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Methods for modifying proton exchange membranes using the sol–gel process

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Abstract

Over the past 20 years, sol–gel processing has expanded into organic–inorganic hybrid materials. This expansion has benefited from the collaborations between the polymers community and the ceramics community, and the discovery that in many instances sol–gel processing and polymer processing are compatible. An active participant in this field has been Dr James E. Mark [Mark JE. Heterog Chem Rev 1996;3:307–320], and his accomplishments deserve this tribute. One example, which derives from his work in organically-modified silicates (ORMOSILS), is hybrid membranes for fuel cells. We present some recent progress in synthesis of hybrid membranes involving Nafion. These membranes have been prepared by infiltration and recasting, and contain silicates, phosphosilicates, zirconium phosphosilicates and titanosilicates.
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1. Introduction

Proton-exchange membrane fuel cells (PEMFC) represent an alternative to internal combustion and diesel engines for cars, trucks and buses [2]. Fuel cells convert chemical energy directly to electrical energy using fixed electrodes and, in this case, a proton-conducting electrolyte. PEMFCs operate at high efficiencies when using pure hydrogen fuel, but have serious problems when using hydrogen obtained from reformed hydrocarbons. For example, the problem with methanol–water reformers is that the reaction is often incomplete, leaving small concentrations of carbon monoxide in the fuel stream. Carbon monoxide is a poison for the fuel cell catalyst [3–5]. One way to reduce the CO poisoning problem is to operate at higher temperature [6].

Another problem is water management. The proton conductivity of the membrane increases linearly with the water content, with the highest conductivity corresponding to a fully hydrated membrane. While it is desirable to operate a fuel cell at a temperature above the boiling point of water from the standpoint of lower susceptibility to CO poisoning, the membranes lose conductivity due to drying. Membrane dehydration also causes the membrane to shrink, which reduces the contact between the electrodes and membrane, leading to the crossover of the reactant gases. Since, the vapor pressure of water increases rapidly above 100 °C, the total pressure needed to maintain hydration increases dramatically. Clearly, further developments in PEMFCs are needed before they see wide scale use.

2. Proton exchange membranes

By far the most common proton-exchange membrane is the polymer Nafion. Nafion is the trade mark (produced by DuPont) of a perfluorinated material composed of carbon–fluorine backbone chains and perfluoro side chains with sulfonic acid ion-exchange groups:

$$(CF_2\text{-}CF_2)_x \text{—} (CF\text{-}CF_2) \text{—}$$
$$|$$
$$O$$
$$|$$
$$(CF_2\text{-}CF)_y \text{—} (CF_2)_z \text{—} SO_3^- M^+$$
$$|$$
$$CF_3$$
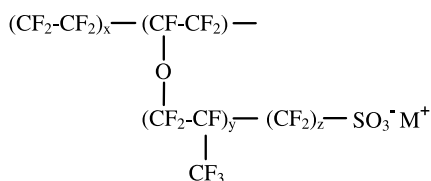
where M is either a metal cation in the neutralized form or a proton in the acid form. The favorable properties of this polymer lie in the combination of the high hydrophobicity of the perfluoronated polymer backbone and the high hydrophilicity of the sulfonic acid branch. The hydration water of the hydrophilic branches provides high proton conductivity in the presence of water.

Although the exact structure is not known, Nafion is modeled typically by a three-zone pore model. Interconnecting channels within the polymer contain (i) a low dielectric region with the hydrophobic fluorocarbon polymer matrix, (ii) a high dielectric region containing ion clusters with the sulfonate exchange sites, counterions, and sorbed water, and (iii) an interfacial region containing the pendant side chains of the sulfonate groups and a small amount of water. The hydration water is composed of three water molecules per sulfonic acid group that form the primary hydration shell. A second phase is located in the nanopores between the hydrated, sulfonated polymeric backbone. The structure is shown schematically in Fig. 1.

The activation enthalpy for water diffusion in Nafion membranes with water contents higher than required for the primary hydration shell is nearly the same as that in pure water. The proton conductivity for Nafion roughly follows the water diffusion coefficient, i.e. the conductivity is provided by the diffusion of hydrated protons such as H_3O^+ and $H_5O_2^+$ [7–9].

The practical problem encountered in PEMFC is keeping the membrane wet under operating conditions. The performance of the PEMFC improves with increasing temperature until 90 °C, which reflects a decrease in the internal resistance of the cell. This decrease is due largely to the decrease in ohmic resistance of the electrolyte. Mass transport, which is limited (i) by diffusion of reactants through the PEMFC assembly to the active catalyst (Pt) sites, (ii) by the movement of protons from the anode to the cathode, and (iii) by the removal of product water, is improved with increases in temperature.

3. Nafion/sol–gel hybrids

To solve both the CO poisoning and the water management problems, there have been numerous efforts to improve Nafion through the incorporation of hydrophilic metal oxides. Among these efforts, sol–gel processing has lead to some promising results. Nafion/sol–gel composites have been prepared via (i) infiltration of Nafion with sol–gel solutions, (ii) mixing sol–gel and Nafion solutions, and (iii) impregnation of sol–gel porous material with Nafion solutions. The three approaches are shown schematically in Fig. 2.

3.1. Infiltration

3.1.1. With silicon alkoxides

Mauritz et al. have investigated the preparation of Nafion/SiO_2 composites by infiltration of Nafion membranes with silicon alkoxides. They exploited the fact that the pendant $SO_3^- H^+$ group clusters catalyze the sol–gel reaction. In their procedure, a Nafion membrane is swelled in an alcohol/water solution. A mixture of tetraethylorthosilicate (TEOS) and alcohol is added to the swelling solution containing the Nafion membrane, where TEOS molecules presumably migrate to the clusters. After the sol–gel reactions, the in situ inorganic phase is cured. This is
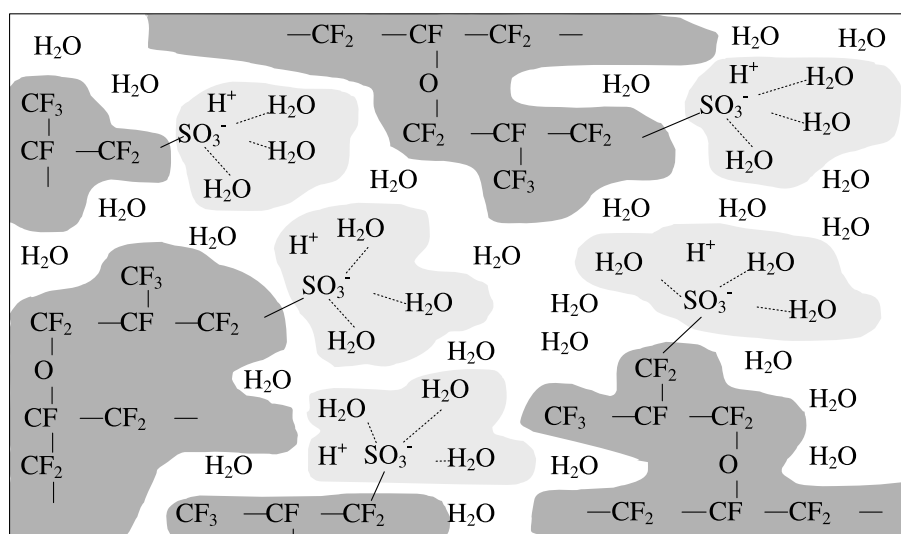

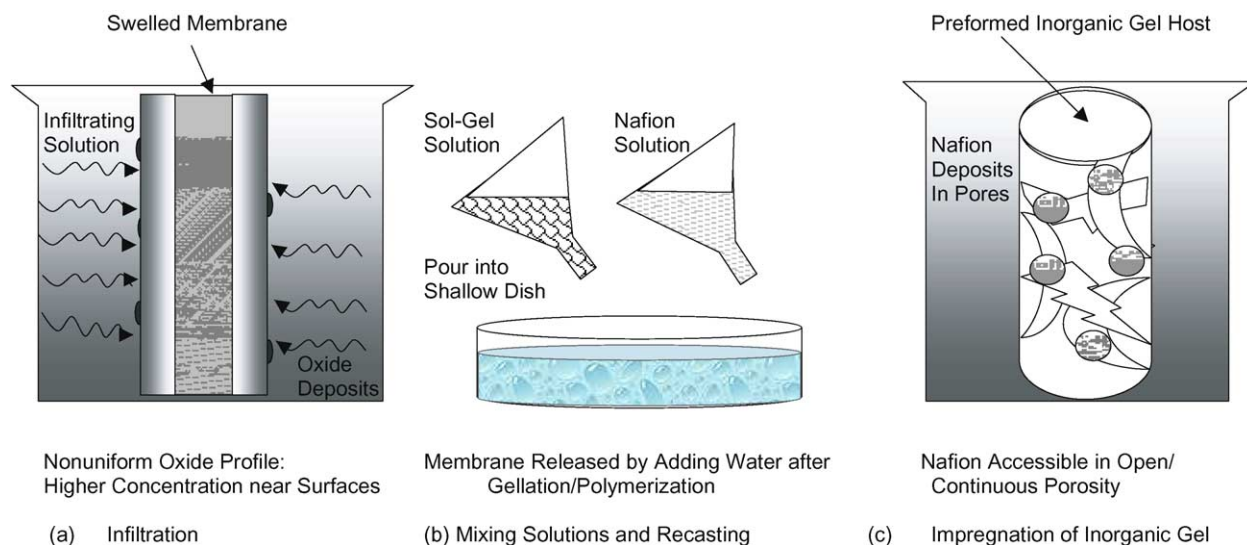Fig. 1. Schematic of the chemical make-up of a Nafion Membrane.

Fig. 2. Schematics of preparation methods for Nafion/sol–gel hybrids, by (a) infiltration, (b) mixing solutions and recasting, and (c) impregnation of inorganic gel.

accomplished by placing the membrane in a vacuum oven at 100 °C, where the solvents, alcohol and water evaporate and the condensation of SiOH groups proceeds [10].

In Nafion 117 (1100 equivalent wt) the weight uptake of the dried samples increases linearly with immersion time [11–13]. This suggests that as immersion time increases the SiO_2 begins to percolate through the Nafion. However, a significant amount of SiO_2 deposits on the surface, making it necessary to clean the surfaces of the membranes with alcohol after the immersion process to avoid forming surface layers of silica. Chemical analysis shows a profile across the membrane thickness with greater SiO_2 concentration near the surface, decreasing to a minimum in the middle [13]. This gradient may be reduced using an acid-catalyzed, pre-hydrolyzed silicon alkoxide solution in alcohol, so that partially hydrolyzed species, such as $(RO)_{4-x}Si(OH)_x$ molecules, migrate to the polar clusters of Nafion at the same time that the membrane is swelled. A slight concentration gradient is hard to avoid because of the difficulty of diffusion in the narrow channels of Nafion membrane.

Nafion/SiO_2 composites showed a higher water uptake at room temperature ($\sim 20\%$) compared with unfilled Nafion ($\sim 15\%$) [14]. Presumably, the sol–gel silica provides a large number of hydroxyl groups that tie up water molecules. The hydrophobicity of the fluorocarbon backbone and pendant side chains appears to be reduced by the incorporation of SiO_2.

3.1.2. With other metal alkoxides

Nafion/ZrO_2 asymmetric composites were obtained by unidirectional infiltration of Nafion membranes with tetra-butylzirconate (TBZ) solutions [15]. The experimental procedure was first immersion in solutions of water–ethanol to swell the Nafion membranes, and then immersion in TBZ–ethanol solutions. A similar behavior, with high metal concentration near the surfaces, was obtained with Nafion/SiO_2–TiO_2 composites using tetrabutoxytitanate (TBT)–TEOS solutions after the Nafion membranes were swollen with water and propanol [16]. However, the preparation of Nafion/SiO_2–Al_2O_3 under similar conditions using TEOS and tri-sec-butoxyaluminium (ASB) produces relatively uniform Al profiles [16]. While ASB is very reactive, the uniform profile in this case may be due to the high diffusivity of ASB within the Nafion. Another scheme consisted of first infiltration with TEOS–propanol solutions, and then a second infiltration with TBT–propanol solutions to create titanium oxide shells on SiO_2 nanoparticles [17].

3.1.3. With ORMOSILS

ORMOSIL nanophases can be formed within a Nafion template. In one case, an ORMOSIL phase was generated with TEOS, diethoxydimethylsilane (DEDMS) and others alkylalkoxides, followed by infiltration of Nafion membranes. The membranes were swollen in methanol–water solutions before premixed TEOS–DEDMS–methanol solutions were introduced [18,19]. The water uptake of these Nafion/ORMOSIL composites was smaller than that of pure Nafion and Nafion/SiO_2 composites due to the lower hydrophilicity of the ORMOSIL phase.

Another modification consisted of infiltration with DEDMS or ethoxytrimethylsilane (ETMS) to react with the residual SiOH groups of nanoparticles of silica obtained with TEOS [20,21]. Nanoscale phase separation was detected when incorporated SiO_2 particles were reacted with monofunctional ETMS. In contrast, reaction with difunctional DEDMS generated co-continuous networks.

3.2. Mixing solutions and recasting

Nafion/SiO$_2$ membranes also can be prepared using Nafion solutions and silicon alkoxides in a mutual solvent. The mixed solution is cast into shallow containers and dried at ambient temperature. This procedure allows the incorporation of continuously increasing amounts of silica. With high silica (>50%), the films are transparent but brittle. Since, the composites are formed from a mixed solution, instead of infiltrating a Nafion film, the silica phase is not restricted to the clusters of Nafion. When part of the TEOS is substituted by 1,1,3,3-tetramethyl-1,3-diethoxy disiloxane (TMDES), phase separation, higher flexibility and higher ionic conductivity are observed [22,23].

3.3. Impregnation in inorganic gel

Finally, particles of Nafion/SiO$_2$ nanocomposites have been obtained by capturing Nafion solutions in silicon alkoxides [24,25] and preformed gels [26]. The Nafion phase (20–60 nm) is trapped within a porous silica network. By controlling the variables of the process (composition, pH, drying), the resulting material can have a wide range of surface area (85–560 m^2/g) and pore diameter (25–2.1 nm), and highly dispersed Nafion is readily accessible to reactants.

4. Rutgers work with phosphate-containing gels

Silicophosphate gels by themselves have been shown to be fast proton-conducting solids [27–29]. The mobility of protons increases when the protons are strongly hydrogen-bonded. Compared with Si–OH, phosphate gels are better for high protonic conduction because the hydrogen ions are more strongly bound to the non-bridging oxygen. Also, the hydrogen in the P–OH group is more strongly hydrogen-bonded with water molecules, resulting in an increase in the temperature necessary to remove the water.

4.1. Infiltration

4.1.1. SiO$_2$–P$_2$O$_5$–ZrO$_2$ (SPZ)

We prepared sols of compositions 60SiO$_2$–30P$_2$O$_5$–10ZrO$_2$ and 70SiO$_2$–20P$_2$O$_5$–10ZrO$_2$ using Si(OC$_2$H$_5$)$_4$ (TEOS), tri-ethyl phosphite P(OC$_2$H$_5$)$_3$ (TEP), and zirconium-n-propoxide Zr(OC$_3$H$_7$)$_4$, (TPZ). The sol was prepared by mixing two solutions [30,31]. Solution A was prepared by mixing TEOS, half the volume of propanol (solvent), TEP, HCl (to control the pH at ~2) and water [molar ratio of water/(TEOS + TEP) = 2] at room temperature and stirred for 1 h. Solution B was prepared by mixing TPZ, the other half of the propanol and acetylacetone (molar ratio of acetylacetone/TPZ = 1) at room temperature and stirred for 1 h. Both solutions were subsequently mixed together and stirred for 1 h. The remaining water was added

drop by drop, and then the solution was stirred for 15 min. The sol has a concentration of 70 g of solid per liter, and a final molar ratio of water/precursors = 5.5.

The preparation of the infiltrated Nafion consisted of first pre-treating the Nafion membrane with 3 vol% H$_2$O$_2$ for 2 h at 80 °C, followed by 50 vol% H$_2$SO$_4$ for 2 h at 80 °C. The membrane was treated three times in distilled H$_2$O at 80 °C to remove any excess acid. After drying for 3 days at 80 °C, the membrane was immersed in the SiO$_2$–P$_2$O$_5$–ZrO$_2$ sol for 3 h. Then, the membrane surfaces were cleaned with propanol to avoid the formation of surface-attached silicate layers. After the treatment, the membrane was placed at room temperature for 5 h and then in an oven at 150 °C for 2 days. The dried infiltrated samples had an average weight increase of about 10%.

4.1.2. SiO$_2$–TiO$_2$–P$_2$O$_5$ (STP)

Solutions were prepared using Si(OC$_2$H$_5$)$_4$ (TEOS), Ti(OC$_4$H$_9$)$_4$ (TBT) and n-C$_4$H$_9$OH (butanol), the molar ratio of TEOS:TBT:butanol was 1.0:0.11:2.3 (nominal composition of 10TiO$_2$·90SiO$_2$ mol%). Nafion™ membranes of 2.0×1.5 cm^2 (125 µm dry thickness, ion exchange capacity of 1.0 meq/g) were first cleaned in 3% H$_2$O$_2$ at 80 °C for 1 h, then rinsed with distilled water and treated in 0.5 M H$_2$SO$_4$ for 1 h at 80 °C. Finally, they were rinsed several times in distilled water at 80 °C. After drying at room temperature under vacuum, the membranes were immersed into solutions. After several hours for the infiltration, the membranes were quickly rinsed with butanol, followed by in situ hydrolysis through immersion in a large volume (30 mL) of HCl solution (pH 2.1) at 50 °C for 30 min, and then in 30 mL of NH$_4$OH solution (pH 8.3) at 80 °C for 30 min. The hybrid membranes were then dried at 120 °C for 30 min. To remove the adsorbed NH$_3^+$ ions, membranes were treated as before with H$_2$SO$_4$ and water at 80 °C [32].

Based on previous results on phosphorus-containing gels [33], the 10TiO$_2$·90SiO$_2$ hybrid membranes were treated after infiltration in 4% phosphoric acid solution for 4 h at 70 °C to incorporate P–OH groups. The membranes were then rinsed in distilled water to remove excess acid. The membranes became somewhat brittle after treatment with phosphoric acid as compared with untreated 10TiO$_2$·90-90SiO$_2$/Nafion membranes. Crystalline α-Ti(HPO$_4$)$_2$·H$_2$O was confirmed inside the membrane from X-ray diffraction analysis.

4.1.3. Precipitates

In addition to silicates with titania and zirconia, we prepared silicates with phosphotungstates (H$_3$PW$_{12}$O$_{40}$). Samples containing silicates, including Nafion/SPZ, Nafion/STP, and Nafion/H$_3$PW$_{12}$O$_{40}$ are gel composites based on a silica network. We prepared Nafion membranes with zirconia–phosphate (ZrP) solutions by a process similar to the infiltration process described for SPZ and STP. However, Nafion/ZrP is structurally different, as ZrP is

particulate, albeit amorphous. In all cases the dry membranes weight was increased by 10–15% after infiltration, with the particulate ZrP samples showing somewhat higher weight gains [34].

4.2. Recasting

The preparation of the recast 90%wt Nafion™/10%wt 60SiO₂–30P₂O₅–10ZrO₂ membranes consisted first of mixing the Nafion™ solution with double its volume of *N,N*-dimethyl formamide at room temperature with stirring for 15 min. The sol was subsequently added and stirred at room temperature for 1 h. This mixture was cast in a Petri dish and heated at 80 °C for three days followed by 24 h at 150 °C. The recast composite membrane was detached from the Petri dish after addition of distilled water. Additionally, both infiltrated and recast membranes were treated with H_2O_2, H_2SO_4 and distilled H_2O, as described for the original Nafion™ membrane. The final cleaning process helped produce samples with reproducible behavior. The weight increase for recast membranes was variable, according to the proportions of the solutions [35].

5. Membranes in fuel cell tests

For a typical fuel cell experiment, commercial Pt/C fuel electrodes (ETEK Inc.) with a Pt loading of 0.4 mg/cm², were impregnated with 0.6 mg/cm² of Nafion (dry weight) by applying 12 mg/cm² of 5% Nafion solution with a brush. The electrode area was 5 cm². The membrane electrode assembly (MEA) was prepared by heating the electrode/membrane/electrode sandwich to 90 °C for 1 min in a Carver Hot-Press, followed by increasing the temperature to 130 °C for 1 min and finally hot-pressing the MEA at 130 °C and 2 MPa for 1 min. The MEA was positioned in a single cell test fixture, which was then installed in a fuel cell test station (Globetech Inc., GT-1000). The test station was equipped for the temperature-controlled humidification of the reactant gases (H_2, O_2 and air) and for the temperature control of the single cell.

For the performance evaluation of the PEMFC, the single cell was fed with humidified H_2 and O_2 at atmospheric pressure (reactant gas and water vapor pressure equal to 1 atm) and the temperature of the H_2 and O_2 humidifiers and of the single cell was raised slowly to 90 , 88 and 80 °C, respectively. During this period, the external load was maintained at a constant value of 0.1 Ω, to reach an optimal hydration of the membrane using the water produced in the single cell. After the single cell had reached stable conditions (i.e. current density remained constant over time at a fixed potential), cyclic voltammograms were recorded at a sweep range of 20 mV s^{-1} and in the range of 0.1–1 V vs. reversible hydrogen electrode (RHE) for 1 h. Cell potential vs. current density measurements were then

made at a relative humidity of 90–100%. The flow rates of gases were two times stoichiometric.

This preliminary study was carried out to know whether or not the incorporation of SiO_2–P_2O_5–ZrO_2 gel in Nafion enhances the current density at a fixed potential, for temperatures $> 130 °C$. By limiting the total pressure to 3 atm, the maximum operating temperature investigated was 140 °C since the vapor pressure of water at this temperature is 3.5 atm. In fact, we measured a significant improvement in the water management of the composite vs. the control Nafion membrane [36]. The higher current densities and lower resistances of the composite membrane can be attributed to the water retention characteristic of the SiO_2–P_2O_5–ZrO_2 gel. In addition, composite membranes were less susceptible to high temperature loss of proton conductivity than unmodified Nafion. These promising results are being investigated further.

6. Summary

Three preparation methods have been used to incorporate inorganic gels in Nafion membranes. In the first case, Nafion, with its ionic clusters and inter-cluster channels, allows in situ polymerization of inorganic or organically-modified inorganic nanophases. The morphology of Nafion has a direct influence on in situ formation of the inorganic phase, in view of the fact that the clusters are only 3–5 nm in size. The typical weight increase with infiltration is 10%. In the second case, the recast composites have the advantage of a completely homogeneous distribution of sol–gel oxides and Nafion, and the extent of the inorganic phase is not restricted to small clusters. The weight increase in recasting exceeds that for infiltration, and can be as high as 50%. In the third case, the impregnation of porous sol–gel materials with Nafion solutions exploits the potential of the sol–gel technique to produce controlled porosity and surface area.

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