

A new water-free proton conducting membrane for high-temperature application

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Abstract

A new water-free proton conducting membrane based on an organic/inorganic hybrid is presented. Siloxane oligomer functionalized with imidazole-terminated side chains (CImSS) is employed as an organic phase and proton transporter. As a mechanical framework, organically modified silicate (ORMORSIL) is prepared by a sol–gel synthesis of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS). Polarity difference between the CImSS and the sol affects the phase separation of the resulting hybrids. Based on the phase separation, morphology of the hybrids and specific interactions between the CImSS and the silicates are investigated and discussed with the temperature- and the pressure-dependent proton conductivity. Under the absence of water, high proton conductivity of around $10^{-4} \text{ S cm}^{-1}$ at 160°C has been obtained for the CImSS/(MTEOS-based silicate) hybrid. This high proton conductivity is believed mainly due to well-developed percolation of the proton-conducting phase (CImSS) and weaker interaction between the CImSS and the MTEOS-based silicate.

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1. Introduction

Proton-conducting polymers have attracted much attention because they are considered promising materials for 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[®], proton transport properties of the water-swollen perfluorinated ionomers largely depend on their water content, which limits their application to the temperature and the pressure below the dew point of water [1,2]. In the water-swollen polymers, proton migrates in the hydrated form such as H_3O^+ , H_5O_2^+ , therefore the loss of transport moieties leads to the significant decrease of the proton conductivity. This puts several constraints on the use of hydrogen-rich reformats usually containing traces of carbon monoxide or methanol as fuels requiring somewhat higher temperatures.

Therefore, it is worthwhile to seek for 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. 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 [6–8]. It has been reported that the heterocycles form similar hydrogen bond networks like water and the transport properties in the liquid state are similar to water [7,8]. The approach of employing these heterocycles as proton solvents in the fuel cell membranes may require their immobilization to prevent the leakage of the heterocycles during the cell operation. Proton mobility of the immobilized heterocycles generally relies on structure diffusion, namely grotthus-type mechanism comprising of proton transfer between the heterocycles and their reorganization [9–13]. The first attempt towards a full immobilization of a heterocycle as a proton solvent in completely water-free electrolytes has been recently developed by Schuster et al. [12] They reported that the structure diffusion consisting of inter-molecular proton transfer and structural reorganization

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by hydrogen bond breaking and forming process is the dominant proton conduction mechanism in the imidazole-terminated ethylene oxide oligomers. However, this model material has not yet been available for practical applications mainly because of its liquid-like physical characteristic. Following this model system, Scharfenberger [13] further developed new water-free proton conducting electrolytes for the practical uses. They have focused on polymer-bound proton solvents and nano-sized particles grafted with imidazole-terminated side chains.

In this study, as a consecutive approach for developing water-free proton conductors, a new solid membrane based on an organic/inorganic hybrid is presented. Since siloxane oligomer functionalized with the imidazole-terminated side chains (CImSS) has been reported as a material with good proton transport ability as well as good self-dissociation constant [13], this moiety is employed as a good candidate for a proton-transporter, though it shows a viscous liquid characteristic [13]. As a mechanical framework, silicates prepared by a sol–gel synthesis of silane monomers are chosen. It has been well known that structures and properties of silicates highly depend on characteristics of silane monomers [14–20]. Organically modified silicates (ORMOSILs) are believed to be promising candidates in the development of new materials for various applications due to their good mechanical and chemical stability and the ease with which they can be prepared and modified. The specific chemical and physical properties of the silicates can be tailored through the proper choice of organic functional groups containing a non-hydrolyzable silicon–carbon bond. In this study, based on the polarity difference, two silane monomers such as tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) are chosen.

It is possibly expected that the polarity difference between the CImSS and the corresponding sol could affect the phase separation during blending accompanied by sol–gel synthesis. Based on the phase separation, morphology of the hybrids and specific interactions between the CImSS and the silicates are investigated. Finally, the temperature- and the pressure-dependent proton conductivity of the hybrids are examined and discussed in terms of the phase separation.

2. Experimental

2.1. Sample Preparation

As an organic phase, siloxane oligomer functionalized with imidazole-terminated side chains (CImSS) is prepared and the chemical structure is presented in Fig. 1. The synthetic details have already been described in the previous work [13]. Before mixing with silane monomers, the CImSS was dissolved in methanol to give homogeneous solution of 1.5 wt.% concentration.

Silicates as an inorganic phase were prepared by sol–gel synthesis of tetraethoxysilane (TEOS, Aldrich, >99%) and methyltriethoxysilane (MTEOS, Aldrich, 99%). For each sol, a 1/4/4.5/0.01 (total silane mixtures/ethanol/water/0.1 M HCl) mixture was stirred for 5 h and then subject 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 (w/w), respectively.

The sol was then added drop by drop to the CImSS solution, where the ratio of CImSS/silanes was fixed at 50/50 (w/w). Immediately following the addition of the sol, the mixture was further sonicated for 1 min and then was stirred for 5 days. The mixture was casted onto a teflon plate. Drying of the sample was carried out slowly in a nitrogen atmosphere for 6 days at room temperature and for 4 days at 60 °C and finally in the vacuum oven for 2 days at 60 °C. Before mixing, the CImSS and the silane mixtures look viscous wax and transparent liquid, respectively. After blending accompanied by the sol–gel synthesis, the liquid mixtures turned into solid hybrids consisting of the CImSS and the silicates (Fig. 2).

2.2. Characterization

Morphology of the samples was observed from a field emission electron microscopy (FE-SEM, GEMINI, LEO 1530) adopting low voltage (<1 keV) imaging technique that needs no heavy metal coating. For clear identification, before the

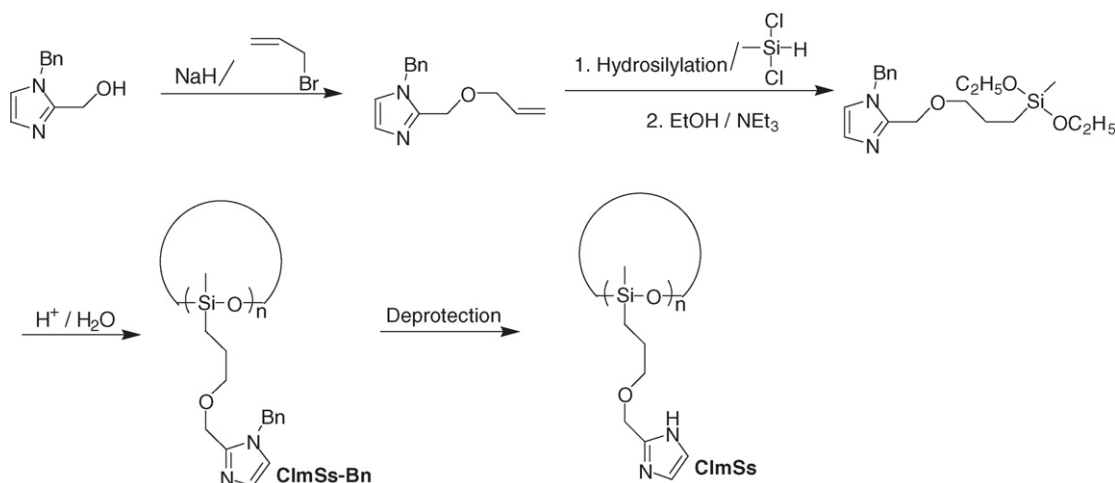


Fig. 1. Structure of siloxane oligomers functionalized with imidazole-terminated side chains (CImSS).

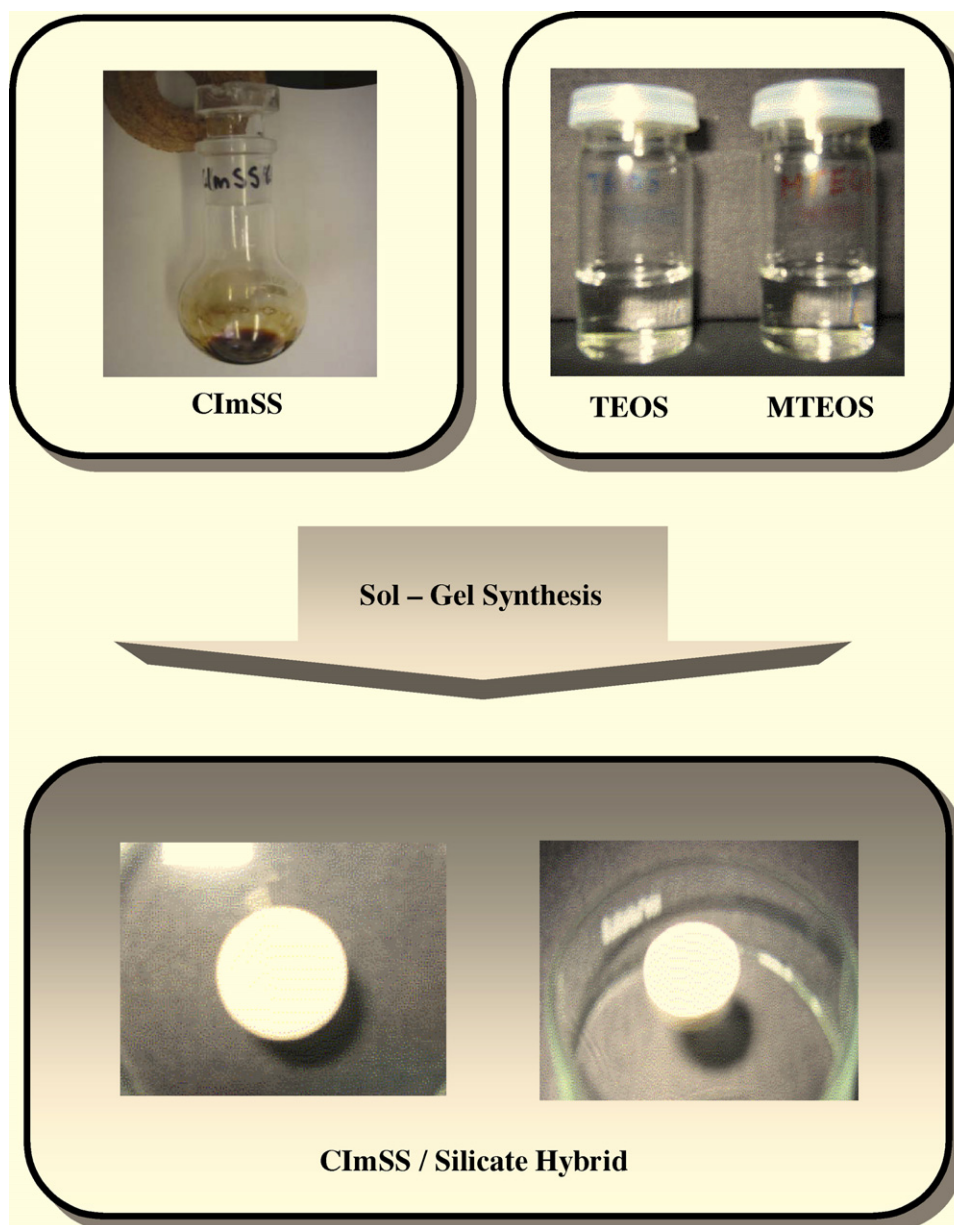


Fig. 2. Micrographs of CImSS-based hybrids at each sample preparation stage: (a) before sol–gel synthesis and (b) after sol–gel synthesis.

measurement, the organic component, i.e., the CImSS was selectively removed by solvent (methanol) etching. Specimen for a proton conductivity measurement was prepared by pressing the dried samples to make a disk shape and the disk was sandwiched between two stainless steel electrodes. FT-IR spectra ($4000\text{--}400\text{ cm}^{-1}$, resolution cm^{-1}) of the samples were recorded with a Nicolet Magna-IR 850 series II spectrophotometer. Temperature-dependent conductivity was measured 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 from 40 to 160°C . The measurement was performed in a Novocontrol cryostat (Novocontrol, Hundsangen, Germany) in which the sample was controlled with a nitrogen gas and measured with a platinum resistor (Pt 100) inserted in one of the electrodes. Pressure-dependent

proton conductivity was measured at a temperature of 100°C with an experimental setup for high-pressure dielectric spectroscopy developed in our laboratory [21]. The sample holder was embedded in silicone oil as a pressure-transducing medium. DC conductivities were obtained from Cole–Cole plots (Z'' versus Z') and were identical with the low-frequency plateaus of the AC conductivities [12,13,26,27].

3. Results and discussion

3.1. Morphological observation

Morphologies of the CImSS/silicate hybrids are investigated with the FE-SEM measurement. For clear identification, the CImSS in the CImSS/silicate hybrids was solvent-etched using

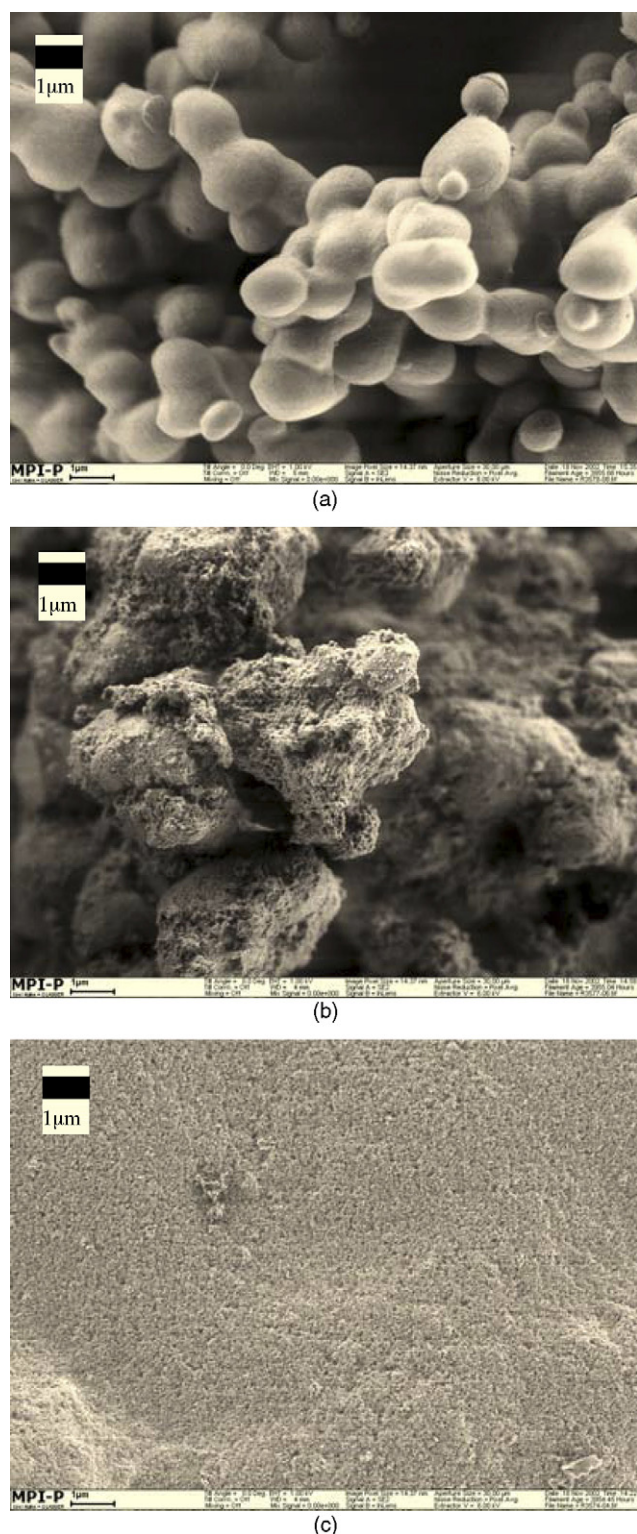


Fig. 3. Scanning electron micrographs (SEM) for CImSS/silicate = 50/50 hybrids as a function of TEOS/MTEOS ratio. TEOS/MTEOS in the silicate: (a) 0/100 (w/w), (b) 50/50 (w/w), and (c) 100/0 (w/w).

a methanol, which could make it possible that the inorganic phase, i.e. silicates are exclusively observed. Depending on the TEOS/MTEOS ratio in the silane mixtures, completely different morphologies are observed (Fig. 3). It is clearly shown that

while it is hard to differentiate the CImSS in the CImSS/(TEOS-based silicate) hybrid, porous structure assigned to the etched CImSS becomes noticeable with increasing the MTEOS content in the silane mixtures, which leads to well-developed connection of the CImSS. This morphological change may be related to the phase separation between the CImSS and the sol during the blending accompanied by the sol–gel synthesis. The CImSS was found very polar and even dissolved in polar solvents such as methanol [13]. Increasing the trifunctional MTEOS content in the silane mixtures significantly lowers the polarity of the precursor sol, because after the hydrolysis the MTEOS has a less chance to yield polar –OH groups than the TEOS [14–18]. It may lead to increase of the polarity difference between the CImSS and the MTEOS-based sol. Therefore, the phase separation becomes pronounced and finally the percolation of the CImSS can be highly developed.

This morphological observation is likely to be quite consistent with the other publications. In the ORMOSILs-based hybrids mainly comprising of ORMOSILs and organic components [14–20], it has been reported that the nature of the ORMOSILs, in other words, the polarity difference between the ORMOSILs and the organic components affects the morphology and the specific chemical interaction between the constituents. For example, in the ORMOSILs-based optical sensors [16], film hydrophobicity increased as a function of hydrophobic silane content. And it affected the miscibility of silicates with the functional organic component. The phase-separated structure and the weak interaction between the constituents were closely correlated with the enhanced oxygen sensor performance.

Further closer investigation on the interaction between the CImSS and the silicate will be discussed in the following FT-IR and TGA measurements.

3.2. FT-IR analysis

FT-IR spectra of the CImSS/silicate hybrids are compared in Fig. 4. The characteristic peaks of the imidazole were comprehensively analyzed in the previous work [22]. The N–H stretch of the imidazole in the CImSS itself causes absorption around 3200 cm^{-1} . The heteroaromatic rings yield several medium peaks in the $1650\text{--}1570\text{ cm}^{-1}$ range due to ring stretching vibrations. In addition, the five-membered heteroaromatic rings show a strong absorption at $800\text{--}3200\text{ cm}^{-1}$ that is assigned to C–H out of plane vibrations at 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 the imidazole in the CImSS become broad and ambiguous. The IR results may indicate that there exists a strong interaction between the CImSS and the silicates. And the interaction seems to highly depend on the nature of the silanes, i.e., the polarity of the precursor sol. Compared to the MTEOS-based sol with three –OH groups, the TEOS-based sol has four –OH groups and is considered to be more polar. It possibly shows better compatibility with the polar CImSS during the blending accompanied by the sol–gel synthesis, which could lead to a homogeneous structure (Fig. 3). It is likely that the FT-IR result verifying the strong interaction between the CImSS and

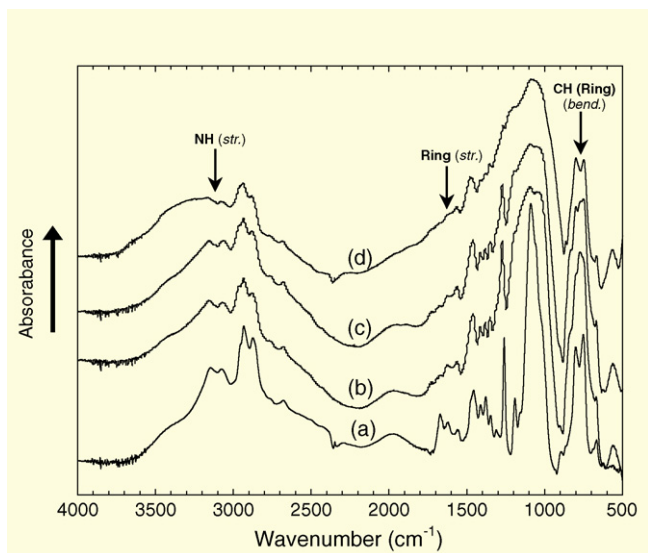


Fig. 4. FT-IR spectra for CImSS/silicate = 50/50 hybrids as a function of TEOS/MTEOS ratio. (a) CImSS; TEOS/MTEOS in the silicate: (b) 0/100 (w/w), (c) 50/50 (w/w), and (d) 100/0 (w/w).

the TEOS-based sol is quite consistent with the homogeneous morphology.

3.3. Thermal analysis

Thermogravimetric analysis (TGA) exhibits that all the CImSS/silicate hybrids are thermally stable up to about 150 °C (Fig. 5). Further increase of the temperature leads to thermal decomposition of the CImSS in the CImSS/silicate hybrids. With increasing the TEOS content in the silicate, the thermal stability of the CImSS/silicate hybrids is improved, which would be due

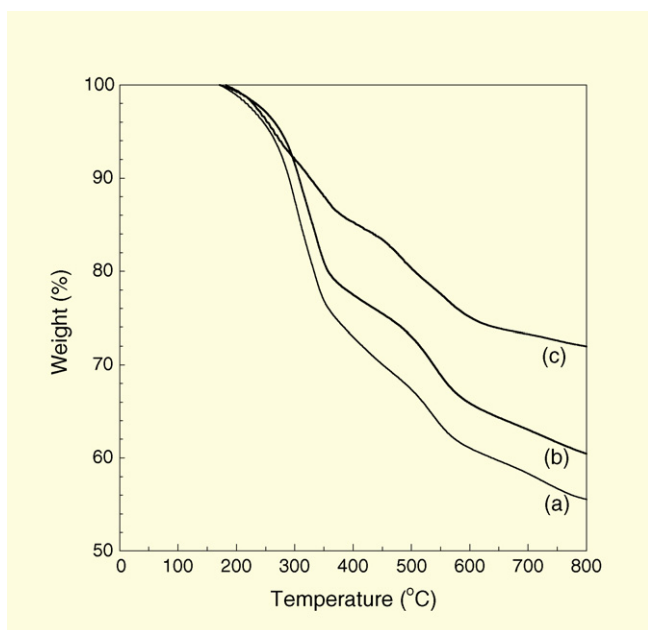


Fig. 5. TGA traces of CImSS/silicate = 50/50 hybrids recorded under N₂ atmosphere with a heating rate of 10 K/min. TEOS/MTEOS in the silicate: (a) 0/100 (w/w), (b) 50/50 (w/w), and (c) 100/0 (w/w).

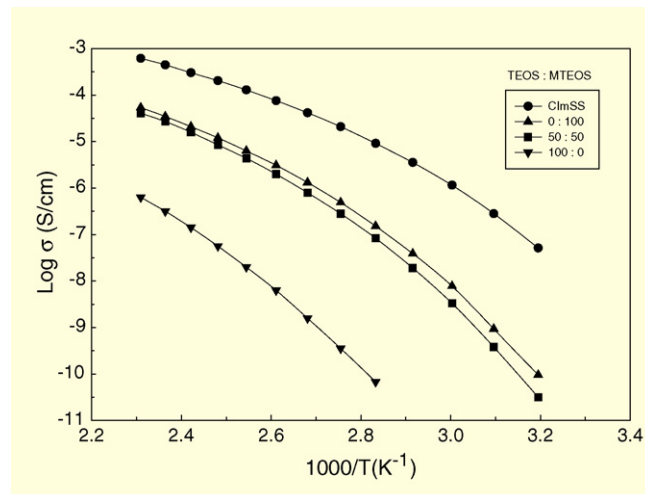


Fig. 6. Temperature-dependent ionic conductivity for CImSS/silicate hybrids as a function of TEOS/MTEOS ratio.

to the stronger interaction between the CImSS and the TEOS-based silicate. It is believed that the stronger interaction may contribute to significant resistance to the thermal decomposition of the CImSS in the CImSS/silicate hybrids.

3.4. Ionic conductivity

Temperature-dependent proton conductivity of the CImSS/silicate hybrids is presented in Fig. 6. The proton conductivity of the pure CImSS exhibits a Vogel–Tamman–Fulcher (VTF)-type temperature dependence and exhibits the highest conductivity of around 10^{-3} S cm⁻¹ at 160 °C. This value is surprisingly high when considering the fact that the charge carriers can be generated only from the self-dissociation of the imidazole units and the immobilized proton donor and acceptor functions exclude any vehicle-type transport and only permit proton mobility via structure diffusion (grotthus mechanism) involving proton transfer between the imidazoles with a corresponding reorganization of the hydrogen bond network. The VTF-type behavior indicates that the segmental motion 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 detailed proton transport mechanism was discussed in the previous works [8,12,13].

Compared to the pure CImSS, relatively lower proton conductivities are observed for the CImSS/silicate hybrids. It verifies that while the CImSS acts as a proton transporter in the hybrids, the silicate has a function to only maintain a mechanical stability without contributing to a proton transport. It is of interest to note that with increasing the TEOS content in the silicates, the proton conductivities of the hybrids have a tendency to decrease. Clear morphological differences between the hybrids are observed in Fig. 3, where while the CImSS/(TEOS-based silicate) hybrid shows a homogeneous structure, the CImSS/((TEOS/MTEOS = 50/50)-based silicate) hybrid and the CImSS/(MTEOS-based silicate) hybrid exhibit highly phase-separated structures. This reflects that with increasing the MTEOS content in the silane mixtures, the percolation of

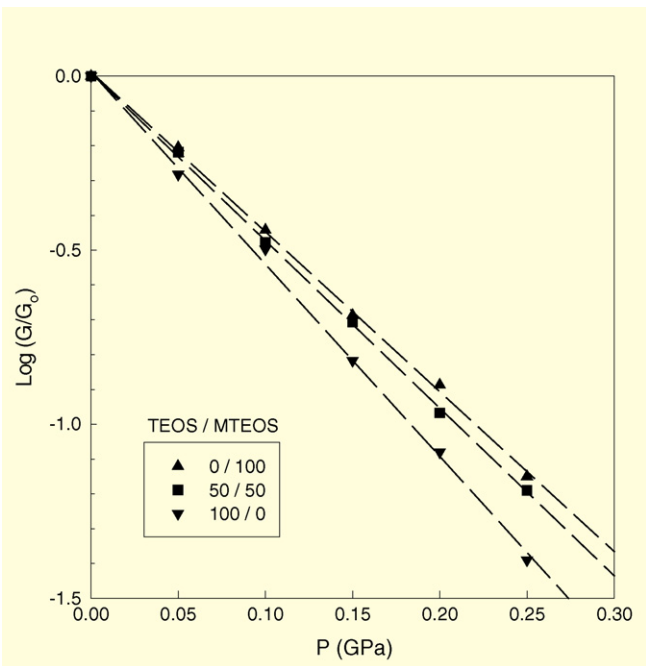


Fig. 7. Pressure-dependence of relative conductance for CImSS/silicate hybrids at 100 °C as a function of TEOS/MTEOS ratio.

the proton-conducting phase (CImSS) is likely to be well developed. It may also suggest that the CImSS in the phase-separated structures is less affected by the silicates and presents similar behavior like the pure CImSS itself. The previous IR and TGA results also verify that there is a strong interaction between the CImSS and the TEOS-based silicate. It would suggest that the segmental motion of the CImSS is largely affected by the TEOS-based silicate and requires high activation energy. Compared to the CImSS/(TEOS-based silicate) hybrid, the well-developed percolation of the CImSS and the weak interaction between the CImSS and the MTEOS-based silicate may allow easier reorganization of the hydrogen bond network, which results in faster proton transfer between the imidazoles.

Pressure-dependence of the relative conductance G/G_0 (G is the conductance at different pressures, while G_0 is the conductance at ambient pressure) for the CImSS/silicate hybrids at a temperature of 100 °C is compared in Fig. 7. For all samples, the relative conductance decreases approximately linearly with increasing pressure from 0 to 0.29 GPa, which seems quite consistent with other published results [23–25]. It is of interest to note that the slope of the relative conductance becomes steeper as the TEOS content in the silicate increases. It will be further explained by considering the activation volume (ΔV) that can be obtained from the above pressure-dependence of the relative conductance.

The slope of the conductance versus pressure at a constant temperature can be converted to the pressure variation of the ionic conductivity using Eq. (1)

$$\left(\frac{\partial \ln \sigma}{\partial P}\right)_T = \left(\frac{\partial \ln G}{\partial P}\right)_T + \frac{\beta}{3}, \quad (1)$$

Table 1

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

TEOS/MTEOS	$\{(\partial \ln G / \partial P)_T\}$ (G Pa ⁻¹)	ΔV (cm ³ mol ⁻¹)
0/100	-10.91	33.07
50/50	-11.08	33.62
100/0	-13.13	39.88

where β is the isothermal compressibility. Since the correction term ($=\beta/3$) is not often known, but is only a small fraction of the total, an approximation can be used [23–27]. The compressibility for most liquids is in the order of 0.8–1.2 GPa⁻¹. Consequently, an approximation correction of $\beta/3 \cong 0.3$ GPa⁻¹ could be applied. The linear variation of the ionic conductivity is used to calculate the ΔV from Eq. (2), with R the Boltzmann constant.

$$\Delta V = -RT \left(\frac{\partial \ln \sigma}{\partial P}\right)_T = -RT \left\{ \left(\frac{\partial \ln G}{\partial P}\right)_T + \frac{\beta}{3} \right\} \quad (2)$$

The ΔV as defined above is not strictly correct for all materials. However, most of the pressure-dependent data in the literature [23–27] are discussed in terms of the ΔV calculated using Eq. (2).

The ΔV of the CImSS/silicate hybrids are calculated with Eq. (2) and summarized in Table 1. It is observed that the ΔV has a tendency to increase with increasing the TEOS content in the silicate. Especially, the increase of ΔV is noticeable for the CImSS/(TEOS-based silicate) hybrid. The ΔV is known to indicate the volume change of the material required for ionic motion [23–27]. The higher ΔV for the CImSS/(TEOS-based silicate) hybrid explains that the mobility of the CImSS becomes suppressed and requires larger volume change for the proton transport. This can be evidenced by poor percolation of the CImSS and its strong interaction with the TEOS-based silicate. Similar to the temperature-dependent proton conductivity, the ΔV for the CImSS/silicate hybrids is observed to highly depend on the microstructure (especially, degree of percolation of the proton-conducting phase (CImSS)) and the specific interaction between the constituents.

4. Conclusions

The new water-free proton conducting membrane based on the organic (CImSS)/inorganic (silicate) hybrid is developed. The phase separation in the various CImSS/silicate hybrids is discussed in terms of the polarity difference between the constituents. It is observed that increasing the trifunctional MTEOS content in the precursor sol significantly lowers polarity of the sol mixtures, which may lead to the larger polarity difference between the CImSS and the sol mixtures. As a result of these phenomena, the phase separation becomes pronounced, which creates the well-developed percolation of the proton-conducting phase (CImSS). The specific interaction between the CImSS and the silicate is examined by FT-IR and TGA measurements. It is suggested that with increasing the TEOS content in the silane

mixtures, the interaction between the CImSS and the silicate becomes stronger.

Compared to the pure CImSS, the CImSS/silicate hybrids show relatively lower proton conductivity. It indicates that in the hybrids, the silicate does not contribute to the proton transport and just presents the mechanical stability, while the CImSS still acts as a proton transporter. High proton conductivity of around $10^{-4} \text{ S cm}^{-1}$ at 160°C is obtained for the CImSS/(MTEOS-based silicate) hybrid under the absence of water. The difference of the proton conductivity in the CImSS/silicate hybrids is explained by the morphological difference and the specific interactions between the constituents. The larger activation volume (ΔV) is observed in the CImSS/(TEOS-based silicate) hybrid. It may explain that the mobility of the CImSS becomes suppressed due to the poor percolation of the CImSS and its strong interaction with the TEOS-based silicate, which would require the larger volume change for the proton transport. It is likely that both the ΔV and the temperature-dependent proton conductivity for the CImSS/silicate hybrids highly depend on the microstructure and the specific interaction between the constituents.

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