

Inorganic-organic Hybrid Proton Conductive Membranes Doped with Phosphoric Acid

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Abstract A new proton conductive inorganic-organic hybrid membrane doped with H_3PO_4 was fabricated via sol-gel process with 3-glycidoxypropyltrimethoxysilane(GPTMS),3-aminopropyltriethoxysilane(APTES)andtetraethoxysilane(TEOS)asprecursors.Theproton conductivity of about 3.0×10^{-3} S/cm was obtained at $120^\circ C$ under 50% relative humidity (R.H). DTA curves showed that the thermal stability of the membrane is significantly enhanced by the presence of SiO_2 framework up to $250^\circ C$. SEM and XRD revealed that the gel is microporous and amorphous. The addition of APTES improved the conductivity of the membranes and the effect of the APTES on the conductivity was also discussed in this paper.

Keywords: Proton conductivity; Sol-gel process; Inorganic-organic composite; Fuel cells.

1. Introduction

The inorganic-organic hybrid materials via sol-gel process have attracted great attentions in recent years because of their potential advantages over the conventional materials [1-3]. From a practical point of view as the separators for fuel cells and sensors, these solid-state proton hybrid conductors have a promising future due to unique advantages, such as flexibility, good mechanical strength, thermal stability and excellent processibility. Although the commercially used perfluorinated membranes, such as Nafion[®] (Du Pont), Aciplex[®] (Asahi Chmeicals) possess very desirable properties such as good mechanical strength, chemical stability and high conductivity[4], however, their applications are limited by high humidity dependence, small operating temperature range below $100^\circ C$, fuel permeability, high cost, and poor hydrophilicity. A new proton conductive material with excellent operating performance for medium temperature ($100\text{--}200^\circ C$) is required intensively due to higher CO tolerance and catalyst efficiency[5,6], better water and heat management. In recent researches, the inorganic-organic hybrid material is one of the most versatile ways due to the preformation and controllable properties by preparing inorganic or inorganic-organic proton conducting materials to be used as fillers for polymeric hybrid membranes [7-9].

In our present work, the polymeric phase was directly incorporated into the inorganic matrix through the epoxy ring-opening and polycondensation reactions of 3-glycidoxypropyltrimethoxysilane (GPTMS). We expect that the Si-O-Si backbone (which provides thermal stability) will be connected with each other by the pseudo

PEO-chain (which provides flexibility and processibility) to form the nanocomposite materials. The 3-aminopropyltriethoxysilane (APTES) was added into the precursors sol to shorten the gelation time and improve the water affinity (atoms with unshared electrons are potential acceptors for hydrogen bonding). The microstructure is schematically showed in Fig. 1. And the low cost phosphorous containing compound, H_3PO_4 was doped to provide the material with proton conductive behavior.

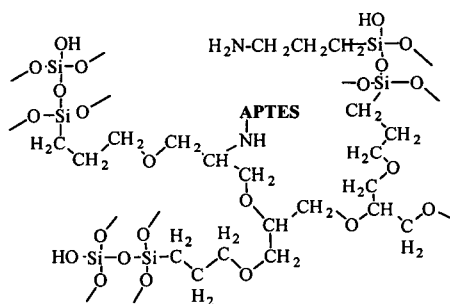


Fig. 1 The schematic molecular structure of inorganic-organic hybrid membrane

2. Experiments

The hybrid membrane was fabricated via sol-gel process by hydrolysis and condensation reaction of GPTMS, TEOS and APTES. H_3PO_4 (85% aqueous solution) was used as phosphorous dopant. All the chemicals were used as received. The synthetic procedure is shown in Fig. 2. The total ratio of ethanol/Si was fixed to be 5 and water containing hydrochloric acid (pH=0.25) was added dropwise to the precursor solution, where 1 mol of the total alkoxy groups in precursors met with 0.01 mol of HCl in 1 mol of H_2O solution. The molar ratio of TEOS/GPTMS/APTES/ H_3PO_4 was $50:(50-x):x:50$, where x was varied from 0 to 30. The sol obtained was cast onto petri dish and kept at $60^\circ C$ for 1 week and $80^\circ C$ for 1 day. The gel was further

annealed at 120°C for 2h at atmospheric pressure to fully polymerize the silica network.

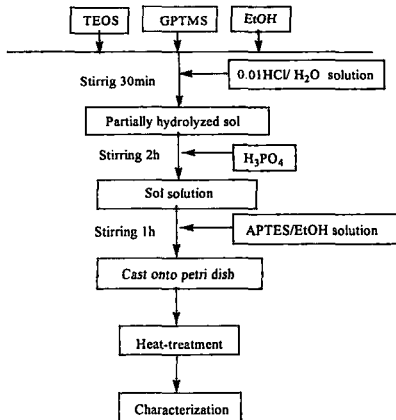


Fig.2 The synthetic procedure for the hybrid membrane

3. Results and Discussion

3.1 Thermal stability

The DTA-TGA curves of the membranes are shown in Fig.3. The curves suggest that the thermal stability of the polymer PEO phase in the composites is highly enhanced by the nanolevel confinement of the inorganic SiO₂ framework. Exothermic peaks at 310 °C, 371 °C and 422 °C are attributed to the oxidation and decomposition of the polymeric side groups, side chains and main chains in the polymeric phase, respectively.

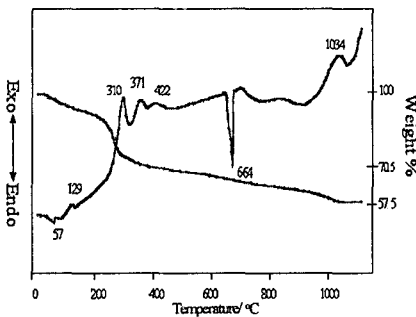


Fig.3 DTA-TGA curves for sample 50TEOS-30GPTMS-20APTES-50H₃PO₄

3.2 FT-IR spectra analysis

Fig.4 compares the infrared (IR) spectra of the gels with different compositions. It is worthy noting that the strong absorption band at 1020 cm⁻¹ was observed in spectra, which assigned to ν(Si-O-P) [10]. It suggests that there are chemical interactions between H₃PO₄ and SiO₂ matrix, which are expected to enhance the retention of the hydrated water and improve the immobility of the phosphorous ions. The absorption band at 2400 cm⁻¹ is assigned to ν(P-OH) [11] and shift to low wavenumber with increasing APTES due to the coordination by amino group. The

separation of absorption band at 1600 cm⁻¹ (ascribed to ν(NH₂)) [12] strongly suggested the reactions between amino group and the H₃PO₄ and/or epoxy ring.

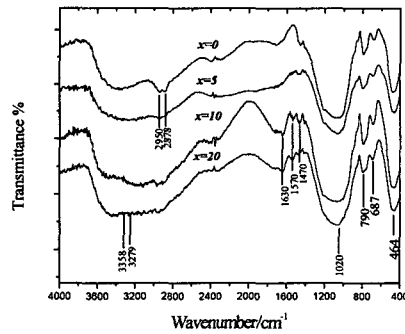


Fig.4 FT-IR spectra for samples 50TEOS-(50-x)GPTMS-xAPTES-50H₃PO₄

3.3 XRD analysis

Fig.5 shows the X-ray diffraction patterns of powder samples with various APTES molar ratios from 0 to 20 in the precursors compositions. The results indicate that there was no obvious evidence for crystallization for SiP₂O₇ or Si₅O(PO₄)₆ [13,14] in the phosphosilicate matrix. The typical amorphous pattern with a broad peak at about 2θ = 21°, characteristic of vitreous SiO₂ [15], was observed by XRD.

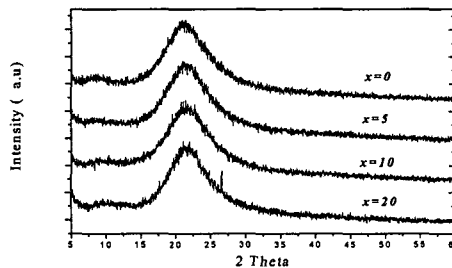


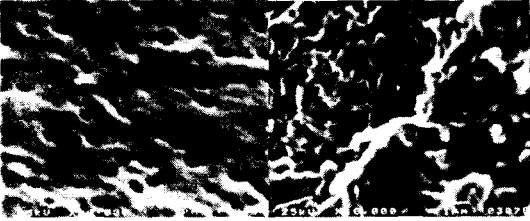
Fig.5 The XRD patterns for samples 50TEOS-(50-x)GPTMS-xAPTES-50H₃PO₄

3.4 Morphology analysis

The morphologies at the surface and fractured section of the hybrid membranes with and without APTES were compared by SEM, as shown in Fig.6. The sample without APTES possessed a homogenous texture with some small pores having a diameter of about 0.1~0.5 μm, which may be formed when the condensation proceed and water and ethanol released from the surface. With APTES addition, there are pores with diameter of about 0.1~0.3 μm on the fractured section (c) and pores accompanied with some channels in the surface (d). These porous structures were obtained by sol-gel process and they are expected to favor the proton transportation in the membrane.



(a)(b)



(c)(d)

Fig.6 SEM images for sample with 0% APTES: (a) fractured section, (b) surface and with 20% APTES: (c) fractured section, (d) surface.

3.5 Electrical conductivity

In our present work, the conductivities of all membranes show dependence on environmental humidity. When the relative humidity of the measuring environment was elevated from 5% to 75%, the conductivities were improved largely, as seen in Fig. 7. It strongly suggests the membranes are microporous in the matrix that can absorb water molecules to favor the proton transportation. It is well known that the surface mechanism explains [16] water-dependent conduction in porous ceramic and glassy materials.

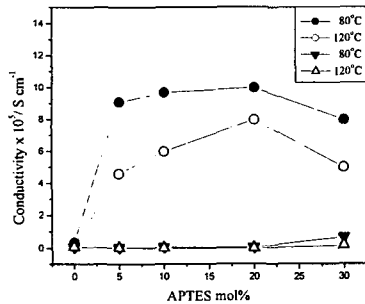


Fig.7 Relationship between the conductivities and APTES molar ratios. Conductivities were obtained at 60 μ m under 5% R.H (Δ , \blacktriangledown) and 75% R.H (\circ , \bullet) with and without heat-treatment at 120°C

As shown in Fig. 7, the effect of APTMS on conductivity is quite different between low and high relative humidity environments. Under higher relative humidity (75%), conductivity of sample further heated at 120 μ m increases with the amount of APTES and shows a maximum conductivity at 20 mol% while for sample without annealing exhibits a Volcano type behavior, showing maximum conductivity in the rang 5~20 mol%. While under low

humidity (5%), the conductivity is kept constant with APTES increases. It means no obvious effect of the amino groups on the conductivity under low relative humidity. According to the above-mentioned mechanism, we suppose that the incorporation of APTES increase the concentration of the defected sites ($\equiv\text{SiO}^+ \cdot \text{H}_3\text{NC}_3\text{H}_6\text{-Si}\equiv$)^[17,18] which are necessary for water dissociation to provide protons as charge carrier. High concentrations of defected sites are necessary for the formation and affinity of the condensed water in the matrix. And the humid ambience benefits the formation of defected sites. On the other hand, since the charge carrier is proton that dissociated from the phosphoric acid, any factor to the concentration change of P-OH can lead to the variety of the electrical conductivity of the membranes. Thus we conclude that the reaction between the basic -NH₂ group and acidic P-OH group will partially decrease the proton concentration in the P-OH bonds resulting in the appearance of the optimum conductivity at about 20 mol% APTES in the precursors compositions.

It is noteworthy that the conductivity decreases slightly with the increasing heating temperature, although the mechanical properties improves after annealing at 120 μ m for 2h. The brittleness and solubility in water were reduced obviously after the further polymerization of the silicate gels. We consider that the decrease in conductivity may attribute to the change of the pore properties by the heat-treatment. It is well known that during the gelation and drying process, organic solvent will extract out of the matrix to form the micropores. The polymeric phase is readily to distribute on the surface of pores and when the temperature is elevated over the glass transition temperature (T_g), the polymeric chains begin to move to readjust its conformations leading to decrease in pore volume and even block the pores in the matrix. Another reason may be the condensation reactions between H₃PO₄ and Si-OH or H₃PO₄ which more readily occurs at higher heating temperature even though there were no evident observations of such condensation in the present work.

Fig.8 shows the temperature dependence of the conductivities of the hybrid membrane with the composition as 50TEOS-30GPTMS-20APTMS-50H₃PO₄, where the conductivities were measured under 50% R.H and plotted as a function of the reciprocal temperature. The maximum conductivity of 3.0×10^{-3} S/cm was obtained at 120°C under 50% R.H and the conductivity kept stable at temperature higher 100°C, suggesting the good potential for medium temperature applications. It is notable that this curve is not exactly linear in the range from 20 to 120°C, indicating proton conduction does not just follow an Arrhenius-type behavior, but also shows the character of Vogel-Tamman-Fucher (VTF) behavior. The latter behavior may be attributed to segmental motion of polymeric phase. Even though the interactions between H₃PO₄ and the SiO₂

or pseudo-PEO are not clear until now. We suggest H_3PO_4 is distributed in both inorganic and organic phases, showing different conducting behaviors.

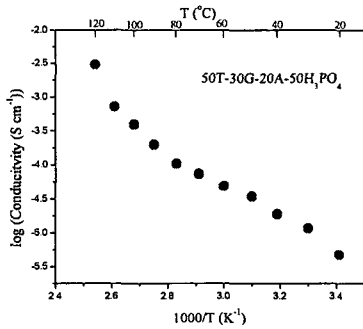


Fig.8 The temperature dependence of the conductivity of the membrane measured at different temperatures under 50%R.H.

4. Summary

A new inorganic-organic hybrid membrane based on the hydrolysis and condensation of GPTMS, APTES, TEOS doped with phosphoric acid has been successfully fabricated via sol-gel process. The addition of APTES can not only shorten the gelation time but also improve the water affinity resulting in the improvement of the electrical conducting behavior. The flexible, transparent and microporous material shows the humidity-dependent conductivity. A high conductivity of $\sim 3.0 \times 10^{-3}$ S/cm are obtained at 120°C under 50% R.H. And thermal stability is largely enhanced due to the presence of SiO_2 framework up to 250 °C. The hybrid membranes have high potentiality to be used as medium temperature fuel cells and good processibility for large area membranes.

5. References

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