ADVANCED MATERIALS

A Novel Water-Free Proton-Conducting Solid Electrolyte based on an Organic/Inorganic Hybrid**

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Proton-conducting polymers have attracted much attention due to their promising application as membranes in fuel cells. The most commonly used polymer has been a perfluorinated ionomer known by its trade name, Nafion. It is well known that, including Nafion, the proton-transport properties of water-swollen perfluorinated ionomers largely depend on their water content, which limits their application to temperatures and pressures below the dew point of water.[1,2] This puts several constraints on the use, as fuels, of hydrogen-rich reformats, which usually contain traces of carbon monoxide or methanol, as they require somewhat higher temperatures. Therefore, it is worthwhile to seek distinctly different proton-conducting materials. One approach is based on the complexation of basic polymers (e.g., polybenzimidazole) with oxo-acids (e.g., phosphoric acid).[3–5] Another approach is the substitution of water by heterocycles, such as imidazole, pyrazole, and benzimidazole.[6–10] They are known to present high-proton conductivity that is comparable to the value of hydrated membranes, especially at high temperatures ranging between 150 and 250 °C. The approach of employing these heterocycles as proton solvents in fuel-cell membranes may require their immobilization to prevent the leakage of heterocycles during fuel-cell operation. The first attempt towards full immobilization of a heterocycle as a proton solvent in completely water-free electrolytes has been recently developed by Schuster et al.[9] They reported that structure diffusion, which consists of intermolecular proton transfer and structural reorganization by a hydrogen-bond breaking and forming process, is the dominant proton-conducting mechanism in the imidazole-terminated ethylene oxide oligomers. However, this material is not yet available for practical applications, mainly because of its liquid-like physical state. Following this model system, in this study, a new water-free proton-conducting solid electrolyte based on an organic/inorganic hybrid is presented. Since a siloxane oligomer functionalized with imidazole-terminated side chains (CImSS)[10] has been reported as a material with a good proton-transport ability as well as a good self-dissociation constant, this moiety is employed as a candidate for a proton transporter, although it shows a viscous liquid characteristic. The CImSS has been synthesized according to a literature procedure[10] (Fig. 1). As a mechanical framework, silicates prepared by a sol–gel synthesis of silane monomers have been chosen. Two silane monomers, such as tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS), were employed after consideration of their different polarities. The polarity difference between the CImSS and the silane monomers could affect the phase separation during the blending accompanied by the sol–gel synthesis.

The morphologies of the CImSS/silicate hybrids were investigated by field-emission scanning electron microscopy (FE-SEM) measurements (Fig. 2). The physical appearance of the CImSS/MTEOS-based silicate hybrid is shown in the inset of Figure 2a, which verifies that the hybrid apparently maintains a solid state. For clear identification, the CImSS in the CImSS/silicate hybrids was solvent-etched using methanol, which preferentially attacks the CImSS as opposed to the harder inorganic silicate, i.e., the silicates are observed exclusively. Depending on the TEOS/MTEOS ratio in the silane mixtures, completely different morphologies are observed. It is clearly shown that while it is hard to differentiate the CImSS in the CImSS/TEOS-based silicate hybrid, the porous structure assigned to the etched CImSS becomes noticeable with increasing the MTEOS content. This morphological change may be related to the phase separation between the CImSS and the sol. A schematic representation of the CImSS/silicate hybrids is presented in Scheme 1. The CImSS observed is very polar, and dissolves in polar solvents such as methanol.[10] Increasing the trifunctional MTEOS content in the silane mixtures significantly lowers the polarity of the precursor sol, because after hydrolysis the MTEOS has less of a chance to yield polar –OH groups than TEOS.[11–15] It may lead to an enlargement of the polarity difference between the CImSS and the MTEOS-based sol. Therefore, the phase separation becomes pronounced and the percolation of CImSS becomes highly developed. This morphological observation is likely to be consistent with other publications. For the ORMOSIL (organically modified silicate)-based hybrids with organic components,[11–17] it has been reported that the nature of the ORMOSIL-based hybrids, in other words, the polarity difference between the ORMOSIL and the organic components, affects the morphology and the specific chemical interactions between the constituents. For example, for ORMOSIL-based optical sensors,[13] film hydrophobicity increased as a function of hydrophobic silane content. It also changed the miscibility of the silicates with the functional organic component. The phase-separated structure and the weak interactions between the constituents were closely correlated to the enhanced oxygen-sensor performance.

The FTIR spectra of the CImSS/silicate hybrids are shown in Figure 3. The characteristic peaks of imidazole have been comprehensively analyzed in the literature.[18] The N–H stretch of imidazole in the CImSS itself causes absorption around

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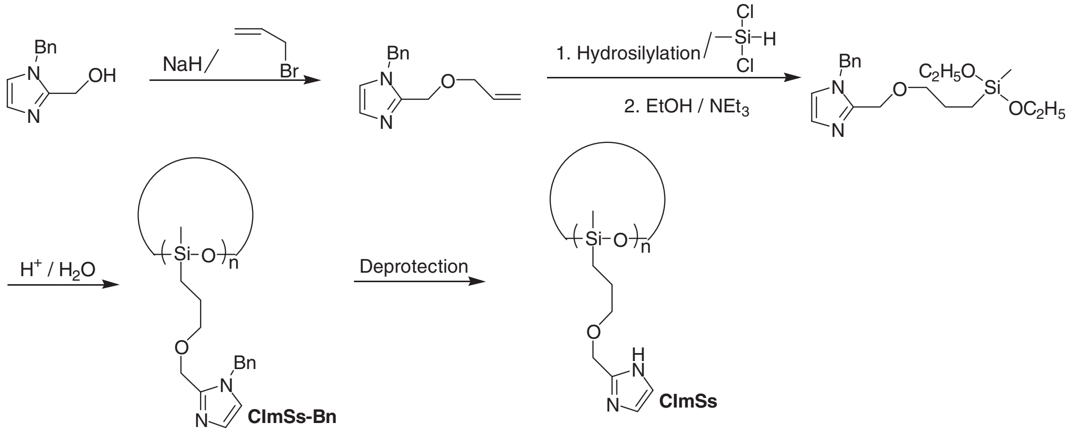


Figure 1. Synthesis and chemical structure of siloxane oligomers functionalized with imidazole-terminated side chains (CImSS).

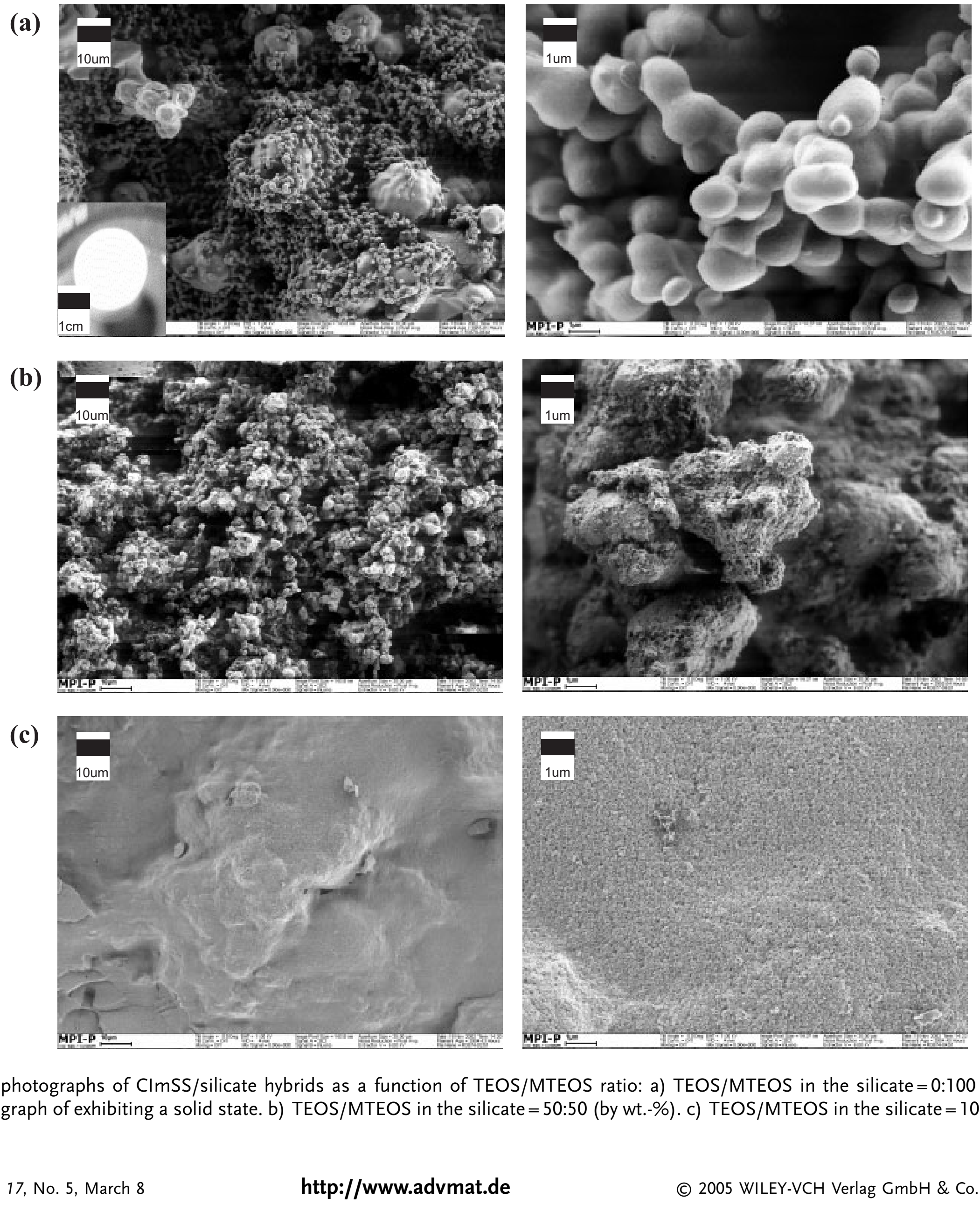
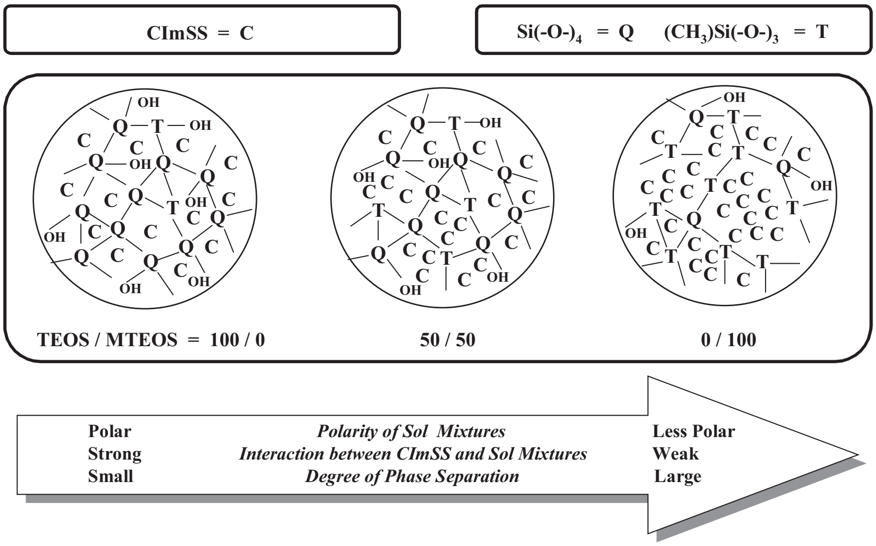


Figure 2. SEM photographs of CImSS/silicate hybrids as a function of TEOS/MTEOS ratio: a) TEOS/MTEOS in the silicate = 0:100 (by wt.-%), the inset is a photograph of exhibiting a solid state. b) TEOS/MTEOS in the silicate = 50:50 (by wt.-%). c) TEOS/MTEOS in the silicate = 100:0 (by wt.-%).



Scheme 1. Schematic representation of CImSS(C)/silicate hybrid structures consisting of condensed Q and T units, where Q indicates Si(–O–)$_4$ and T indicates CH$_3$Si(–O–)$_3$, respectively.

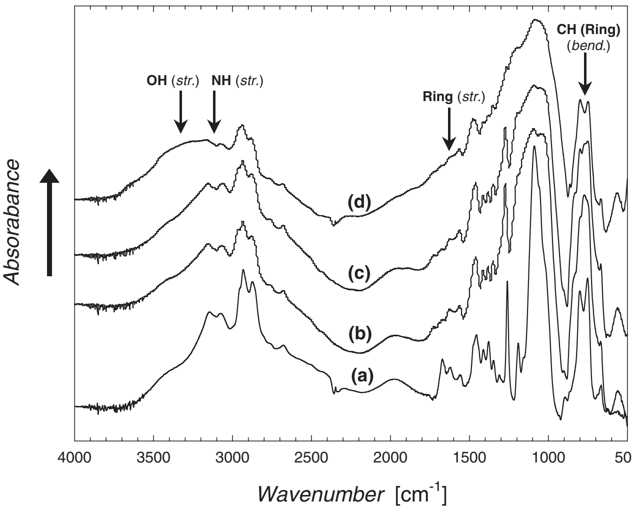


Figure 3. FTIR spectra of CImSS/silicate hybrids as a function of TEOS/MTEOS ratio. a) CImSS, b) TEOS/MTEOS in the silicate = 0/100 (by wt.-%), c) TEOS/MTEOS in the silicate = 50/50 (by wt.-%), and d) TEOS/MTEOS in the silicate = 100/0 (by wt.-%).

3200 cm^{-1}. The heteroaromatic rings yield several medium peaks in the 1650–1570 cm^{-1} range due to ring-stretching vibrations. In addition, the five-membered heteroaromatic rings show a strong absorption at 800–3200 cm^{-1} that is assigned to C–H out-of-plane vibrations of unsaturated bond systems. In the CImSS/silicate hybrids, it is noticeable that as the TEOS content increases, the N–H stretch and the ring vibrations, which are characteristic peaks of imidazole in the CImSS, become broad and ambiguous. This IR result may indicate that strong interactions exist between the CImSS and the silicates. Compared to the MTEOS-based sol with three –OH groups, the TEOS-based sol with four –OH groups is considered to be more polar, which implies that a better compatibility with the polar CImSS could be developed.

The glass-transition temperature (T_g) of CImSS in the CImSS/silicate hybrids was investigated by differential scanning calorimetry (DSC). Figure 4 shows that the T_g of pure CImSS is observed around 10 °C. It is of interest to note that the T_g of CImSS in the CImSS/silicate hybrids tends to increase and become ambiguous with increasing TEOS content in the siliane mixtures. In the FTIR analysis, it had already been observed that there were strong interactions between the CImSS and the TEOS-based silicate. It is likely that as the interactions become stronger, the segmental motion of the CImSS becomes hindered and requires a higher activation energy, which could lead to the increase of T_g.

The temperature-dependent proton conductivity of CImSS/silicate hybrids is presented in Figure 5. The proton conductivity of pure CImSS exhibits a VTF (Vogel–Tamman–Fulcher)-type temperature dependence, and a high conductivity of around 10^{-3} S cm^{-1} at 160 °C. This value is surprisingly high when considering that: i) the charge carriers can only be generated from the self-dissociation of imidazole units, and ii) that the immobilized proton donor/acceptor functions exclude any vehicle-type transport and only permit proton mobility via structure diffusion (Grotthus mechanism), which involves a proton transfer between the imidazoles with a corresponding reorganization of the hydrogen-bond network.[10] The

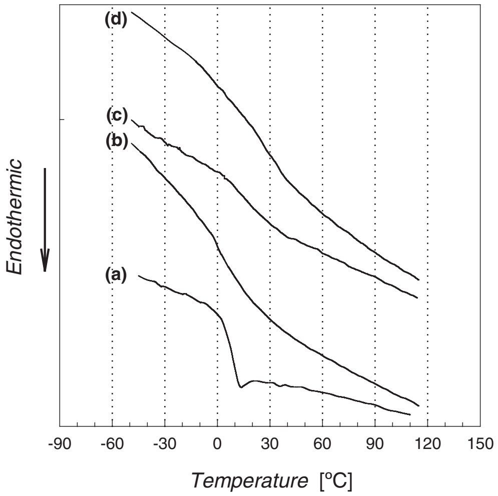


Figure 4. DSC thermograms of CImSS/silicate hybrids as a function of TEOS/MTEOS ratio: a) CImSS, b) TEOS/MTEOS in the silicate = 0:100 (by wt.-%), c) TEOS:MTEOS in the silicate = 50:50 (by wt.-%), and d) TEOS/MTEOS in the silicate = 100:0 (by wt.-%).

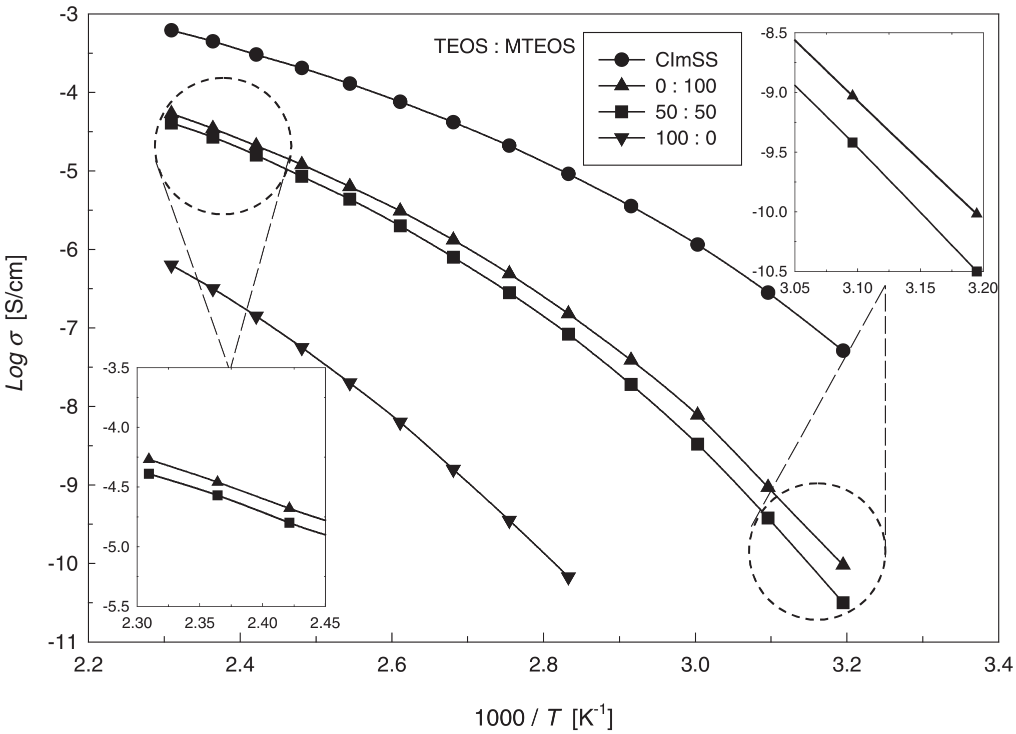


Figure 5. Temperature-dependent proton conductivity of ClmSS/silicate hybrids as a function of TEOS/MTEOS ratio.

VTF-type behavior indicates that the segmental motion of ClmSS may play an important role in the long-range proton transport as an element of dynamical percolation within the hydrogen-bonded domain formed by the terminating imidazoles. The proton-transport mechanism has been discussed in detail in previous publications.[6–10] Compared to the pure ClmSS, slightly low proton conductivities are observed for the ClmSS/silicate hybrids. It is of interest to note that with increasing TEOS content, the proton conductivities of the hybrids have a tendency to decrease. From the morphological differences in Figure 2, it has been observed that percolation of the proton-conducting phase (ClmSS) becomes pronounced with an increase in MTEOS content. The previous IR and DSC results also verify that there are strong interactions between the ClmSS and the TEOS-based silicate. It would suggest that the segmental motion of ClmSS is significantly affected by the TEOS-based silicate and requires high activation energy. The well-developed percolation of the ClmSS and the weak interactions between the ClmSS and the MTEOS-based silicate may allow easier reorganization of the hydrogen-bond network, which contributes to a faster proton transfer between the imidazoles. Comparing the ClmSS/(TEOS/MTEOS = 50/50)-based silicate hybrid with the ClmSS/MTEOS-based silicate hybrid, it is found that the difference between the proton conductivities of the two hybrids becomes larger as the measuring temperature decreases (shown in the insets of Fig. 5). This may be related to the difference of T_g between the hybrids. The previous DSC results have revealed that the ClmSS in the (TEOS/MTEOS = 50:50)-based silicate shows a higher T_g (≈ 20 °C) than the ClmSS (≈ 10 °C) in the MTEOS-based silicate. Schuster et.al[9] reported that the T_g of imidazole-based oligomers could play an important role in long-range proton transport, and its effect on the proton conductivity becomes more noticeable at lower temperatures. Therefore, the change of T_g reflecting the mobility of ClmSS in the hybrids can be considered as good evidence to verify the enlarged difference of proton conductivity between the hybrids at lower temperatures.

The activation volume (ΔV) for proton transport is obtained from the pressure-dependent ion conductance by using Equation 1:

$$\Delta V = -RT\,(\partial \ln\sigma/\partial P)_T = -RT\,(\partial \ln G/\partial P)_T + \beta/3 \qquad (1)$$

where β is the isothermal compressibility, G is the ion conductance at different pressures, and R is the Boltzmann constant. The details for the calculation have been expressed in other publications.[19–23] The ΔV of the ClmSS/silicate hybrids is observed to increase with an increase in the TEOS content in the silicate (Table 1). In particular, the increase of ΔV is noticeable for the ClmSS/TEOS-based silicate hybrid. The ΔV is known to indicate the volume change of material required for ionic motion.[19–23] The higher ΔV of the ClmSS/TEOS-based silicate hybrid explains that the mobility of the ClmSS becomes suppressed and requires a larger volume change for proton transport. This can be evidenced by the poor percolation of ClmSS and its strong interaction with the TEOS-based silicate. Similar to the temperature-dependent proton conduc-

Table 1. Activation volume (ΔV) of CImSS/silicate hybrids at 100 °C as a function of TEOS/MTEOS ratio.

TEOS/MTEOS	$(\partial \ln\sigma/\partial P)_T$ [GPa^{-1}]	ΔV [cm^3 mol^{-1}]
0:100	−10.91	33.07
50:50	−11.08	33.62
100:0	−13.13	39.88

tivity, the ΔV of the CImSS/silicate hybrids is observed to be highly dependent on the microstructure and the specific interactions between the constituents.

New water-free proton-conducting solid electrolytes based on organic (CImSS)/inorganic (silicate) hybrids have been presented. A remarkably high proton conductivity of around 10^{-4} S cm^{-1} at 160 °C is obtained for the CImSS/MTEOS-based silicate hybrid in the absence of water. The proton conductivity and the activation volume (ΔV) of the CImSS/silicate hybrids have been explained by considering the morphological difference and the specific interactions between the constituents. The larger polarity difference between the CImSS and the trifunctional MTEOS causes a pronounced phase separation, which leads to the well-developed percolation of a proton-conducting phase (CImSS). The specific interactions between the CImSS and the silicate are examined by FTIR and DSC measurements. With increasing MTEOS content, the interactions between the CImSS and the silicate are observed to become weaker.

Experimental

Preparation of CImSS/Silicate Hybrids: The details for the synthesis of CImSS have been already described in the literature [10]. The CImSS was dissolved in methanol to give a homogeneous solution of 1.5 wt.-% concentration. Silicates as an inorganic phase were prepared by the sol–gel synthesis of tetraethoxysilane (TEOS, Aldrich, > 99 %) and methyltriethoxysilane (MTEOS, Aldrich, 99 %). For each sol, a total silane mixture/ethanol/water/0.1 M HCl (1:4:4.5:0.01) mixture was stirred for 5 h and then subjected to ultrasonic energy (Digital sonifier model 250 & 450, Branson) for 1 min in a sonication bath to obtain a homogeneous sol, where the ratios of TEOS/MTEOS in the total silane mixtures were 100:0, 50:50, and 0:100 (by wt.-%), respectively. The sol was then added drop by drop to the CImSS solution, where the ratio of CImSS/silanes was fixed at 50:50 (by wt.-%). Immediately following the addition of sol, the mixture was further sonicated for 1 min and was then stirred for 5 days. The mixture was cast onto a Teflon plate. Drying of the sample was carried out slowly in a nitrogen atmosphere for 6 d at room temperature, followed by 4 days at 60 °C, and finally in a vacuum oven for 2 days at 60 °C.

Characterization: FTIR spectra (4000–400 cm^{-1}) were recorded with a Nicolet Magna-IR 850 series II spectrophotometer. The glass-transition temperature (T_g) was examined with a Mettler DSC TA 3000 instrument at a heating rate of 10 K min^{-1}. The morphology of the samples was observed using a FE-SEM (GEMINI, LEO 1530) adopting a low-voltage (< 1 keV) imaging technique that needs no heavy metal coating. The temperature-dependent proton conductivity was measured by using a Schlumberger SI1260 impedance/gain phase analyzer with a homemade dielectric interface in the frequency range from 10^{-1} to 10^6 Hz, and in the temperature regime of 40 to 160 °C. The pressure-dependent proton conductivity was measured at a temperature of 100 °C with an experimental set-up for high-pressure dielectric spectroscopy developed in our laboratory [24]. The DC conductivities were obtained from Cole–Cole plots (Z' vs. Z'') and were identical to the low-frequency plateaus of the AC conductivities [9,10,22,23].

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