

High Temperature Proton Conducting Polymer Electrolytes based on Hydrocarbon - Silicate Molecular hybrids

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Proton conducting properties of temperature tolerant bridged hydrocarbon - silicate molecular hybrid membranes have been investigated. The conductivity of the hybrid membranes based on pure hydrocarbons were found to exceed 10^{-2} S/cm level with various PWA doping ratios. The binary hydrocarbon hybrids between diethylbenzene /octane or hexane/octane show large conductivities exceeding 10^{-2} S/cm with thermal stability at 160°C under humidified condition.

Key words: organic/inorganic hybrid, bridged polysilsesquioxane, proton conducting membrane, polymer electrolyte membrane, 12-Phosphotungstic acid (PWA)

1. INTRODUCTION

Intermediate temperature operation of PEFCs above 100°C has been suggested to lead many technological advantages in the application to electric vehicles or on-site power generation. For example, electrodes kinetics are improved at elevated temperatures, CO tolerance of the electrocatalysts is enhanced, while the amount of precious Pt metals can be reduced. Improved tolerance of the electrodes towards CO contaminated hydrogen-rich gases allows for the use of reformed natural gas, gasoline and even methanol. Also, a reduction of electrode polarization losses leads to higher energy conversion efficiency of the cell. However, polymer electrolyte membranes⁽¹⁻¹⁹⁾ which can be tolerant at elevated temperatures are challenging goal in the research of materials science of polymer electrolyte fuel cells.

Hybrid materials with nano-size interfaces between organic and inorganic domains offer exceptional opportunities to create materials with unique properties. We have reported in our previous papers⁽¹⁴⁻¹⁹⁾ that a family of bridged polysilsesquioxanes are novel proton conducting organic/inorganic hybrid macromolecular materials. These were prepared by sol-gel processing of monomers that contain polymer bridging groups and two or more functional silyl groups. The materials were synthesized using amphiphilic bridged monomers and heteropolyacids such as 12-phosphotungstic acid (PWA) clusters to form proton conducting polysilsesquioxane macromolecular membranes. Flexible, homogeneous and large-sized hybrid macromolecules are structurally controlled by varying the hydrocarbons attached to multifunctional alkoxy silane moieties. The proton conductivities of the octane (Oct), hexane (Hex) and diethylbenzene (DEB) hybrids were studied along with the dependence to the doping ratio of PWA. Also, binary polymer mixture between octane/hexane or octane/DEB were synthesized and the conductivities of those binary hybrids were studied.

Conductivities exceeding 10^{-2} Scm⁻¹ have been achieved in these hydrocarbon - silicate molecular hybrid membranes

2. EXPERIMENT

Organic/inorganic nano-hybrid macromolecules are synthesized through organically bridged tri-alkoxysilane (bridged polysilsesquioxanes) precursors, as previously reported⁽¹⁴⁻¹⁹⁾. Temperature tolerant polymers such as polyethers, alkylenes and aromatics were used to bridge alkoxy silane functional groups for organic/inorganic hybrid monomers. Sol-gel processing provides a versatile synthetic route to tailor hydrophobic/hydrophilic interfaces, where the polymerization of bridged tri-alkoxysilanes proceeds by a series of hydrolytic and condensation reactions involving addition of heteropolyacids such as PWA.

Figure 1 shows the molecular structure of the hydrocarbon based organically bridged polysilsesquioxane monomers used in the present work, where bifunctional hydrocarbons (hexane (Hex), octane (Oct), diethylbenzene (DEB)) were terminated by reactive alkoxy silanes. All of these hydrocarbon hybrids were proved to possess thermal stability due to the inclusion of inorganic phase⁽¹⁴⁻¹⁹⁾.

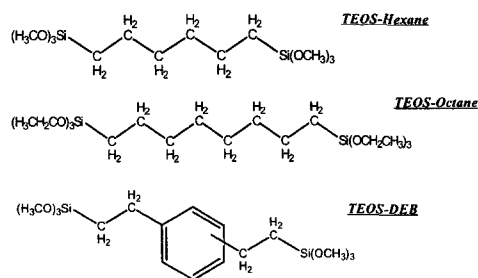


Figure 1 Molecular Structure of the hybrids

The bridged silsesquioxane precursors were hydrolyzed and condensed to form hybrid

macromolecules through a catalytic reaction with PWA ($\text{H}_3\text{PO}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$). The sol-gel synthetic process used in the present study were reported in our previous study⁽¹⁴⁻¹⁹⁾. The hybrid monomers were prepared as alcohol solutions (methanol, ethanol, isopropanol and 2-buthanol) and mixed with PWA and further mixed with water, resulting in a sol solution. The sol solution was cast on to a polystyrene Petri Dish and annealed at room temperature for more than 24 hours to form transparent, homogeneous, flexible gel membranes with thicknesses of 100 - 300 μm . The membranes were then aged under controlled humidity (60°C, 95%R.H., 24h) to form hydrated ion exchanged electrolytes. Finally, the membranes were boiled in water for 12h to wash impurities and solvents out of the matrix, resulting in the desired organic/inorganic hybrid membranes. This process is unique for the sol-gel processing of bridged polysilsesquioxanes with organic/inorganic interfaces.

The hybrid membranes become proton conducting by incorporating of PWA in the macromolecules; PWA acts as a catalyst and a protogenic moiety at the same time.

3. RESULTS AND DISCUSSIONS

Figure 2 shows proton conductivities of hexane (Hex), octane (Oct) and diethylbenzene (DEB) hybrids as a function of water content in the membrane, which is obtained by the initial drop in the thermal gravimetric analysis (TGA). The proton conductivities are not strongly dependent on the water content in the membranes. However, the conductivity of exceeding 10^{-2} S/cm is quite large in spite of the low water content, less than 60 wt.%, in the membrane. The highly conductive ion exchange membrane such as Nafion contains more water (> 60 wt.%) , so the present hybrid membrane is very conductive with small amount of water. The conductivities of 10^{-2} S/cm with less than 20 wt.% water in the membrane suggests the presence of fast ion conductive channels in the organic/inorganic hybrid macromolecules.

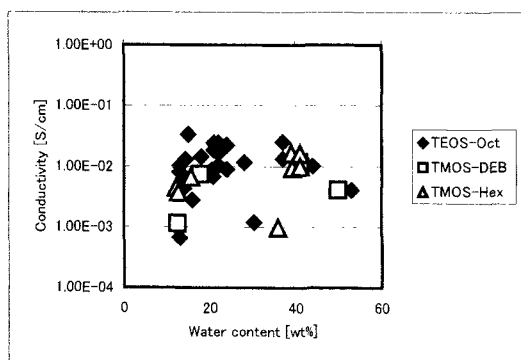


Figure 2 Proton conductivities of hexane, octane and diethylbenzene hybrids

Figure 3 shows proton conductivities of (a) octane (Oct), (b) hexane (Hex) and (c) diethylbenzene (DEB) hybrid membranes as a function of PWA doping ratios (mol.%).

diethylbenzene (DEB) hybrid membranes as a function of PWA doping ratios (mol.%). As the molecular weight of PWA is large (2880), the equivalent weight of the hybrid membrane doped with 10 mol. % PWA is approximately 10000 (0.1 meq./g) , which is about 10 times larger than that of Nafion membrane (900 - 1100). This means that the proton concentration of the hybrid membrane is about 10 times smaller than that of Nafion membrane, suggesting the fast proton transport in the hybrid macromolecules. The large conductivity exceeding 10^{-2} S/cm can be achieved with relatively small proton concentration. The proton conductivity of the hexane hybrid is not dependent on the PWA content, however, it is shifted in octane as well as diethylbenzene hybrid membrane. In these materials, the conductivity can not be well controlled by PWA content alone.

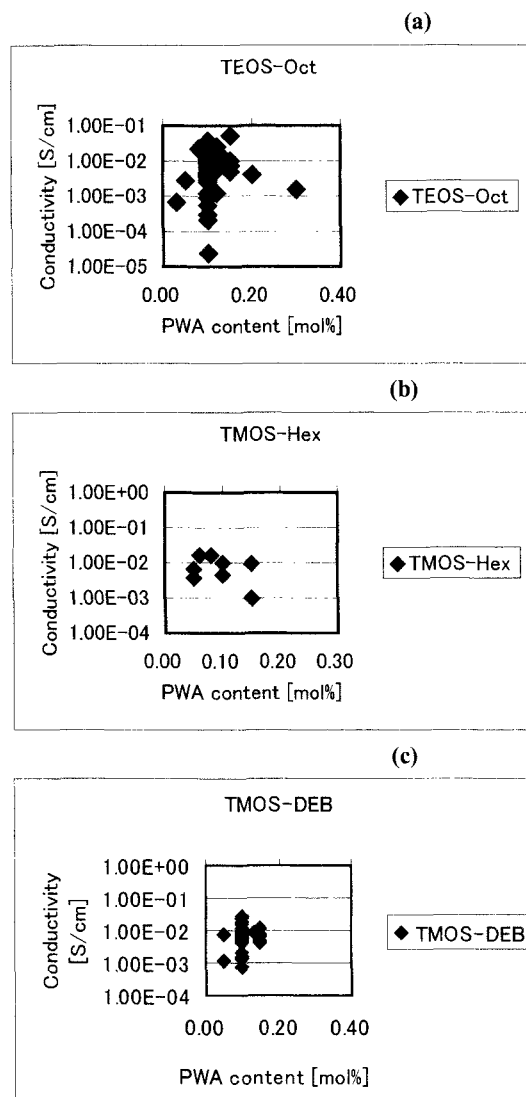


Figure 3 Proton conductivities of (a) octane (Oct), (b) hexane (Hex) and (c) diethylbenzene (DEB) hybrid membranes as a function of PWA doping ratios (mol.%).

Figure 4 show the proton conductivities of the binary membranes of (a) octane/hexane hybrids and (b) octane/diethylbenzene hybrids, respectively. The conductivity was measured at 60°C under 95% relative humidity for all cases. The mixing ratio of the two hydrocarbon hybrids are systematically varied from 100% of octane, 70%, 50%, 30% to 0% (with respect to pure DEB membrane) and PWA was doped in the membrane either at 10 wt. % and 20 wt.%, respectively. The conductivity of the binary hybrid was found to be exceeding 10^{-2} S/cm in spite of the mixing ratio and PWA doping ratio. The maximum conductivity was found in the pure octane hybrid membrane with 10 wt.% PWA doping ratio which has 3×10^{-2} S/cm. The hydrocarbon hybrid membrane based on octane, hexane or DEB has superior proton conducting property at an application level to PEFC.

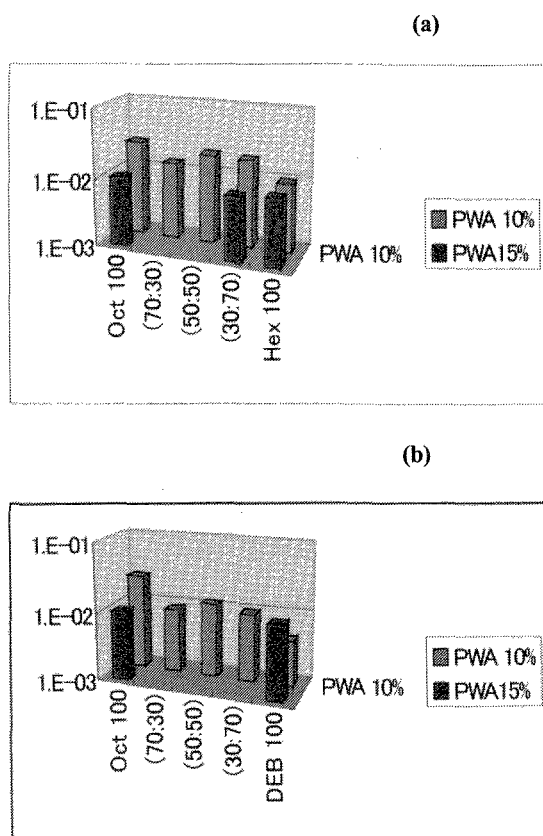


Figure 4 Proton conductivities of the binary membranes of (a) octane/hexane (Oct/Hex) hybrids and (b) octane/diethylbenzene (Oct/DEB) hybrids, respectively.

Figure 5 shows the proton conductivity of the pure DEB hybrid membrane with different PWA doping ratio from 5 mol.% to 20 mol. % at 160°C under saturated humidities. As the water vapor pressure increased rapidly above a boiling point of water, the pressure in the measuring cell at 160 °C was approximately 0.6 MPa in this experiment. The conductivity of the membrane with 5 mol. % PWA

did not decrease for more than 7 hours even at 160°C, while that of the membrane doped with more than 10 mol. % PWA gradually decreased after 7 hours. The DEB membrane with 5 mol. % was found to possess thermal stability even at 160°C.

The stable conductivity above the water boiling temperature is of primarily importance for high temperature operation of PEFCs and the hybrid membranes presented in the work show large proton conductivities and stability at elevated temperatures. The conductivities of the membranes were modified by varying the molecular structures and PWA doping ratios. The understanding of the proton conducting mechanism of the amphiphilic hydrocarbon hybrids is necessary for fast proton conduction with affordable thermal stability.

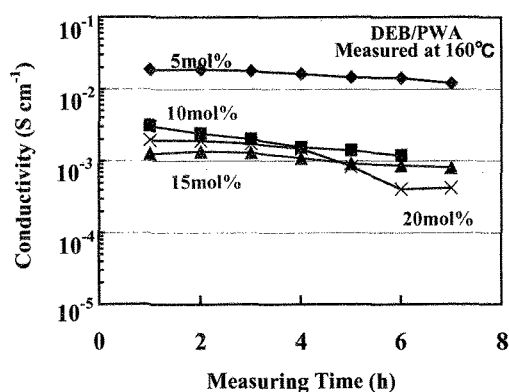


Figure 5 The proton conductivity of the pure DEB hybrid membrane with different PWA doping ratio from 5 mol.% to 20 mol. % at 160°C under saturated humidities

4. CONCLUSION

Proton conducting organic/inorganic nano-hybrid amphiphilic materials have been synthesized by the sol-gel processing of bridged polysilsesquioxanes, where the organic component of the building blocks are flexible hydrocarbons such as octane, hexane or diethylbenzene. The hybrid membrane consists of binary mixture of those hybrids doped with heteropolyacids (PWA) exhibiting large proton conductivities ($>10^{-2}$ S cm⁻¹). Also, the conductivity of DEB hybrid was stable at 160°C under saturated humidity. The conductivity of the hydrocarbon hybrid membrane can be tailored by varying the molecular structure of the organic bridges and the equivalent weight of PWA incorporated in the membrane. The understanding of proton conducting mechanism of the hybrids is necessary for fast ionic conduction of the thermally tolerant hybrid membranes. The conductivity exceeding 1×10^{-2} S cm⁻¹ level is an application level for intermediate temperature operation of PEFCs. The hydrocarbon based organic/inorganic hybrids in this work suggests the presence of a robust conductive channel structure within the flexible macromolecules.

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