

NOVEL INORGANIC/ORGANIC HYBRID ELECTROLYTE MEMBRANES

Zhiwei Yang, Decio Coutinho, Fangxia Feng, John P. Ferraris*,
Kenneth J. Balkus Jr.*

Department of Chemistry and The UTD Nanotech Institute,
University of Texas at Dallas
Richardson, Texas 75083-0688, USA

Introduction

Proton exchange membrane fuel cells (PEMFCs) hold promise as next generation clean energy sources for transportation as well as small-scale stationary power generation. The advantages of PEMFCs include high power density, fast startup and immediate response for power demand change.¹ Recently, the interest in high temperature (>130 °C) PEMFCs has grown because of possible advantages over low temperature PEMFCs. These include the enhanced ability of the FC system to directly use reformed fuels by increasing catalyst tolerance of impurities in the fuel feed stream, simplification of water-management for PEMFC systems, and reduction of radiator size in automotive applications due to enhanced rejection of heat by the FC system.

A key part of a PEMFC is the membrane that conducts protons and insulates electrons. Perfluorosulfonic acid (PFSA) polymers, such as Dupont's Nafion®, have been used as PEMs in PEMFCs for decades because of their superior performance and durability. The conduction of protons in the PFSA polymer is realized through the mobility of H⁺-nH₂O clusters among the -SO₃⁻ end groups, called the vehicular mechanism,^{2,3} which requires the PFSA polymers to be fully hydrated to perform well. This limits their applications under ambient atmosphere and elevated temperature (>100 °C) conditions. The previous efforts for high temperature PEM development mainly include modifying PFSA by compositing with hygroscopic materials and developing novel aromatic-based polymers, which directly incorporate sulfonic acid groups. Since H⁺ conduction in these membranes still depends on water (vehicular mechanism), they always suffer from low H⁺ conductivity at elevated temperature and low to zero humidity conditions because of the water loss, and/or swelling in the presence of water.

In recent years, Brønsted acid-base systems such as organic amine/ trifluoromethanesulfonimide (HTFSI) melting salts have been reported to be highly proton conducting at elevated temperatures (100–200 °C) and water-free conditions. The H⁺ conduction of these electrolytes could result from hopping of H⁺ from one amine/acid active site to another without transport of small molecules (Grotthuss mechanism).^{3,4}

In this study, novel inorganic/organic hybrid membranes containing immobilized amine/HTFSI groups were explored. Considering the activation energy of proton transport could depend upon the distance between the active sites as well as nature of electrolytes, a higher density of the active functional groups was introduced into the membranes to reduce the distance among active sites. The membranes are comprised of a 3-dimensional cross-linked silicon-oxygen backbone and organic amine groups. The silicon-oxygen backbone, which is stable to free radical attack, provides the PEM with the necessary thermal/chemical/mechanical properties. The organic amine groups were doped with HTFSI to form H⁺ conducting sites. The thermal stability and proton conductivities of these novel membranes were studied using TGA and ac impedance.

Experimental

Preparation of membranes.

HTFSI-doped PEI/SiO₂ membranes: Polyethylenimine (PEI) (linear, M.W. = 215K, prepared according to literature method⁵) was dissolved in absolute ethanol to form 10wt% solution. 3-glycidyl-oxypolytrimethoxysilane (GLYMO) (97%, Fluka, 1:1 weight ratio vs. PEI) was added and stirred for ½ hour at room temperature. The desired amount of HTFSI (50wt% in ethanol) was added dropwise and stirred for another ½ hour at room temperature. The resultant solution was cast on a level PTFE surface, air dried at room temperature for 1 day, and then annealed at 80 °C, ambient atmosphere overnight to form a freestanding, flexible membrane.

Polysilsesquioxane membranes with amine/HTFSI groups: Three kinds of membranes comprising different types of organic amines were prepared through sol-gel processes by using N-[3-(trimethoxysilyl)propyl]-ethylenediamine (EDATMS) (97%, Aldrich), N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (IPTES) (Gelest Inc.) and N-[3-(trimethoxysilyl)propyl]-polyethylenimine hydrochloride (PEITMS) (Aldrich), respectively. In a typical membrane preparation, 0.5 g of IPTES was dissolved in 1 ml of methanol. 0.1 g of (GLYMO) (97%, Fluka) was added and stirred for overnight at room temperature. 1.3 g of HTFSI solution (50wt% in dry ethanol) was added and stirred for ~2 hours at room temperature. The resultant mixture was cast on a glass paper (HOVOSORB®, Hollingsworth & Vose Company), then dried in air for 2-3 days and annealed at 80 °C overnight to form a flexible membrane.

Thermal stability. The thermal decomposition of the membranes under O₂ atmosphere was evaluated by thermogravimetric analysis (TGA) using a Perkin Elmer Pyris 1 TGA. The heating rate was 10°C/min until no further weight loss was detected.

Proton conductivity measurements. Pt black (fuel cell grade, E-TEK) was symmetrically deposited on both sides of the membrane with a loading of ~5 mg/cm², followed by hot-pressing at ~85 °C and ~300 psig for 1-2 min to form crude MEA. The proton conductivities of MEA were measured by AC impedance using a PC controlled VoltaLab® PGZ301 (Radiometer Analytical S.A.) over the frequency range of 100 KHz to 0.1 Hz, using a 10 mV amplitude ac single. All measurements were carried out under ambient atmosphere. The experimental temperature and humidity were well controlled using a fuel cell testing station and 5 cm² single cell (Fuel Cell Technologies Inc.). The relative humidity of the cell was calculated from humidifier temperature against the cell temperature.

Results and Discussion

HTFSI-doped PEI/SiO₂ membrane. PEI has been chosen in this study because PEI has the highest amine density among the other polyamine polymers. Since the prepared linear PEI (cal. M.W.=215k) has a soft point of ~80 °C, GLYMO was used to cross-link PEI to increase its heat resistance. When mixed with PEI in alcohol solution, the epoxy ends of GLYMO covalently bonded to the amine groups of PEI, and the trimethoxysilane ends of GLYMO hydrolyzed and condensed together to form inorganic silica clusters through so called sol-gel processes, which greatly improved thermal stability of the composite membranes (Figure-1).⁶

Under water-free conditions, the proton conductivity of the membrane increased with increasing temperature, indicating that the proton conduction here follows Grotthuss mechanism only. Increasing relative humidity of the fuel cell operating atmosphere leads to an increase in the membrane's proton conductivity by introducing additional proton conduction through the vehicle mechanism (Figure 2).

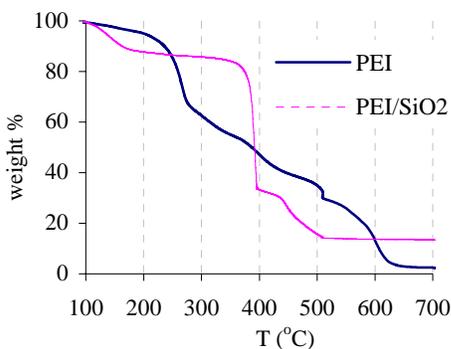


Figure 1. TGA of PEI polymer and GLYMO cross-linked PEI

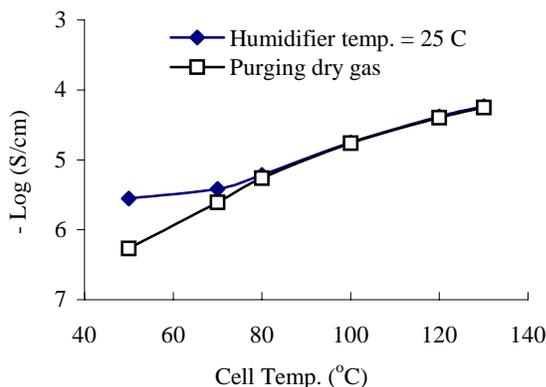


Figure 2. Proton conductivity of HTFSI doped PEI/SiO₂

Polysilsesquioxane membranes with amine/HTFSI groups.

The membrane precursors were organosilanes, which hydrolyze and condense to form a 3-dimensional cross-linked Si-O network with pendant organic amine groups that were doped with HTFSI to form proton-conducting sites. The mechanical properties of the membranes, especially flexibility and swelling in hot water, were greatly improved by adding GLYMO to increase the level of cross-linking. In this case, the epoxy end of GLYMO reacts with the amine groups to form covalent bonds, while the trimethoxysilane end of GLYMO hydrolyzes and condenses with the silane through a sol-gel process. The prepared membranes exhibited good thermal stability in an O₂ atmosphere (Figure 3), and hot water.

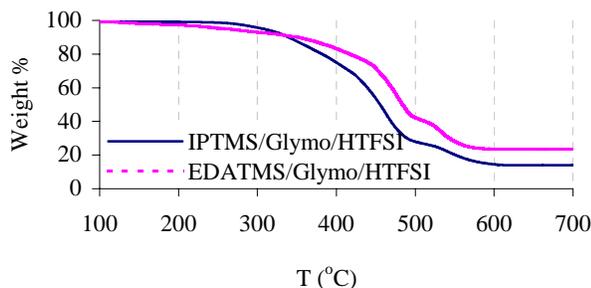


Figure 3. TGA of polysilsesquioxane hybrid membranes

Figure 4 shows the proton conductivities of an IPTES/GLYMO/HTFSI membrane with the corresponding molar ratio of 1.0 / 0.1 / 0.6 (per nitrogen site / GLYMO / HTFSI). Under water-free conditions, the membrane showed excellent proton conductivity, which increases with temperature, reaching a maximum of 10⁻³ S/cm at 130°C, while under fully hydrated conditions, the proton conductivity increased by ~1 order of magnitude. The proton conductivity of the membranes was also affected by GLYMO content and doping level. An increase of GLYMO content results in better mechanical strength but less proton conductivity. An increase in HTFSI content results in an increase in the doping level of organic amine groups, and a better proton conductivity but less mechanical strength. Membranes made from EDATMS/GLYMO/HTFSI and PEITMS/GLYMO/HTFSI showed similar behavior as IPTES/GLYMO/HTFSI membranes.

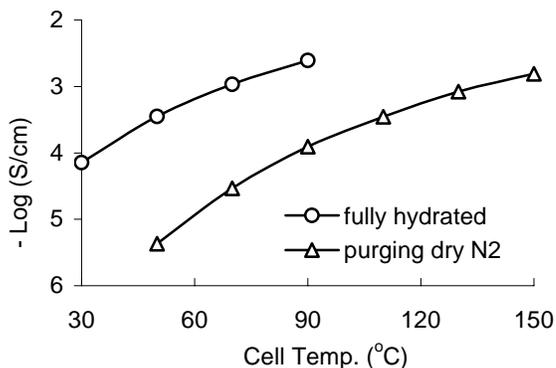


Figure 4. Proton conductivity of polysilsesquioxane membrane comprising IPTES/GLYMO/HTFSI in molar ratio of 1.0 / 0.1 / 0.6

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