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Silicon hydrogensulfates: solid acids with exceptional 25°C conductivities and possible electrochemical device applications

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S1. HCl trap information

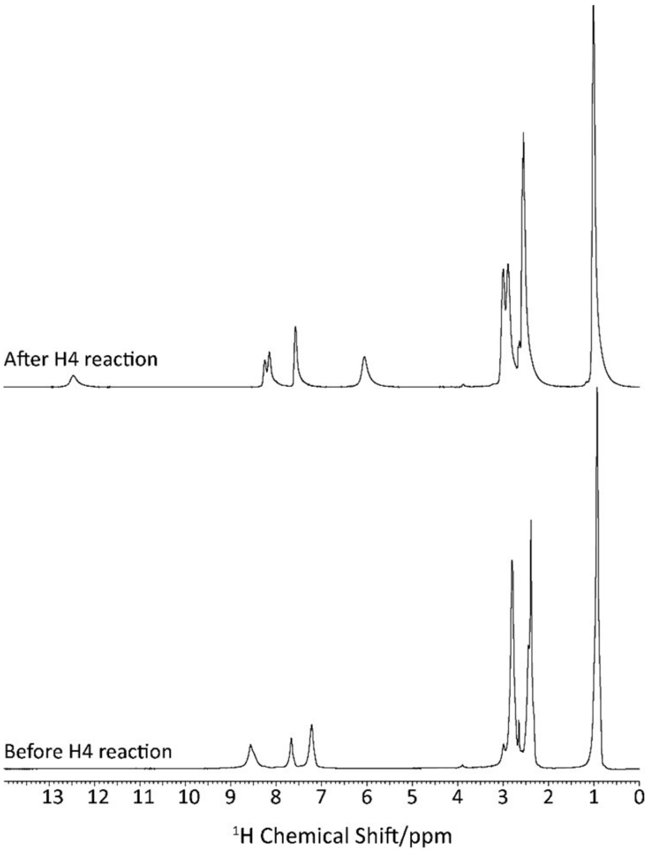

Figure S1 -^{1}H NMR of the HCl trap before (bottom) and after (top) exposure to the atmosphere of the H4 reaction. HCl uptake can be observed by the protonation of DEMA (peak ~6 ppm) and α-picoline (peak ~ 12.5 ppm). The trap can absorb up to 14% of its weight in HCl.

S2. MetOxH1 NMR characterization

The solid-state NMR data were collected using a Bruker 400 MHz AVANCE III spectrometer equipped with a 4 mm double resonance broad-band magic angle spinning probe at 25 °C. ^{29}Si DP-MAS spectra collected on the solid-acid products obtained from reactions that had been treated with lithium amide to remove mobile protons and so protect the sample against need for ^{1}H decoupling measures. Samples were center packed into 4 mm MAS rotors using Teflon plugs above and below the sample to maximize the amount of sample in the active volume of the spectrometer. Data were obtained using a 1.0 μs π/12 pulse corresponding to a B_1 field of 35 kHz, a recycle delay of 10 seconds, 1-8 k scans, a MAS rate of 5 kHz and no ^1H decoupling. Decoupling was not required due to the reaction of lithium amide with a significant portion of the ^1H nuclei of the solid acid material, resulting in a substantially reduced ^1H dipolar network. ^{13}C DP-MAS NMR data were collected for the MetOxH1 material, by center packing the lithium amide quenched material into a 4 mm MAS rotor using plugs of Teflon. The spectra were collected using a 5.0 μs π/2 pulse, 10 second recycle delay, 256 scans, a MAS rate of 10 kHz, and approximately 60 kHz TPPM ^1H decoupling. All solid-state NMR spectra were collected with a MAS rate of 5 kHz, and were externally referenced to TMS in the solid state using adamantane ($^1H\delta$=1.63 ppm, $^{13}C\delta$=38.48 ppm) and tetrakis(trimethylsilyl)silane ($^{29}Si\delta$=-9.69 ppm) for ^1H, ^{13}C and ^{29}Si spectra respectively[1].

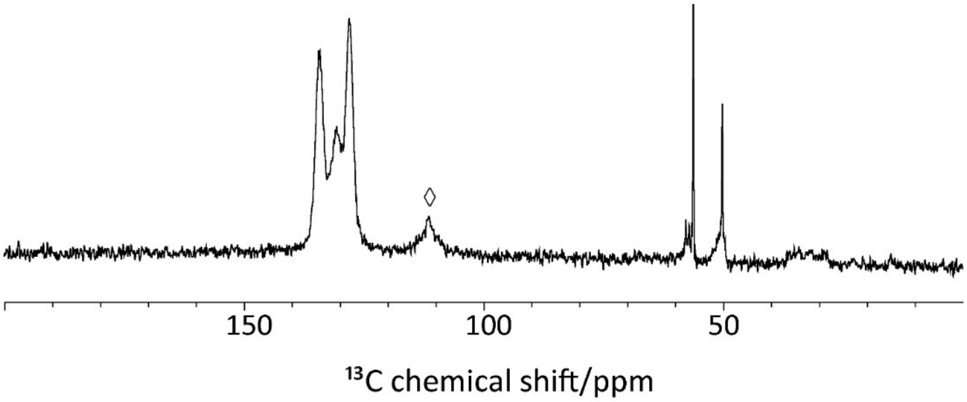

Figure S2 - ^{13}C NMR of MetOxH1 quenched with $LiNH_2$. Two different methoxy sites suggest 2 compounds in a solid mixture – see ^{29}Si NMR for confirmation, Supplementary Figure S3. Methanol was detected in the liquid phase remaining from the reaction, which also confirms methoxy groups are replaced along with phenyl groups. The compounds still have remarkable conductivity. The diamond indicates the peak due to the Teflon plug used in the measurement.

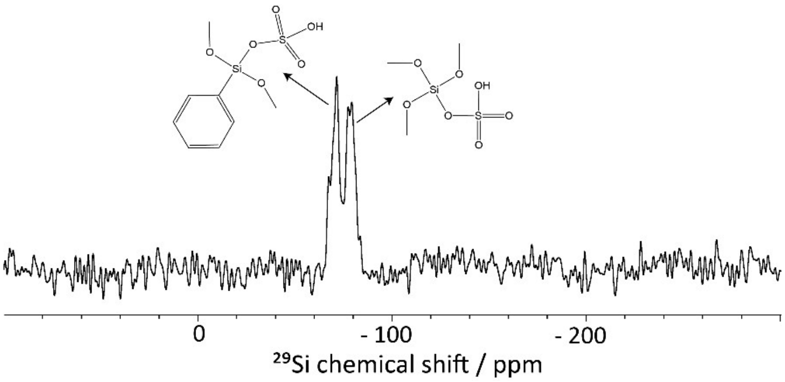

Figure S3 - ^{29}Si NMR of MetOxH1 quenched with $LiNH_2$. The two different peaks indicate a mixture of products: the most upfield (negative) peak is attributed to $Si(CH_3O)_3(HSO_4)$ and the most downfield peak is attributed to $Si(CH_3O)_2Ph(HSO_4)$. See Discussion section on the main text.

S3. Me_3H1 NMR characterization

All the liquids NMR spectra were collected using a Varian MR 400 MHz equipped with a 5 mm broadband observe probe. The samples were externally referenced to TMS in the liquid state. The Me_3H1 ^{13}C spectrum was collected using a relaxation delay of 1 s, 64 scans and a 45° pulse with a duration of 6.88 µs. ^1H decoupling was done using a waveform waltz16. The Me_3H1 ^{29}Si spectrum was collected using a relaxation delay of 30 s, 64 scans and a 45° pulse with a duration of 13 µs. ^1H decoupling was done with a waveform waltz16. Me_3H1. ^1H spectrum was collected a relaxation delay of 1 s, 1 scan and a 45° pulse with a duration of 5.3 µs.

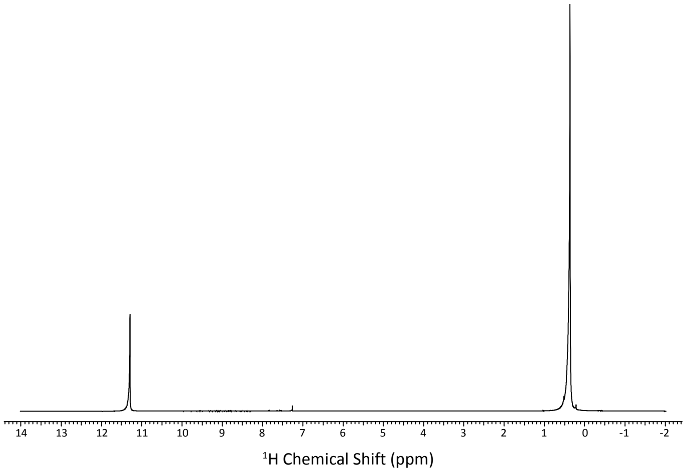

Figure S4 – ^1H NMR spectrum of Me_3H1, neat liquid. The methyl resonances are observed at 0.5 ppm and the acid proton resonance is located at 11.3 ppm. These observations are consistent with the suggested formula of $Si(CH_3)_3HSO_4$.

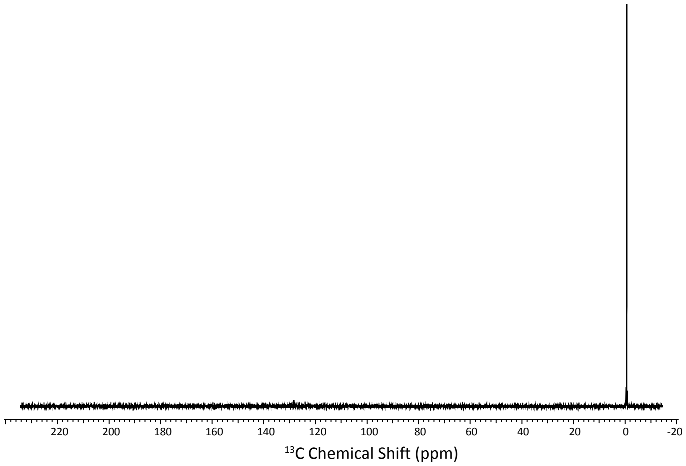

Figure S5 – ^{13}C NMR of the neat liquid Me_3H1. The single peak at 0 ppm is attributed to the CH_3 carbons.

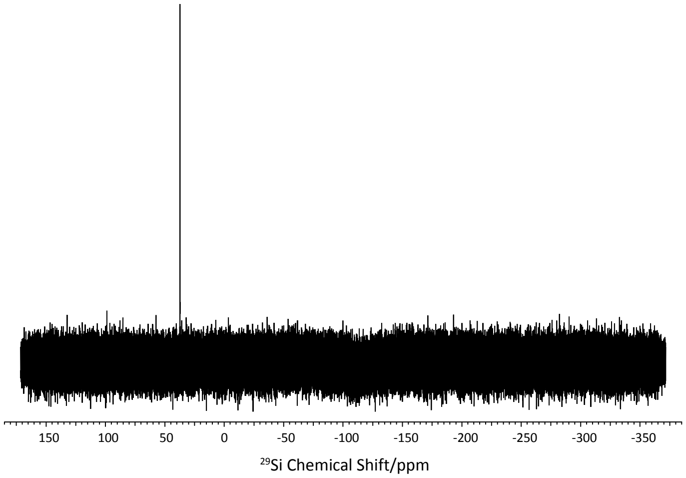

Figure S6 – ^{29}Si NMR of the neat liquid Me_3H1. The single resonance at 48 ppm is attributed here to the single silicon environment in the molecule $Si(CH_3)_3HSO_4$.

S.4 Thermodynamic stabilization of intermediate phases by mixing.

To illustrate the advantages of having a mixed product in the synthesis of phases of interesting properties but probable metastabilities, we reproduce[2] the case of binary nitriles containing succinonitrile, a system much studied for the existence of a plastic crystal phase of very short reorientation time. Succinonitrile in the pure state readily crystallizes on cooling to a non-rotational state which normally excludes it study at lower temperatures in the interesting region approaching the glass transition. However, it is found that addition of second components lower not only the melting point but also the rotator phase transition temperature leading to the phase diagram shown in Figure S7. As Figure S7 shows clearly appropriate mixtures of substances that are in soluble in the crystal lattice of a first component provide an excellent means of permanently stabilizing physical states of phenomenological interest such as rotator phases. This is the reason that the generation of closely related but mutually insoluble rotator phases with interesting protonic properties during a synthetic process such as that for metoxH1, is welcomed.

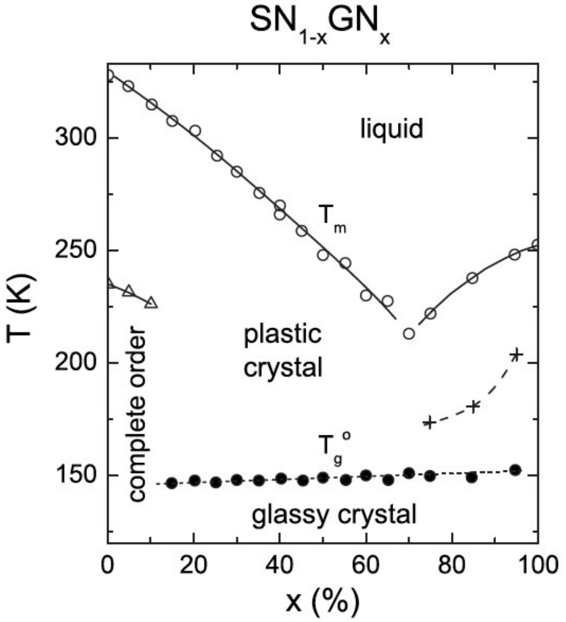

Figure S7 - The phase diagram of succinonitrile (SN) + glutaronitrile (GN) showing depression of transition to ordered crystal state and preservation of rotator phase down to glass transition temperature T_g. Reproduced from supplemental reference[2].

S4. FT-Raman of H4

The FT-Raman spectra were collected from 100 to 3500 cm^{-1} using a FT-IR/FT-Raman Bruker IFS66V/S spectrometer using a YAG laser (1064 nm) and a Ge detector. The spectral resolution is 4 cm^{-1}. The samples were inside glass vials under argon atmosphere during the measurements.

The most intense peak in the Raman spectrum of H4 is ν_sSiO at 419 cm^{-1}. That is the first difference from the spectrum of pure sulfuric acid, with its most intense peak at 914 cm^{-1} attributed to the ν_1 mode[3,4] (ν_sS-O-H). This mode is also present in H4, at the exact same frequency. That suggests that the strength of the hydrogen bonding in H4 is comparable to that of sulfuric acid. That is very different from the case of $CsHSO_4$, where the ν_1 mode is located at considerably lower frequencies (860 cm^{-1} at room temperature), albeit dependent on the crystallographic phase[5,6]. That indicates a decrease in the strength of hydrogen bonding when compared to pure sulfuric acid and H4. The second glaring difference between the two spectra is the transformation of sulfuric acid's split ν_3 (ν_sS=O) peak at 1048 cm^{-1} after the reaction. This mode appears as a single peak in H4, similarly to other bisulfates, like $NaHSO_4$[7] and $CsHSO_4$[5,6].

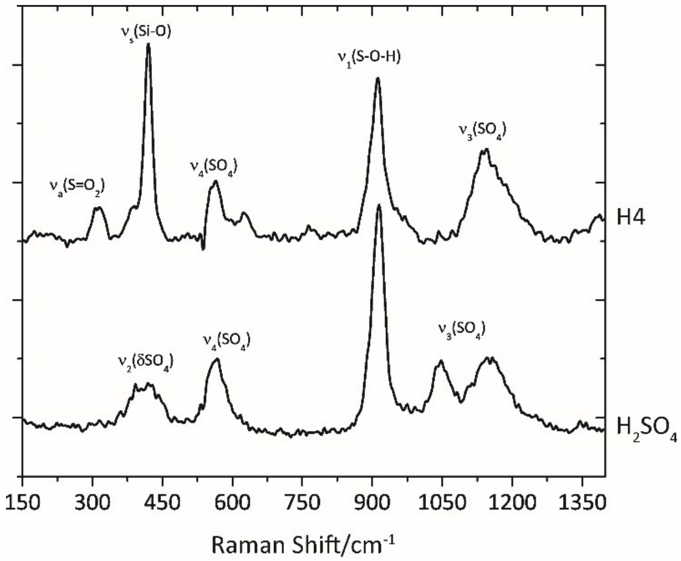

Figure S8 - FT-Raman spectra of H4 (top) and sulfuric acid (bottom). Note how the ν_3 peaks, at 1100 cm^{-1}, are split in sulfuric acid; in the H4 spectrum, the ν_3 mode is a single peak. This is analogous to the cases of other hydrogensulfates, like $NaHSO_4$[7] and $CsHSO_4$[5,6]. Legend: s = symmetric, a = asymmetric; ν = stretch, δ = bend.

S5. Nyquist plots

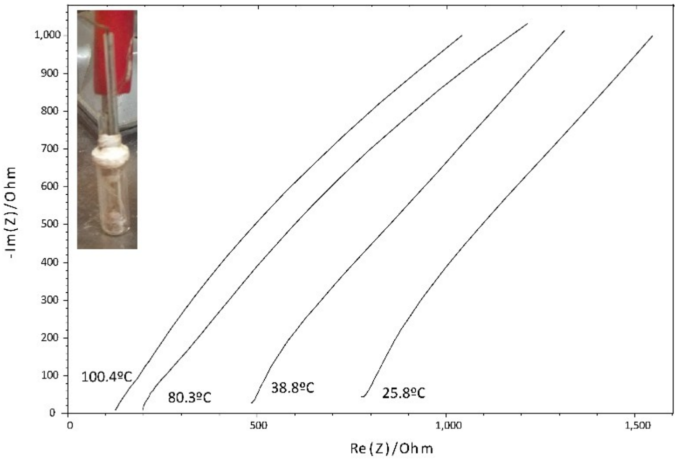

Figure S9 – Nyquist plots of H4 at different temperatures. Insert: in-house made conductivity cell used in this work.

S6. Fuel Cell Measurements

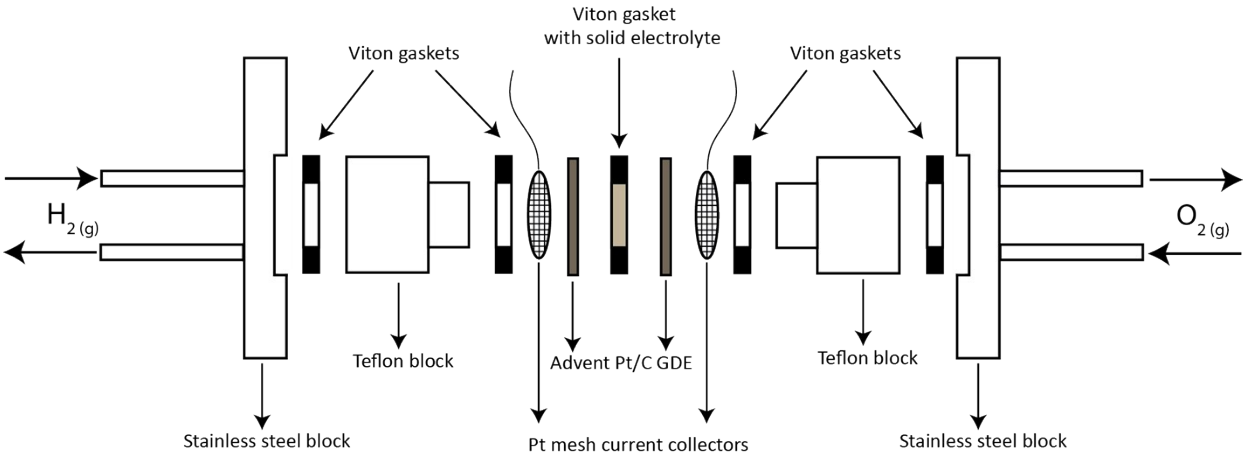

Figure S10 - Exploded view illustration of the fuel cell assembly used in this work. Adapted from reference[8].

S7. Supplementary References

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