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Structure of and Interactions between P/SiWA Keggin Nanocrystals Dispersed in an Organically Modified Electrolyte Membrane

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Hybrid organic−inorganic proton conducting gels (PWA/ICS−PPG or SiWA/ICS−PPG) were made from 3-isocyanatopropyltriethoxysilane and poly(propylene glycol)bis(2-aminopropyl ether), resulting in a hybrid silicon precursor (ICS−PPG) in which was dispersed phosphotungstic acid (PWA) or silicotungstic acid (SiWA) in ethanol. In this system, heteropoly acid takes on the additional role of catalyst, initiating the hydrolysis/condensation reactions of the sol−gel composite. The existence of amidonium ions [C(OH)═NH$^+$] was established from the IR and Raman spectra of PWA/ and SiWA/ICS−PPG composites below and close to the crystallization limits (70−75%). The crystallization of the Keggin ions inside the ICS−PPG host was determined from the XRD spectra of the composites and confirmed also using vibrational spectroscopy, which shows the appearance of H_3O^+ modes at 1700−1710 cm^{-1}. The amidonium ions help in the immobilization of the negatively charged Keggin ions in the membranes, ensuring their uniform distribution in the sol−gel host. The proton conductivity of the composites, measured using impedance spectroscopy, increases with increasing concentration of the heteropoly acid from 10^{-6} S/cm (<10 wt % PWA or SiWA) to 10^{-3} S/cm for >70 wt % of PWA or SiWA in the ICS−PPG.

Introducion

The sol−gel process, with its variety of end applications, has become a tool for chemists to make new materials with desirable properties. Its main advantages are its simplicity; homogeneity of synthesized products, resulting from the intimate mixing of various components on a molecular level; and low processing temperature, enabling the preparation of multicomponent and hybrid organic−inorganic materials. The progress in sol−gel chemistry of organic−inorganic hybrids is reviewed elsewhere.[1−7] The development of organically modified electrolytes (so-called ormolytes),[8−10] as a fast-growing branch of sol−gel hybrid materials, is oriented toward their application in electrochromic devices,[11,12] fuel cells,[13] and solid-state lithium batteries.[14] Proton conducting membranes represent an important part of ionic conductors, especially as candidates to replace Nafion-like materials in H_2 (methanol) fuel cells.[15−17]

The hybrid sol−gel matrix for ionically conducting purposes, in which the organic and inorganic parts are linked by chemical bonds, can be constructed by using reactive silicon alkoxide 3-isocyanatopropyltriethoxysilane. Phosphotungstic acid $H_3PW_{12}O_{40}\cdot nH_2O$ (PWA), having iono-optic properties, is a good candidate for being incorporated into sol−gel matrixes. It belongs to a large group of polyoxometalates[18] and has a high protonic conductivity at room temperature,[19] 0.02−0.1 S/cm; electrochromic and photochromic properties; a relatively small size (∼10 Å); and a high solubility in water and in many organic solvents.

The focus of our study is to stabilize this compound by incorporating it into a modified silica sol−gel matrix and, in doing so, to preserve its multifunctional properties. In our previous work, PWA was incorporated in titanium oxide gel, producing a novel low-temperature chromogenic material.[20]

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The proton conductivity of silica gels containing heteropoly acids was studied by Tatsumisago et al.,[21,22] Mioč et al.,[23] and Staiti et al.[24] for application as solid electrolytes in the fields of optical switching devices[21] and fuel cells.[24] The conductivity of PWA/SiO_2 gel films using tetraethoxysilane as a network-former was found to be very high ($10^{-2}-10^{-1}$ S/cm) at room temperature,[22,25] which is comparable to the conductivity of pure PWA.[19] The doping limit of PWA in silica gel films is 47 wt %. Above this limit, the gel films are opaque and inhomogeneous.

Recently, it was suggested that PWA, as an aqueous solution, could represent an efficient electrolyte for low-temperature fuel cells,[26] although the risk of its continuous leakage during cell operation is high. To overcome the stability problems and to increase the lifetime of the cell, phosphotungstic acid and silicotungstic acid (SiWA) immobilized in silica gel were prepared, and their proton conductivities studied.[24] It was found that up to 30 wt % of the PWA and up to 45 wt % of the SiWA can be entrapped within the gel's structure.[24] The proton conductivity of the solid materials at room temperature is $10^{-3}-10^{-4}$ S/cm, depending on the heteropoly acid loading and relative humidity. The interactions between the Keggin units of PWA or SiWA with the silica network, studied by IR spectroscopy, were stronger for SiWA than for PWA. Solid-state advanced electrochemical studies of PWA and SiWA encapsulated in sol−gel silica were performed by Cox and co-workers,[27,28] Judeinstein and Schmidt,[29] Mioč[30] et al., and Alberti[25] et al.

The aim of this work is to show that an organic−inorganic gel matrix derived from ICS−PPG hybrid precursor, i.e., ethoxy silane functionalized by polypropylene glycol, is a suitable host for the incorporation and immobilization of high amounts of heteropoly acid. The isocyanate group reacts with either the amino groups of poly(propylene glycol)bis(2-aminopropyl ether)[9] or with the hydroxyl group of the poly(ethylene glycol) methyl ether,[10,14] resulting in a hybrid silicon precursor on which sol−gel reactions are performed to obtain an organically modified silica network. The polymer units are bonded to the inorganic part via urea[9] or urethane linkages.[10,14] IR spectroscopic measurements were used extensively to reveal the preservation, entrapment, aggregation, and the interactions of PWA with the sol−gel-derived network. The proton conductivities of the gel samples were measured by impedance spectroscopy. X-ray diffraction analyses were performed to determine the influence of PWA incorporation on the amorphous character of the silica host. The results of our work are compared with some results of PWA/SiO_2 gels made by others[22−24,29] using different silicon precursors for the sol−gel synthesis.

Experimental Section

Preparation of Proton-Conducting Gel Samples. The unhydrolyzed hybrid silicon precursor ICS−PPG was prepared according to the following procedure:[9] Poly(propylene glycol)-bis(2-aminopropyl ether) (20 g, $M_r \approx 4000$; Aldrich) and 2.5 g of 3-isocyanatopropyltriethoxysilane (ABCR) were mixed with 20 g of tetrahydrofuran (THF) under reflux (64 °C) for 6 h. After evaporation of the THF under vacuum, a viscous ICS−PPG precursor was obtained, which is stable at room temperature for several months. For further sol−gel synthesis of a protonic conductor, a portion of the ICS−PPG, depending on the desired weight concentration of PWA or SiWA in the gel, was used. The weight concentration is expressed as wt % PWA $= m_{\mathrm{PWA(anhydrous)}}/(m_{\mathrm{PWA}} + m_{\mathrm{ICS-PPG}})$. For example, to prepare a gel electrolyte containing 75 wt % of PWA, 6.3 g of PWA containing 11% of crystalline water (Aldrich) in ethanol (3 mL) was mixed with 1 g of ICS−PPG. The SiWA (Aldrich) used in our experiments contained 13% of crystalline water. A homogeneous mixture was obtained after a few minutes of vigorous stirring. The PWA(SiWA):ICS−PPG ratio strongly influences the time of gelation (from a few minutes to hours).

Instrumental and Measuring Techniques. *X-ray diffraction (XRD)* measurements of PWA/ICS−PPG membranes, obtained by aging the gel samples in a Teflon dish, were made using a Philips PW1710 automated X-ray diffractometer. Thermogravimetric (TG) measurements for determining the water content in PWA and SiWA were done on a TG951 Module TA2000 instrument from TA Instrument Inc., Castle Point, DE.

FT-IR spectra were measured using an FT-IR Perkin-Elmer 2000 system spectrometer (the spectral range used was 4000−400 cm^{-1}). The spectra of the PWA/ICS−PPG composites were recorded after the sols had been deposited directly on CdTe supporting plates and left on the plates to dry. The FT-Raman spectra of the membranes were measured on a Perkin-Elmer 2000 Raman spectrometer. The resolution of all of the measured spectra was 4 cm^{-1}.

Impedance measurements were made using a 1286 Solartron electrochemical interface and a 1250 Solartron frequency response analyzer. Impedance spectra were recorded between 65000 and 0.001 Hz. For the gels, two parallel F:SnO_2-covered glass plates served as electrodes. To achieve a good contact, the electrodes were immersed in the sol prior to gelation. The distance between the electrodes was 0.3 cm, and their surface area was approximately 1 cm^2 (the exact value was determined individually for each sample).

Results and Discussion

Thermal Stability. PWA and SiWA lose crystalline water up to 250 °C in two steps (Figure 1A and B). Around 100 °C, the number of H_2O molecules decreases from the initial 19 (PWA) or 24 (SiWA) to 6. Hexahydrates remain stable up to 170 °C[30] (Figure 1). Above this temperature, the number of water molecules is further decreased until an anhydrous phase is formed at 250 °C ($H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$). Above 400 °C, the Keggin structure is destroyed and results in the formation of WO_3, agreeing with the measurements obtained by Mioč[30] et al. and Klisch.[31] Previous experiments made with peroxopolytungstic acid (W−PTA)

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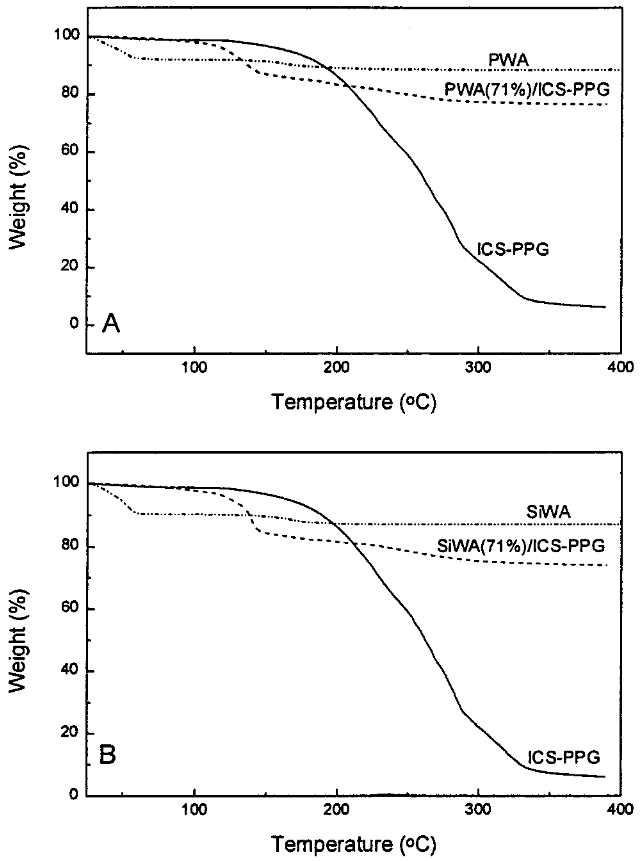

Figure 1. TG curves of (A) PWA, PWA (71 wt %)/ICS−PPG; (B) SiWA, SiWA (71 wt %)/ICS−PPG; and (A, B) ICS−PPG in different temperature ranges.

incorporated in ICS−PPG[32] show that the thermal stability of this composite is improved with respect to that of the pure W−PTA on account of the better thermal stability of ICS−PPG below 80 °C. PWA/ICS−PPG and SiWA/ICS−PPG behave similarly (Figure 1A and B), revealing only 2% weight loss between room temperature and 100 °C, contrasting with the 10% weight loss for pure PWA and SiWA over the same range.

Matrix Cross-Polymerization and Gelation. To obtain more structural information, IR spectra of PWA/ICS−PPG and SiWA/ICS−PPG composites were measured and analyzed. The IR spectrum of 3-isocyanatopropyltriethoxysilane exhibits a strong band centered at 2250 cm^{-1} that is attributed to the stretching mode of N=C=O groups.[32,33] After reaction with poly(propylene glycol)bis(2-aminopropyl ether), this band disappears in the IR spectra, which indicates that the reaction takes place nearly quantitatively. In the IR spectra of the pure ICS−PPG matrix film, the region 1700−1500 cm^{-1} shows bands attributed to urea groups (Figure 2): the doublet C=O stretching band (amide I) at 1684 and 1637 cm^{-1} and the in-plane NH bending mode coupled with the C−N stretching at 1558 cm^{-1} (amide II).[32] The sol−gel reaction of ICS−PPG precursor is sketched in Scheme 1.

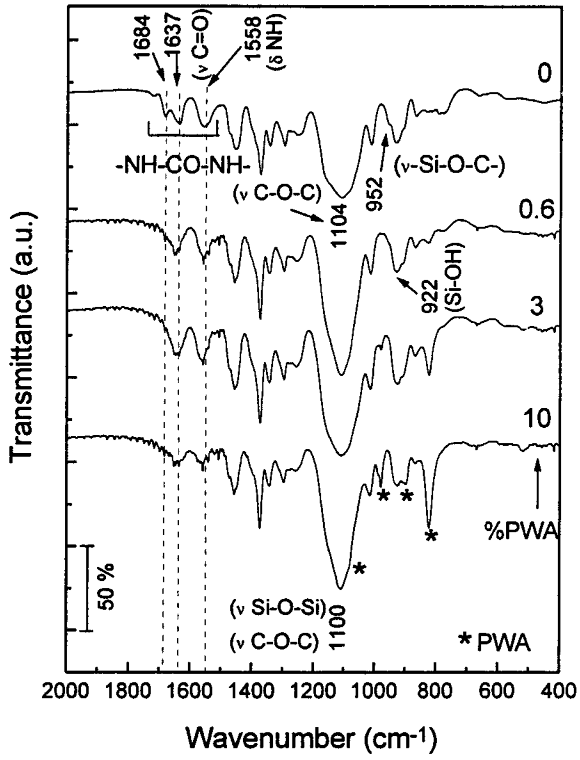

Figure 2. IR transmittance spectra of PWA (0−10 wt %)/ICS−PPG (on CdTe plates) between 2000 and 400 cm^{-1}.

The presence of two distinct amide I modes at 1637 and 1684 cm^{-1} in the unhydrolyzed samples means that two kinds of oxygens of the C=O groups are present: those free of hydrogen bonds (1684 cm^{-1}) and those H bonded (1637 cm^{-1}) to the urea groups of the neighboring ICS−PPG molecules. The addition of PWA (up to 10%) changes the band pattern in the spectral range of the amide I modes, revealing a single 1640 cm^{-1} band, characteristic of H-bonded C=O groups,[32,34] whereas the 1680 cm^{-1} counterpart is no longer visible. This indicates that the incorporation of PWA into the ICS−PPG network and subsequent gelation causes all of the C=O groups to form hydrogen bonds with either H_2O molecules, which were introduced into the ICS−PPG along with the PWA, or with the neighboring urea groups. Even a small amount (~1%) of the heteropoly acid is enough for the disappearance of the band attributed to free or less strongly H-bonded oxygens of C=O groups, agreeing with the effect that HCl and peroxopolytungstic acid have on the gelation of ICS−PPG.[32] However, at SiWA or PWA concentrations below 10%, the amidonium $[C(OH)=NH^+]$ ions are not yet formed (see below) as in the case of nylon-6/H_2SO_4 complexes.[34]

SiO_4 Clustering and Development of the Organic−Inorganic Bonding. The analytically important bands that allow us to follow the effects of adding heteropoly acid to ICS−PPG are also those corresponding to vibrations of SiOH and SiO^- groups, which we expect to form after the addition of the heteropoly acid catalyst (<10%). The IR spectra (Figure 2) of sols hydrolyzed with PWA show the disappearance of the band at 952 cm^{-1} (shown with arrow on the spectrum

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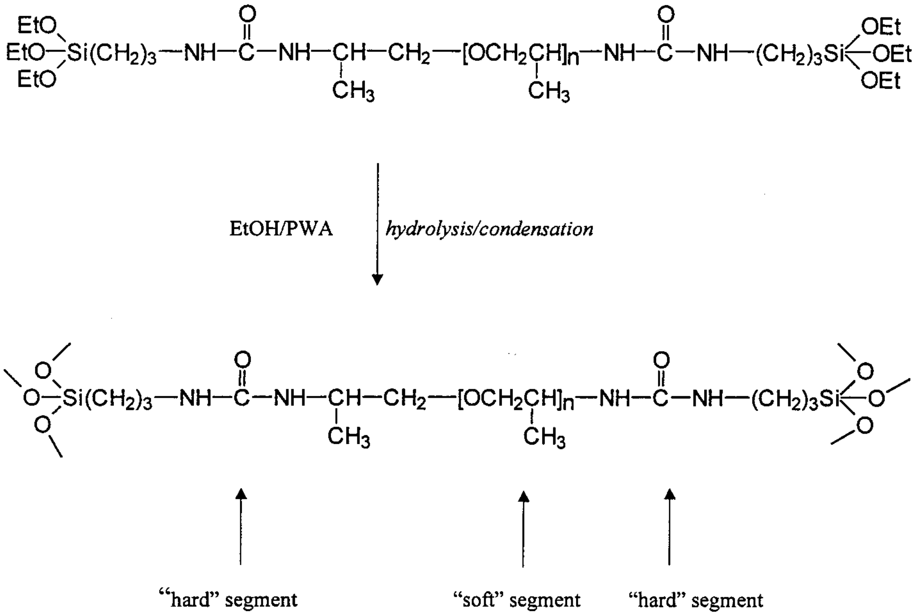
Scheme 1



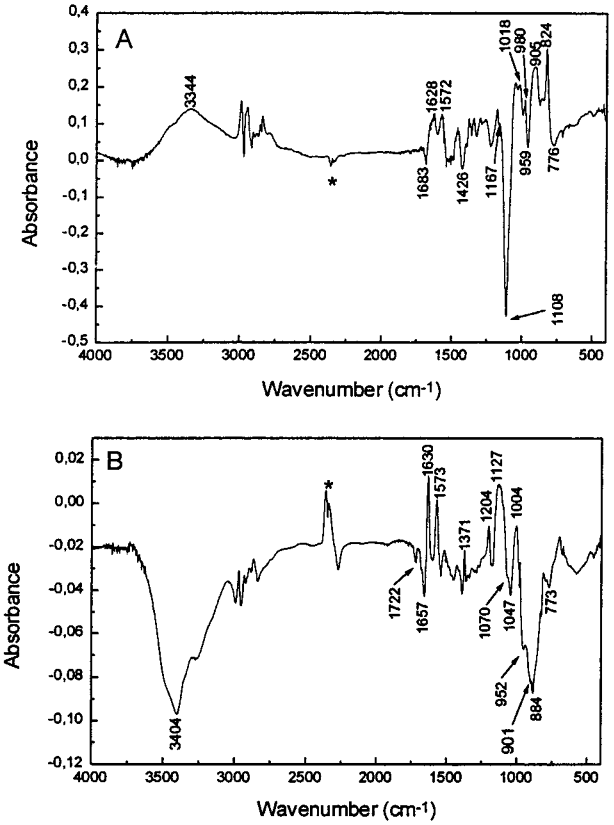


Figure 3. (A) IR difference spectrum of unhydrolyzed ICS−PPG subtracted from freshly hydrolyzed ICS−PPG (with 4% of PWA) and (B) IR difference spectrum of freshly hydrolyzed ICS−PPG subtracted from aged (7 days) ICS−PPG. Spectra were recorded on CdTe plates. (* indicates CO_2 absorption.)

of ICS−PPG), but this band is ascribed to the vibrations of the Si−OEt groups and only accidentally coincides with the position of the expected Si−OH mode. To find the possible SiO^- or SiOH bands, we made subtraction IR spectra (Figure 3A) of an unhydrolyzed ormosil from a freshly hydrolyzed sample (4% PWA). The band at 959 cm^{-1} appears in the unhydrolyzed spectra (protruding downward), which belongs to the Si−OEt mode, indicating that PWA acts as a catalyst for hydrolysis/condensation reactions. Conversely, in a positive direction, the 905 cm^{-1} band appears, which we ascribe to SiO^- group modes following the assignment of Viart et al.[35] who observed this mode in TMOS gels hydrolyzed either with HNO_3 or formamide. This band is characteristic of free SiO^- groups of broken $(SiO)_6$ rings and was first observed in the IR spectra of SiO_2 with a mesoporous structure and irradiated samples.[35]

The presence of SiO^- groups in our samples suggests the formation of SiO clusters, which, in the first step after the addition of PWA, form broken SiO rings that become fully formed during aging. The SiO^- mode is also observed in the subtraction spectrum of a freshly hydrolyzed sol from that of an aged (7 days) sample (Figure 3B). The downward-protruding band confirms that it exists only in the freshly hydrolyzed gel sample. The effect of aging could be seen from the broad OH band centered at 3404 cm^{-1}, which is not present in the spectra of aged gels. In contrast to our results, in recent IR spectroscopic studies of urea-cross-linked organically modified silanes, de Zea Bermudez et al.[33] did not observe the formation of SiOH or SiO^- groups modes in IR spectra of a urea propyltriethoxysilane precursor hydrolyzed with H_2O (without using a catalyst). In addition, the extinction of the mode attributed to the $Si(OR)_3$ groups (950−960 cm^{-1}) and the appearance of the SiO^- band (905 cm^{-1}) was also found in the IR spectra of aged ICS−PPG sols hydrolyzed with HCl or peroxopolytungstic acid.[32] This indicates that water is not a strong enough agent for the hydrolysis/condensation of ICS−PPG precursor, and a catalyst (e.g., strong acid) is needed to achieve fully gelled samples. The difference spectra also show that the addition of PWA alters the urea group modes, as already seen in the IR spectra of Figure 2.

Keggin Ion Structure and Behavior. From the X-ray diffractograms (Figure 4A and B), it is evident that composites with a PWA or SiWA loading up to 70

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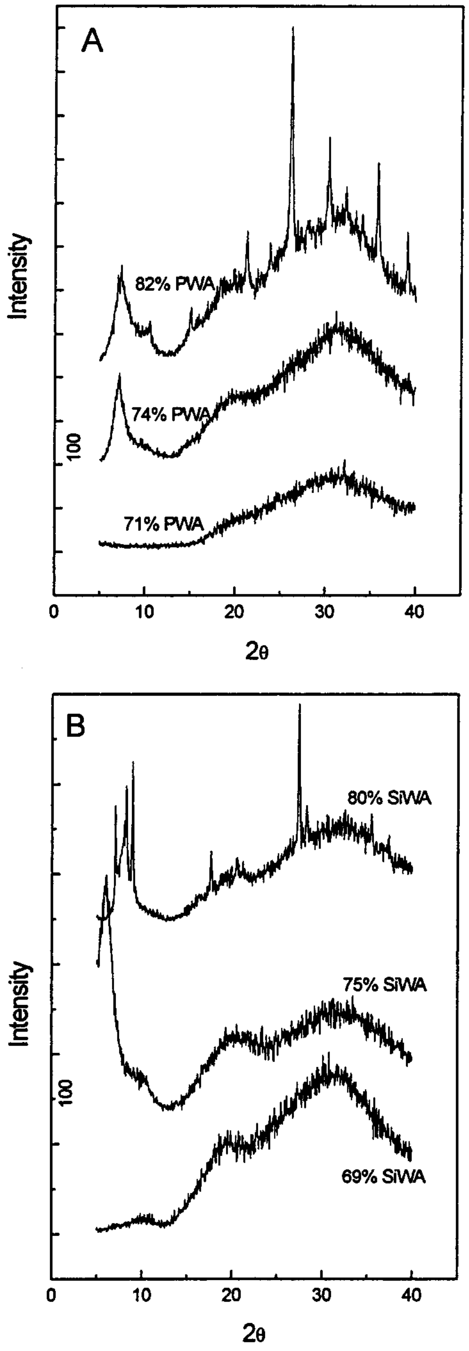

Figure 4. X-ray diffraction patterns of (A) PWA/ICS−PPG and (B) SiWA/ICS−PPG with different contents of heteropoly acid.

wt % are completely amorphous. Such concentrations of heteropoly acid in the silica host (i.e., 70−75 wt %) outrange those in which SiWA or PWA is incorporated in the silica derived from a TEOS precursor.[24] This indicates the advantage of an organic−inorganic hybrid host over a pure inorganic host for the dissolution of high quantities of polyoxometalates. Composites containing more than 75 wt % PWA or SiWA start to exhibit diffraction peaks characteristic of the heteropoly acid. A low-angle diffraction peak (inter-reticular distances = 1−1.5 nm) (Figure 5) is observed for concentrations >70 wt %, indicating that short-range organization remains present. Peaks are rather broad, and the corresponding correlation length deduced from Scherrer formula is 58 Å.

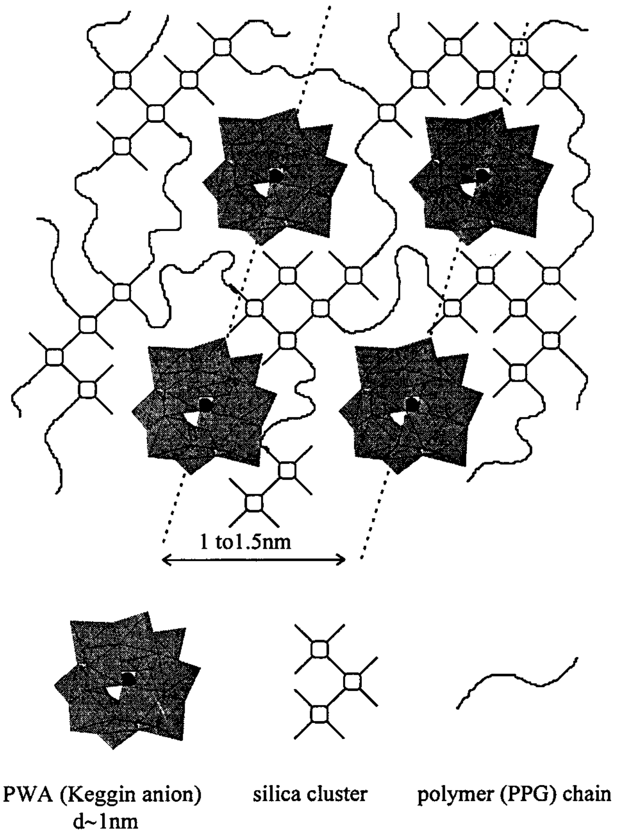

Figure 5. Schematic representation of heteropoly anions dispersed in the silica−polymer host.

Figure 6A and B shows IR spectra of pure heteropoly acids and the influence of ICS−PPG addition on the heteropoly anion skeletal modes appearing between 700 and 1100 cm^{-1}. As expected, with the increasing concentrations of PWA and SiWA, the bands attributed to the Keggin unit's skeletal vibrations (indicated with asterisks) become more intense, which confirms their assignment to the modes of Keggin ions. The characteristic bands of Keggin ions have been assigned according to Deltcheff et al.[36] in terms of W−O−W vibrations of edge- and corner-sharing W−O$_6$ octahedra linked to the central P−O$_4$ or Si−O$_4$ tetrahedra. The stretching modes of edge-sharing (W−O$_b$−W) and corner-sharing (W−O$_c$−W) units appear between 795 and 890 cm^{-1}, whereas the Si−O and P−O modes are at 924 cm^{-1}, 1017 cm^{-1} (SiWA), and 1078 cm^{-1} (PWA). The stretching modes of the terminal W−O$_d$ groups are observed at ~980 cm^{-1} for both heteropoly acids. All of these characteristic bands are also present in the spectra of heteropoly acid entrapped in ICS−PPG, which indicates the preservation of the Keggin ion geometry in the sol−gel composite.

It is known that all of the W−O modes are sensitive to changing electrostatic interactions, e.g., when larger ions (tetrabutylammonium, tetramethylammonium, etc.) replace smaller ones,[36] and to H-bonding interactions, which are established between the incorporated H$_2$O molecules and neighboring urea groups in the ICS−PPG host. For example, when ICS−PPG is added to SiWA, the W−O$_d$ mode shifts from 982 cm^{-1} (SiWA) to 971

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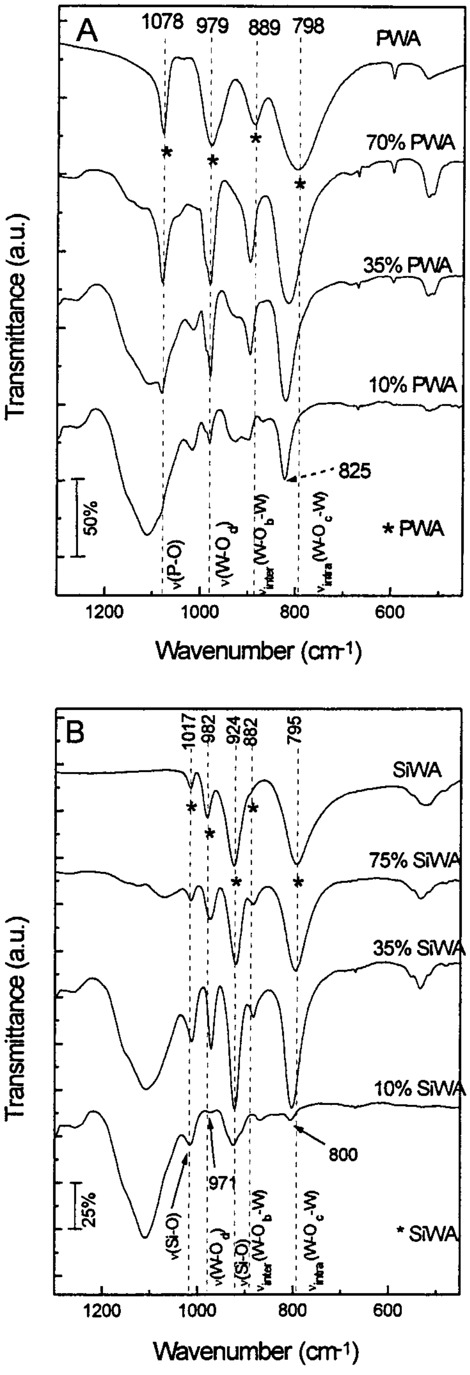

Figure 6. IR transmittance spectra of (A) PWA, PWA (10−80 wt %)/ICSS−PPG and (B) SiWA, SiWA (10−80 wt %)/ICS−PPG between 1300 and 450 cm^{-1}.

cm^{-1} [SiWA (10%)/ICS−PPG], whereas the W−O$_c$−W mode shifts from 795 to 800 cm^{-1} (Figure 6B). This can be straightforwardly explained as an effect of dipolar interactions between the neighboring SiWA molecules, which are diminished by the dispersion of anions in the composite. However, other interactions, such as H bonding, cannot be excluded from participating in the observed frequency shifts of the modes attributed to the Keggin ions. For example, in IR spectra of PWA/ICS−PPG, the highest frequency shift was noted for the W−O$_c$−W$_{intra}$ mode, which shifts from 798 to 825 cm^{-1} (Figure 6A), whereas the same mode in the spectra of SiWA/ICS−PPG is shifted only from 795 to 800 cm^{-1} (Figure 6B) when the concentration of ICS−PPG varies from 0 to 90%. The most apparent difference is noticed for the W−O$_d$ mode, which appears in the IR spectra of both compounds, at 982 cm^{-1} for SiWA and 979 cm^{-1} for PWA. The addition of ICS−PPG to SiWA shifts this band to lower frequencies ($\Delta\nu = 11$ cm^{-1}), whereas the W−O$_d$ band of PWA remained almost unshifted.

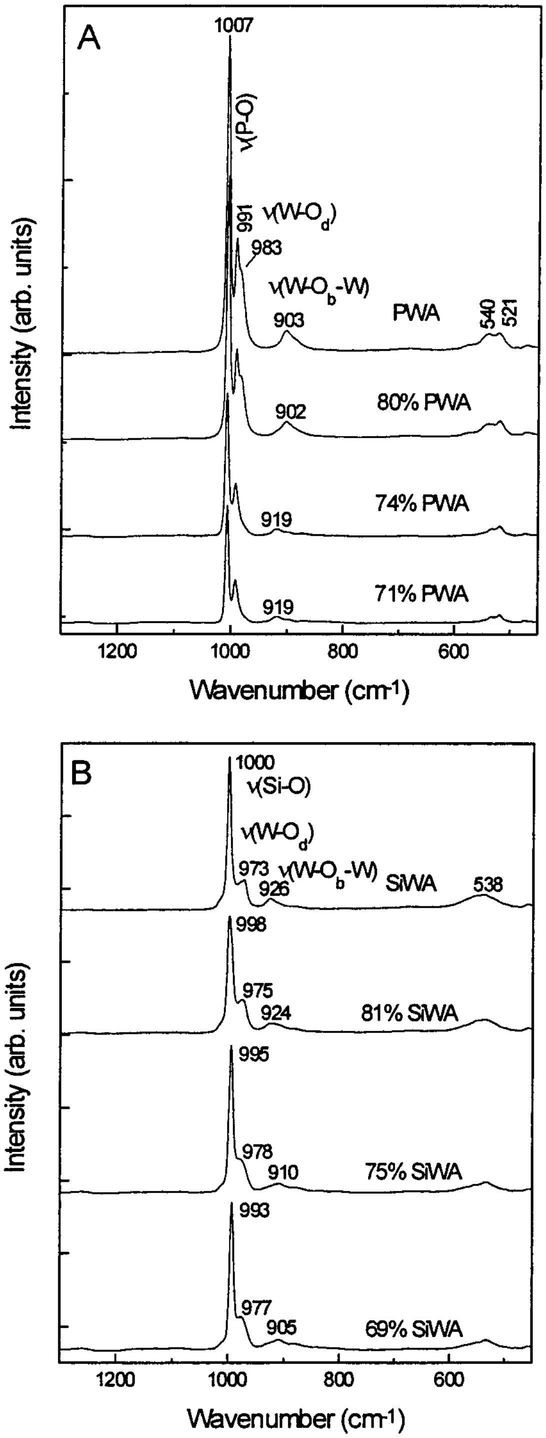

Figure 7. Raman spectra of (A) PWA, PWA (71−80 wt %)/ICS−PPG and (B) SiWA, SiWA (69−81 wt %)/ICS−PPG samples.

Raman spectra of the composites with high heteropoly acid loadings are shown in Figure 7. The assignment of Keggin anion skeletal vibrations is not straightforward as it is not clear from the literature whether the two most intense bands correspond either to the vibrations of the inner P−O$_4$ (or Si−O$_4$) tetrahedron[30] or to the

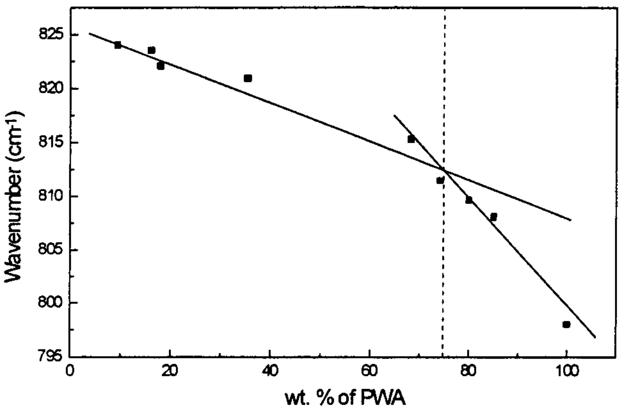

Figure 8. Broadening of the ν_{intra}(W$-$O$_c$$-$W) (peak width is measured at its half-height) (left *y* axis) as a function of PWA concentration in PWA/ICS$-$PPG (●) and frequency dependence of the ν_{intra}(W$-$O$_c$$-$W) (right *y* axis) as a function of PWA concentration in PWA/ICS$-$PPG (□).

W$-$O$_d$ terminal vibrations.[36] The assignment of PWA Raman bands is discussed in our previous paper.[20]

The sharp and intense bands at 1007 and 991 cm^{-1} most likely correspond to P$-$O$_4$ vibrations (Figure 7A), whereas bands at lower wavenumbers are attributed to W$-$O$_d$ (983 cm^{-1}) and W$-$O$_b$$-$W (903 cm^{-1}) vibrations [ν(W$-$O$_c$$-$W) is not active in Raman]. This agrees with the IR spectra as no change is observed in the position of the P$-$O mode after the addition of ICS$-$PPG, whereas the ν(W$-$O$_b$$-$W) mode at 889 cm^{-1} and the ν(W$-$O$_d$) mode at 979 cm^{-1} shift to higher wavenumbers with a decreasing concentration of PWA in the composites.

Blue frequency shifts of both IR-active modes with decreasing concentration of PWA in the composite corroborate the frequency shifts that these modes exhibit in the Raman spectra. At 71 and 74% PWA in ICS$-$PPG, the W$-$O$_d$ band is imbedded in the P$-$O stretching band at 991 cm^{-1}. The blue frequency shift of the W$-$O$_d$ band, when the concentration of PWA is decreased below the crystallization threshold, can be explained by the kinematic coupling between the W$-$O$_d$ and W$-$O$_b$$-$W modes, which shifts the W$-$O$_d$ mode to higher frequencies.

In the case of SiWA, the explanation for the observed band shifts is more difficult, unless we assume a mixed character (Si$-$O + W$-$O$_d$) for the bands at 1000 and 926 cm^{-1}. In this way, we can explain the red frequency shifts of both bands upon ICS$-$PPG addition (Figure 7B), which is then in accordance with the ν(W$-$O$_d$) shift in the IR spectra (Figure 6B).

Keggin Ion Sublattice. A more detailed inspection of the vibrational mode behavior of Keggin ion modes in the concentration range from 0 to 100% PWA in ICS$-$PPG reveals that the rate of the W$-$O$_c$$-$W band frequency and the half-peak width dependence change close to a concentration of 75% PWA (Figure 8). This change coincides with the appearance of the short-range ordering, as noted from the XRD spectra of the composites (Figure 4A). Considerable broadening of the W$-$O$_c$$-$W mode (Figure 8) is found when the concentration of PWA is increased in the ICS$-$PPG host. The W$-$O$_c$$-$W mode of PWA (800 cm^{-1}) exhibits a half-peak width of about 100 cm^{-1}, which is narrowed to 20 cm^{-1} upon incorporation in the ICS$-$PPG host. Below the agglomeration threshold, all of the PWA bands show considerable narrowing, indicating that the vibrations become less disturbed by dipole$-$dipole interactions when the concentration of ICS$-$PPG increases. Similar vibrational band narrowing was noted in IR spectra of Langmuir$-$Blodgett (LB) films obtained from DODA (dimethyldioctadecylammonium) and DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphorylholine) with incorporated PWA.[37] The band narrowing of PWA modes in LB films was explained to appear because the interatomic distances between PWA anions are enough large to neglect anion$-$anion interactions. In addition, the narrowing of the bands is also observed in IR spectra of peroxopolytungstic acid incorporated in the ICS$-$PPG gel.[32] This is not surprising as the metatungstate ion has the same basic structure as the heteropoly anion and exhibits an IR spectrum closely resembling that of PWA. On the contrary, the width of the W$-$O bands remains unchanged when PWA becomes entrapped in the silica gels without organic modification.[23,24] This implies the specific H-bond interactions between PWA and the hybrid organic$-$inorganic gel skeleton resulting from the intimate mixing of PWA in ICS$-$PPG. The interactions ensure the separation of PWA units by the silica$-$polymer network (Figure 5). Accordingly, from XRD results, it is clear that 75 wt % heteropoly acid is the highest loading limit that will permit a homogeneous material to be obtained, which is characterized by nonagglomerated PWA or SiWA units in the ormosil host. A simplified schematic structure of evenly dispersed PWA in the organic$-$inorganic host is shown in Figure 5.

Another indication that the interactions between the Keggin ions and the ICS$-$PPG host change close to the agglomeration threshold can be obtained from an inspection of the OH modes appearing in the IR spectra of PWA/ and SiWA/ICS$-$PPG composites (Figure 9A and B). When the concentration of heteropoly acid is increased above 80%, a new band at 1700$-$1710 cm^{-1} appears, which is due to the presence of H_3O^+ and/or $H_5O_2{}^+$ ions.[23]

The appearance of hydroxonium modes above the crystallization threshold (~75%) agrees with expectations because these modes are typical for the secondary structure of the hydrated and crystalline PWA and SiWA, in which strong hydrogen bonds, existing between the cations, give rise to the structured and broad OH$-$O stretching mode between 3500 and 3000 cm^{-1} and the deformational band of H_3O^+ ions at ~1700 cm^{-1} (Figure 9). Conversely, IR spectra of SiWA and PWA composites containing a small amount (5$-$20%) of heteropoly acid reveal that the broad and structured OH$-$O band in the range 3500$-$3000 cm^{-1} is absent, and in its place, the relatively narrow NH$\cdots$OH$_2$ stretching mode appears close to ~3400 cm^{-1}. This indicates that, at higher heteropoly acid concentrations, a system of strong and short OH$-$O bonds originating from H-bonded $H_5O_2{}^+$ and/or H_3O^+ ions is developed.

In the concentration range 40$-$75% PWA and SiWA in the ICS$-$PPG host, the appearance of the 1680 cm^{-1} band,[34,38] which is accompanied by a broad and structured OH band[39] between 3400 and 2500 cm^{-1}, indicates

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(37) Clemente-Leon, M.; Agricole, B.; Mingotaud, C.; Gomez-Garcia, C. J.; Coronado, E.; Delhaes, P. *Langmuir* **1997**, *13*, 2340.

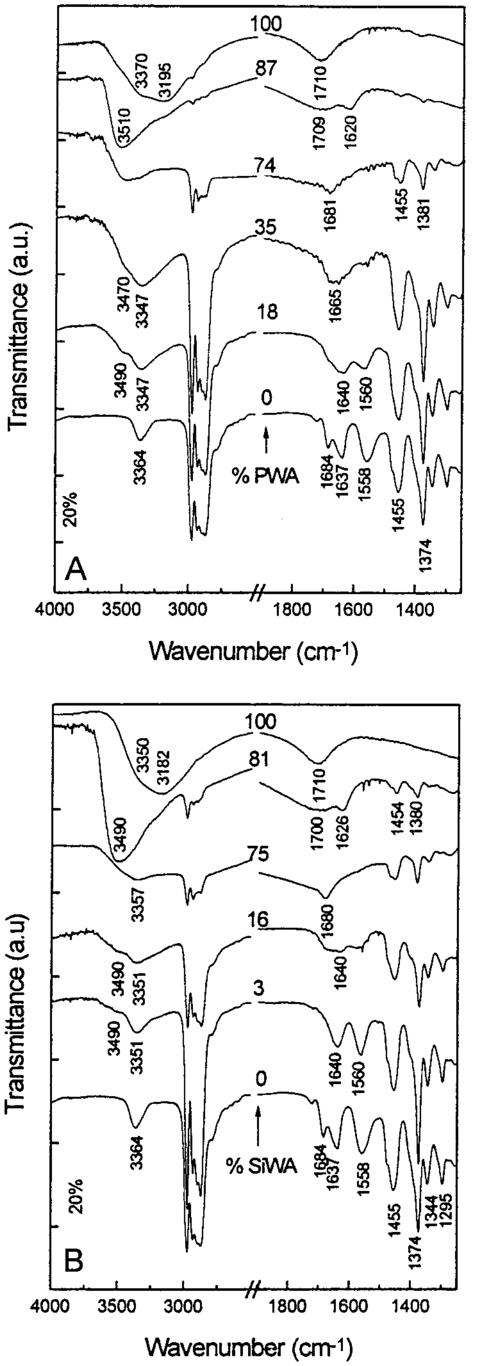

Figure 9. IR transmittance spectra of (A) PWA, PWA (0−87 wt %)/ICS−PPG and (B) SiWA, SiWA (0−81 wt %)/ICS−PPG (on CdTe plates) in the spectral ranges 4000−2500 cm^{-1} and 1900−1250 cm^{-1}.

the protonation of the C═O groups and the transformation of C═(O)NH groups into amidonium ions [C(OH)═NH$^+$].[34] We assume that the amidonium ions increase the strength of the interactions between the negatively charged Keggin ions and the ICS−PPG host and beneficially influence the immobilization and entrapment of PWA and SiWA in the sol−gel network.

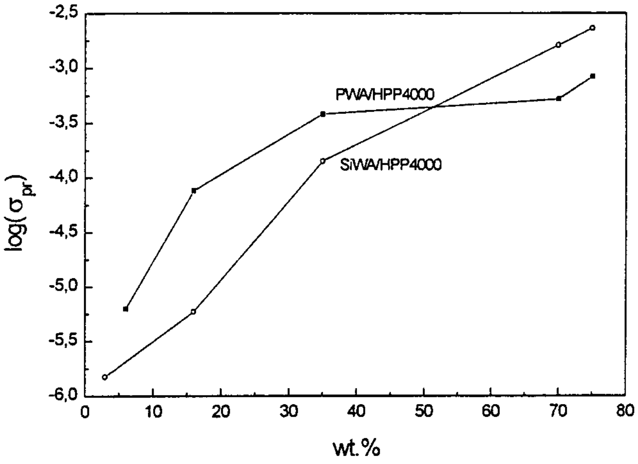

Figure 10. Decadic logarithm of conductivity as a function of PWA concentration in PWA/ICS−PPG and of SiWA concentration in the SiWA/ICS−PPG.

To summarize, IR spectroscopy confirms a homogeneous dispersion of heteropoly acid in the ICS−PPG host. Its successful immobilization is verified also by soaking a film of PWA (70%)/ICS−PPG gel in water. Compared to the spectrum of a fresh sample (before soaking), no drastic alteration in the intensity or frequency of the heteropoly anion skeletal modes is observed. PWA is effectively immobilized in the ICS−PPG host so that it does not dissolve out, even though the crystalline PWA is highly soluble in water. It seems that the amidonium ions formed at PWA and SiWA concentrations below and close to the crystallization threshold help in the immobilization of Keggin ions by increasing the electrostatic interactions between the Keggin ions and the positively charged [C(OH)═NH]$^+$ ions in the ICS−PPG host.

Proton Conductivity. The proton conductivity (σ_{pr}) of the SiWA/ and PWA/ICS−PPG composite gels is evaluated from impedance spectra according to the procedure described in ref 32. The results are summarized in Figure 10 and show that the proton conductivities gradually increase with an increasing amount of PWA or SiWA in the composites. Compared to that of PWA/ICS−PPG, the better conductivity of SiWA/ICS−PPG gels for high SiWA loading (70 and 75%) can be explained by a higher proton concentration in the material. Specifically, SiWA ($H_4SiW_{12}O_{40}\cdot nH_2O$) has one proton more in the molecule than does PWA ($H_3PW_{12}O_{40}\cdot nH_2O$). The opposite behavior of proton conductivity is found for a low concentration (16%) of heteropoly acid in ICS−PPG. The reason for this remains unclear. In both cases, the increase in σ_{pr} with heteropoly acid concentration from 10^{-6} S/cm (<10 wt % of PWA or SiWA) to 10^{-3} S/cm (>70 wt % of PWA or SiWA) in the ICS−PPG host is due to the high loading of heteropoly acids and their uniform distribution in the sol−gel matrix, enabling the transport of protons through the gel.

It is clear that the amidonium ions play an important albeit indirect role in attaining the high proton conductivity of the synthesized hybrids. In this respect, the presence of urea groups and their ability to become protonated is a prerequisite for achieving high loadings of heteropoly acids in the composites. The main reason for the effective immobilization of the Keggin ions is the presence of electrostatic interactions established between the positively charged amidonium ions and the negatively charged Keggin ions.

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(39) Cook, D. *Spectrochim. Acta* **1966**, *22*, 419.

Water molecules that are incorporated in the composite during the insertion of heteropoly acid are the main source of mobile protons. It is reasonable to assume that the conduction path of mobile protons occurs along the C−O−C bonds of the soft segments[40] of the PPG chains. However, we were not able to extract from the IR spectra any additional evidence about the specific interactions involving the protons and modes attributed to the C−O−C bonds. Nevertheless, above the crystallization threshold, there is clear evidence for the existence of H_3O^+ modes at 1700 cm^{-1}, indicating that the water protons are responsible for the high proton conductivity obtained for our organic−inorganic hybrids.

Conclusions

The organic−inorganic network ICS−PPG is a suitable host for the incorporation of high concentrations of heteropoly acid, that is, up to 75 wt % PWA or SiWA can be homogeneously incorporated in ICS−PPG without agglomeration, crystallization, or phase separation of the sample. Preservation, immobilization of the Keggin structure, and uniform distribution of the Keggin ions in the host was confirmed by vibrational spectroscopy, which revealed that the amidonium $[C(OH){=}NH^+]$ ions play an important role in the immobilization of the negatively charged Keggin ions inside the sol−gel host. PWA/ICS−PPG and SiWA/ICS−PPG gels are good ionic conductors with proton conductivities up to 10^{-3} S/cm, making them promising semisolid electrolytes for applications in fuel cells, for example.

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