTRACT: The extensive implementation of hydrogen-powered technology today is limited by a number of fundamental problems related to materials research. Fuel-cell hydrogen conversion technology requires proton-conducting materials with high conductivity at intermediate temperatures up to 120 °C. The development of such materials remains challenging because the proton transport of many promising candidates is based on extended microstructures of water molecules, which deteriorate at temperatures above the boiling point. Here we show the impregnation of the mesoporous metal–organic framework (MOF) MIL-101 by nonvolatile acids H_2SO_4 and H_3PO_4. Such a simple approach affords solid materials with potent proton-conducting properties at moderate temperatures, which is critically important for the proper function of on-board automobile fuel cells. The proton conductivities of the H_2SO_4@MIL-101 and H_3PO_4@MIL-101 at $T = 150$ °C and low humidity outperform those of any other MOF-based materials and could be compared with the best proton conductors, such as Nafion.

For the past decade, metal–organic coordination polymers have been extensively studied because of their exceptional adsorption properties and related applications such as separation, sensing, and catalysis.[1] However, in spite of the pioneering works of Kitagawa,[2,3] such materials have not drawn much attention as ion conductors because of their primarily nonionic, hydrophobic nature and low stability in acidic aqueous environments or at high temperatures. Only very recent examples[4−7] have demonstrated that the proton conductivity in metal–organic frameworks (MOFs) could approach the specifications required for fuel cell proton-exchange membranes (PEMs).[8−12] Crystalline porous MOFs with hydrated water could possess interesting proton-conducting properties, but only at ambient temperatures.[4,13−18]

The synthesis of coordination polymers with high-temperature proton conductivity can be generally divided onto two distinct approaches. First, inherently acidic frameworks can be obtained either by self-assembly of the corresponding functionalized ligands or by postsynthetic modifications of the MOFs. These result in reticular structures with covalently attached acidic groups decorating the pores of the extended coordination network.[5,19,20] The alternative way is to imbue the pores of coordination polymers with nonvolatile guest molecules as a medium that provides multiple proton delocalization pathways for efficient proton transport. For example, the inclusion of weakly acidic triazole,[6] imidazole,[21] or histamine[7] molecules into porous metal–organic structures resulted in new hybrid materials with decent proton conductivities at temperatures above 100 °C, which is essential for practical mobile applications of PEM materials. Lastly, a very recent report of $CsHSO_4$–xMIL-101 ($x = 0.01$–0.07) nanocomposites,[22] which exhibited a considerable increase in $CsHSO_4$ proton conductivity (up to 2 orders of magnitude) due to a salt-disordered state in the MIL pores, represents a novel development of MOF-related proton-conducting materials.

In general, the ionic conductivity depends on the amount and mobility of charge carriers (protons). Therefore, the inclusion of stronger acids into porous structures should greatly improve the proton-conducting properties of such hybrid materials. Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are arguably among the best candidates because of their strong acidity and low volatility. However, choosing such acids greatly limits the scope of MOFs as potential porous hosts. Chromium(III) carboxylates are among a few known examples of porous coordination compounds capable of withstanding such strong acidic conditions.[20,23,24] In this report, we describe the synthesis of two solid materials based on the chromium(III) terephthalate MIL-101 porous structure and imbued with either H_2SO_4 or H_3PO_4. These hybrid compounds demonstrate high proton conductivity (σ) over a broad temperature range. In fact, the achieved σ values of 1×10^{-2} S·cm^{-1} at 150 °C and $\sigma = 3 \times 10^{-3}$ S·cm^{-1} under ambient conditions not only beat those of any other MOF-based compounds but are among the highest values reported to date for proton-conducting materials.

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The confirmed framework and chemical stability at elevated temperatures make such materials promising for automobile fuel-cell PEM applications.

The hybrid proton-conducting materials were prepared by mixing the MIL-101 mesoporous chromium(III) terephthalate (see Figure S1 in the Supporting Information) with aqueous solutions of H_2SO_4 (2.7 M) or H_3PO_4 (2.6 M). After the saturation, the excess liquid was removed and the compounds were dried at elevated temperatures, resulting in the solid products H_2SO_4@MIL-101 (**1**) and H_3PO_4@MIL-101 (**2**). Elemental analysis of these solids revealed atomic ratios of S/Cr = 1.49 (**1**) and P/Cr = 1.23 (**2**), which are equal to 4.47 H_2SO_4 and 3.69 H_3PO_4 molecules per MIL-101 formula unit $[Cr_3O(bdc)_3]^+$ (bdc= 1,4-benzenedicarboxylate) or 50 H_2SO_4 and 42 H_3PO_4 molecules per MIL-101 nanocage, respectively. It is worth mentioning that the inclusion of acids was fast and reversible, as complete acid removal could be done by water washing in merely 10 min. Thermogravimetric analysis (Figure S7) of the title samples confirmed the release of only water molecules in the temperature range up to 200 °C, while the irreversible destruction of the MIL-101 framework took place upon heating above 220−250 °C. On the basis of the gravimetric weight loss, the molar water content of the samples could be estimated as 10 H_2O and 5 H_2O per formula unit in **1** and **2**, respectively. Taking into account the above-mentioned molar amounts of the acids, MIL-101 appears to confine in its pores ~70% H_2SO_4 (~10 M) in **1** or ~80% H_3PO_4 (~14 M) in **2**. Excitingly, powder X-ray diffraction (PXRD) analysis of the inclusion compounds **1** and **2** (Figure S3) confirmed the stability of the MIL-101 host framework at least up to 150 °C. For some reason, however, the PXRD patterns of the acid-impregnated samples showed no reflections at lower angles, and the intensity of the other peaks was decreased compared with guest-free MIL-101. We explain this by X-ray adsorption and/or scattering by the liquids filling the MIL-101 nanopores as well as some local distortions and mosaicity of the MIL-101 crystal structure upon filling of the pores. Most importantly, the crystallinity of the MIL-101 host framework and its pristine PXRD pattern were fully restored upon water washing of **1** and **2**. That is, the encapsulation of strong inorganic acids in such high concentrations into the pores of MIL-101 did not seem to change the host structure, even at elevated temperatures.

Alternating-current (ac) impedance measurements of **1** and **2** were carried out using a two-probe method with Pt-pressed electrodes over the temperature range from 40 to 150 °C under different humidity conditions of 0.6, 3.0, and 5.0 mol %. Typical impedance plots for **2** (Figure 1) feature a part of a semicircle at higher frequencies and a tail at low frequencies at room temperature, which deals with the mobile ions being blocked by the electrode−electrolyte interfaces. At higher temperatures, two clear semicircles appear in the impedance plots in the high-frequency region, corresponding to the bulk and grain-boundary resistance along with electrode contributions. The higher-frequency minima/intercepts along the *x* axes of the impedance plots were used to calculate the bulk resistances of the samples. The detailed experimental results of the proton conductivity measurements on **1** and **2** are shown in Figure 2 as temperature-dependent values (σ vs T^{-1}) for both the heating and cooling regimes. As could be anticipated, the proton conductivities of the as-synthesized title materials at low temperatures and ambient humidity [0.6 mol %, relative humidity (RH) = 20%] were quite high: 4.0 × 10^{-2} S·cm^{-1} for **1** and 2.5 × 10^{-4} S·cm^{-1} for **2**. Such values match well to the conductivities of the corresponding liquid acids, taking into account the partial filling of the pores of the MIL-101 framework and its nonconducting properties.[25] This confirms the proposed model of the title materials as acidic solutions adsorbed by the highly extended surface of MIL 101 and confined within its nanopores (Figure S1). Increasing the temperature of **1** did not seem to affect its proton conductivity (a maximum of σ = 6.0 × 10^{-2} S·cm^{-1} could be observed at 80 °C), which decreased only at temperatures above 80 °C. On the contrary, heating of sample **2** resulted in a gradual increase in the proton conductivity, although the slope of the curve decreased at the same time. Such a convex profile of the temperature-dependent conductivity curves for the as-synthesized samples upon heating could be very well explained by the continuous loss of the water, which is supported by the TGA data. Heating to 150 °C releases ~7 H_2O molecules from **1** but only 1 H_2O for **2**, so dehydration has a stronger influence on the properties of **1**, as reflected by prominent bending of the corresponding curve. The conductivities of samples at *T* = 150 °C were found to be 1 × 10^{-2} S·cm^{-1} for **1** and 3 × 10^{-3} S·cm^{-1} for **2** (both values at a low humidity of 0.6 mol %, RH = 0.13%). The overall higher proton conductivity for **1** than for **2** strongly supports the hypothesis of our work that higher acidity of the guest medium should contribute to the proton-

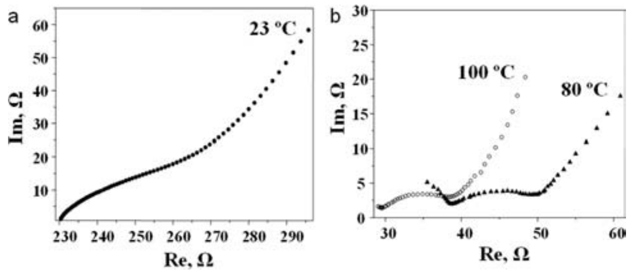

Figure 1. Impedance spectra of sample H_3PO_4@MIL-101 (**2**) at 3 mol % humidity and different temperatures: (a) 23 °C; (b) 80 °C (▲), 100 °C (○).

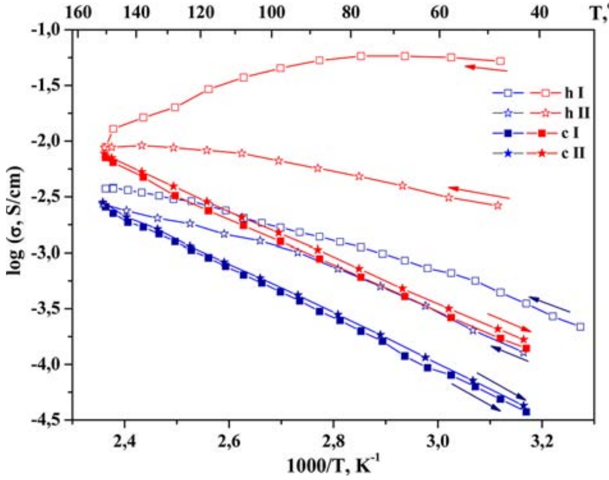

Figure 2. Temperature dependence of the proton conductivities of H_2SO_4@MIL-101 (**1**) (red) and H_3PO_4@MIL-101 (**2**) (blue) at 0.6 mol % humidity in heating−cooling cycles. Open and filled symbols indicate heating (h) and cooling (c) regimes, respectively, in the first run (squares) and the second run (stars).

conducting properties of the hybrid material, as K_a for H_2SO_4 is undoubtedly higher than K_a for H_3PO_4. The moderate-temperature proton conductivities of the title materials are greater than those of any other MOF-based compounds, with the runner-up being $\sigma = 1.7 \times 10^{-3}$ S·cm^{-1} at 150 °C for histamine-impregnated [Al(OH)(ndc)] (ndc = 1,4-naphthalenedicarboxylate).[7] Among any other solid materials, only Nafion ($\sigma = 9 \times 10^{-3}$ S·cm^{-1} at T = 80 °C and RH = 34%) and some other polymers[26] possess comparable proton-conducting performance under specified conditions (Figure 3).[12,27−29]

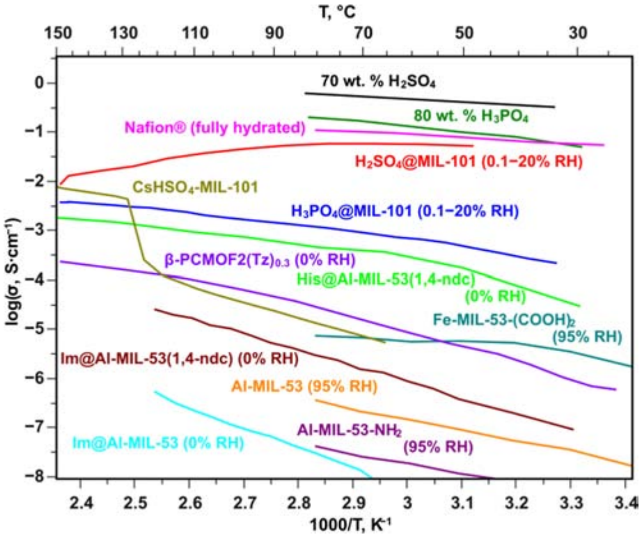

Figure 3. Summary of the proton-conducting properties of H_2SO_4@MIL-101 (**1**) and H_3PO_4@MIL-101 (**2**) together with those of some well-known proton-conducting reference materials (liquid acids, Nafion, MOFs, etc).

Strikingly, the cooling conductivity plots of both **1** and **2** were strictly linear, indicating no significant changes in the sample hydration (Figure 2). Apparently, the duration of the cooling experiment was not enough for the sample pellets to readsorb the moisture in an appreciable amount. As a result, the dependence of the conducting properties on the sample hydration is stronger at lower temperatures, where the condensation of airborne moisture in the pores is more favorable. The second cycle of heating−cooling experiments showed a similar trend as the first one, with an activation energy for proton transport of ~0.42 eV, but the deviations between the heating and cooling profiles were less pronounced. Most importantly, the cooling lines for the two experiments almost coincided, indicating that the proton conductivity properties of the title compounds follow a predictable pattern once the sample hydration is stabilized at higher temperatures (150 °C), irrespective of the initial water content. The discrepancies between the heating and cooling regimes are only due to the kinetics of the water adsorption or desorption. Should the relative humidity of the atmosphere be maintained constant over the whole temperature range, the proton conductivity of the materials would likely follow the linear trend without any deviations. Another important conclusion is that any temperature changes along with the corresponding alterations of the samples' hydration have no effect on the acid content, as any potential acid leaching or evaporation would influence the proton conductivity rather strongly. In other words, the durability of the materials **1** and **2** is not that low, as could be expected from simple acid-impregnated porous structures. The linear Arrhenius plots of **1** and **2** with the same slope for the cooling regimes (Figure 2) indicate that the proton transfer mechanism remains consistent for both materials over the whole range of conditions. The dependence of the proton conductivity upon moisture was further investigated for **2** when the air humidity was raised from 0.6 to 3 mol % and then to 5 mol % (Figure 4); this led to a substantial gain to the conducting properties of the samples (3−5 times). Apparently, the water molecules play an important role in increasing the proton concentration by facilitating phosphoric acid dissociation as well as by expanding the proton-conducting pathways through the hydrogen-bonding network, which eventually enhance the mobility of the protons. As a result, the greater proton conductivity of 1.0×10^{-2} S·cm^{-1} at T = 140 °C for **2** was observed for 5 mol % H_2O in air.

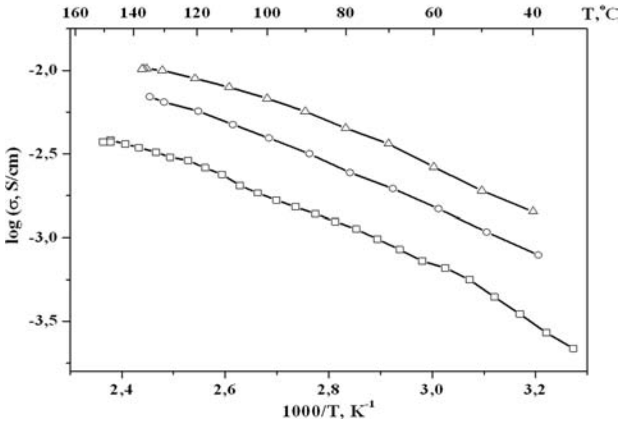

Figure 4. Temperature dependence of the conductivity of H_3PO_4@MIL-101 (**2**) at different water vapor contents: (bottom) 0.6 mol %; (center) 3 mol %; (top) 5 mol %. The corresponding RH values at 150 °C are 0.15, 0.64, 1.1%, respectively. Heating rate = 1.5 deg/min.

The proton transport activation energy of compound **2**, averaged from heating regime data (Figure 4), shows $E_a(\mathbf{2}) \approx 0.25$ eV, which is consistent with the higher hydration of the samples at ambient temperatures. Such activation energy values are typical for the relay (Grotthuss) mechanism in aqueous acid solutions, which involves fast proton transfer between adjacent $H_2O\cdots H_3O^+\cdots HSO_4^-/H_2PO_4^-$ triads and simultaneous conformational rotations of these species. The alternative vehicular proton transport mechanism usually is associated with E_a values greater than 0.4−0.5 eV.[30,31] The variations in the carrier mobility confirmed that the proton transfer primarily takes place within the thin acidic layer, which is spread over the high internal surface area of MIL-101. The remarkable stability of such acid−water microstructures at temperatures above 100 °C is plausibly supported by strong capillary effects of the MIL-101 nanopores, which prevent water evaporation below some critical levels that would cease the existence of the proton-conducting network.

In summary, we have reported the impregnation of the porous MIL-101 structure by nonvolatile acids H_2SO_4 and H_3PO_4. Such a simple approach affords solid materials with potent proton-conducting properties at moderate temperatures, which is critically important for the proper function of on-board automobile fuel cells. The proton conductivities of H_2SO_4@

MIL-101 and H_3PO_4@MIL-101 at T = 150 °C and low humidity outperform those of any other MOF-based material and can be compared to those of the best proton conductors. The acid molecules reside in the pores of the host framework and are not removed either by heating or upon any associated changes of the sample hydration while handled in a humid atmosphere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic methods, TGA and DSC data, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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