NANOCOMPOSITE FUEL CELL MEMBRANES

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Introduction

Nanostructured polymers are synthesized from macromolecules demonstrating supramolecular interactions. Examples are: hydrogen bonding, hydrophobic interactions, organometallics, electrostatic interactions, liquid crystal polymers and van der Waals [1]. Composite membranes are prepared using polyimide (PI) and polybenzimidazole (PBI) with heteropolyacids (HPAs) [2]. Nanostructured PEMs may be prepared from supramolecular polymers and HPAs.

Nanocomposite membranes have been investigated by several groups [2-9]. Nanoporous tungstosilicate based on 12- phosphotungtic acid has been prepared using crosslinked linear polyethyleneimine as a polymer matrix [2]. Nanocomposites of Nafion and silica are being made using sol-gel process [3]. Heteropolyacids (HPAs) are used as inorganic proton conductors because they exhibit high proton conductivity but also are stable at high temperatures [4].

Surface Polymerization – covalently bonded polymers and supramolecular polymers

Most work on surface polymerization has involved covalent bonding of polymers to a particle surface. It is also of interest to investigate the use supramolecular polymers for surface polymerization. Surface polymerization has been widely done in with covalent bonding for silicon dioxide and Si- H groups. Germanium has also been surface polymerized by Xu et al [10] by covalently immobilized polymer brushes from surface-initiated ATRP. Well-defined polymer-Ge hybrids, consisting of covalently tethered polymer brushes of pentafluorostyrene (PFS), (2-dimethylamino)ethyl methacrylate (DMAEMA), and PFS-DMAEMA diblock copolymers, were prepared. This is a process for covalent bonding of an ATRP initiator monolayer on the Ge-H surface. Well-defined polymer-Ge hybrids could be readily prepared via surface-initiated ATRP on the substrates.

Membrane blends

Blended membranes are made so that the properties of both the polymers can be useful to the ultimate purpose of the membranes. Polyether sulfone (PES) have been blended with polymers such as polyvinylidenefluoride (PVDF), polyacrylonitrile, polyurethane, chitosan, cellulose acetate, sulfonated poly(ether ether ketone) (SPEEK) and poly (amide- imide) (PAI). The PAI blends with PES have been made to be used in ultrafiltration membranes [11]. Blended membranes were formed from SPEEK and PES and thermal degradation studies, glass transition temperature, proton conductivity and water uptake were studied for these blended membranes [12]. Blends have also been made with polybenzimidazole (PBI) and sulfonated partially fluorinated poly (arylene ether sulfone) [13]. Blends of PES with PBI have been made as a part of this project.

Surface polymerization

Polymer coating of heteropolyacids (HPA) is done in order to prevent the HPAs from being washed out of the membrane. In addition, functional groups attached to the polymer can provide enhancement of proton conductivity because they can be reacted with sulfonic acid.

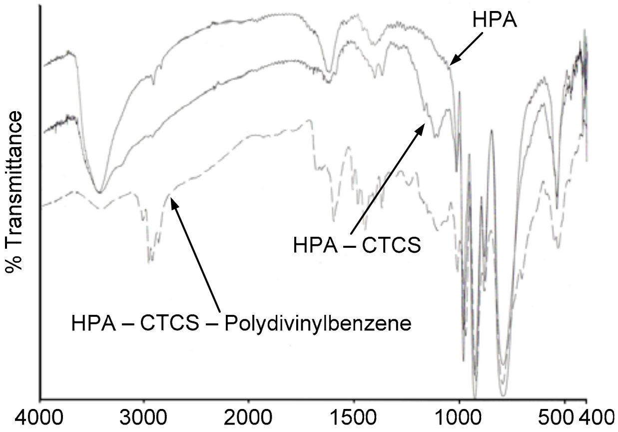

Figure 1 – FTIR of surface polymerized HPA.

Atom transfer radical polymerization (ATRP) was used for as a surface polymerization technique. The surface initiator is grafted onto the HPA surface and is initiated by electrons from the redox reaction of metal halide (CuBr) [14 –16]. Then, the monomer is initiated and followed by propagation and termination.

Polymer Sulfonation

The sulfonation of polyether can be done in two ways, in addition to making a sulfonated polymer from sulfonic groups attached to a monomer. The sulfonation can be achieved by either using chlorosulfonic acid in dichloroethane or using sulfur trioxide in dichloromethane [17]. Sulfonation can also be carried out by the reaction of the monomers with concentrated sulfuric acid [18]. The process with chlorosulfonic acid is carried out at room temperature. Sulfonation of vulcanized ethylene-propylene- diene terpolymer has been sulfonated by acetyl sulfate [19]. Acetyl sulfate was prepared by reacting acetic anhydride and sulfuric acid. Polyarylene ether sulfone was sulfonated by acetyl sulfate as well [20]. SPEEK membranes have also been prepared by sulfonation by chlorosulfonic acid in dichloroethane. Sulfur trioxide, a gas at room temperature, has been used in dichloromethane to sulfonate polyether sulfone pellets [21]. The polymer was dissolved in dichloromethane and stabilized sulfur trioxide was then added in dichloromethane under nitrogen atmosphere.

Results

Composite membranes and composite blends were prepared with PES and HPA. Three types of HPAs were used for the study. Phosphomolybdic acid, phosphotungstic acid and silicotungstic acid (SiW) were used to study the proton conductivity of the membranes. PES and PBI was dissolved in dimethylacetamide (DMAc) and followed by adding and mixing of HPA at 50-60^{0}C with specified weight ratio. The solution was poured in the mold and solvent was then evaporated in a vacuum oven at 80-100^{0}C. The blended membranes were acid doped in 85% phosphoric acid for 7 hours.

More permanent ways of sulfonation are being explored and the most appropriate methods to sulfonate the polymer are by reacting with acetyl sulfate or chlorosulfonic acid. The SiW could not be added to PES at greater than 50% by weight. The membrane, at even 50 %, was extremely brittle and had reached the saturation concentration of SiW.

Surface polymerization of SiW was done to investigate the effect of concentration of SiW on the membrane characteristics.

The surface polymerization procedure was as follows: SiW (16 g) was pulverized, sieved, and dried in a vacuum oven at 100 ^{o}C. Dried SiW particles (12 g) were added and reacted at 85 ^{o}C with 2-4(-chlorosulfonylphenyl)-ethytrichlorosilane (CTCS, 4 g)) for 36 hours in anhydrous toluene (110 g) as a solvent in inert gas (nitrogen). The mixture was then filtered and washed with anhydrous toluene in order to remove excess CTCS. The residue (SiW-CTCS) was dried in a vacuum oven at low temperature (50 °C) for 24 hours. Functionalized SiW-CTCS (6 g) was reacted with.

CuBr (0.06 g), $CuBr_2$ (0.03 g), Spartein (0.06 g), and monomer (divinylbenzene) in anhydrous toluene (60 g) at 85 ^{o}C for 24 hours under nitrogen.

Finally, the mixture was filtered, washed several times with anhydrous toluene and dried in a vacuum oven at low temperature (50 °C) prior to use.

Figure 2 – Surface-coated and non-surface-coated SiW composite (50 wt.%) PES membrane.

Membrane Characterization

The grafted surface initiator and polymer on the SiW was characterized using FTIR. The SiW sample was scanned from 400 to 4000 cm^{-1}. SiW, SiW – CTCS, and SiW – CTCS – polydivinylbenzene transmission data are shown in the **Figure 1** from the top to the bottom respectively. Comparing the SiW, SiW – CTCS curves, the peak is shifted at 1100 cm^{-1} which can be associated with the presence of surface initiator (CTCS) on the SiW. In addition, the peak is shifted at 2900 cm^{-1} on the SiW – CTCS – polydivinylbenzene if compared with SiW – CTCS which means the polymer has been attached onto the SiW surface through surface initiator. The HPA content within the composite membrane could be increased when the HPA was coated with polydivinylbenzene. The comparison of surface-coated (left) and non-surface-coated (right) SiW composite membrane pictures are shown in **Figure 2**. The higher quality of the surface coated SiW composite membrane indicates that the interface compatibility of polymer matrix and HPA may have been increased by the surface coating. The characterization of the composite membranes was done using an electrochemical impedance spectroscopy. The EIS plot of composite blended membrane with 60 wt. % phosphotungstic acid has been shown in **Figure 3**. This is a plot of real and imaginary impedance. The real impedance is the resistance while the Y- axis represents the imaginary impedance. Blended composite membrane with 40 % by wt. content of silicotungstic acid has conductivity of 1.2 x 10 $^{-2}$ S/cm with acid doping. It is expected to increase further after acid doping. The conductivities were measured from 1Hz to 1MHz at 700mV potential. The four point probe method was used to check for the conductivity of the membranes. The summary of the composite membranes conductivity is listed in Table 1. These values were found to be fairly less than Nafion®, whose conductivity is 0.1 S/cm [22]. The process of sulfonation is expected to increase the conductivity of these membranes.

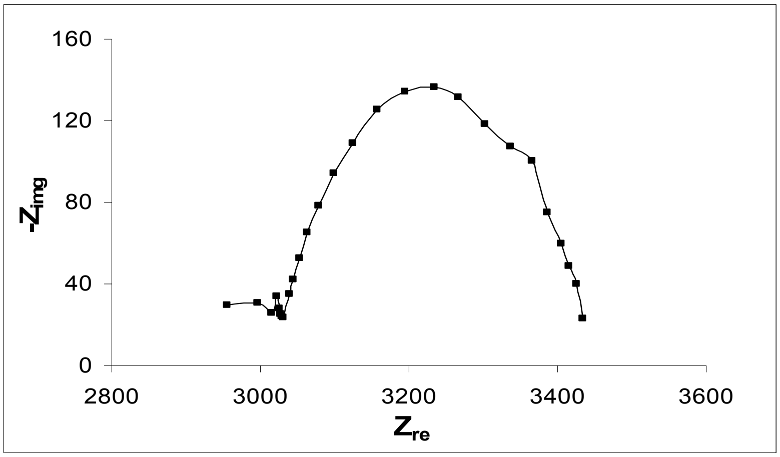

Figure 3 – Nyquist plot of 60 wt. % PWA – PES – 10%PBI (of PES) acid doped.

Future work

The SiW will be surface polymerized using ATRP with styrene as monomer. The surface polymerized SiW can be sulfonated through the reaction with acetyl sulfate in dichloromethane at 40 °C through the styrene functional in order to increase the conductivity [23]. The synthesized composite membrane will be tested using the single test cell for generating current – voltage polarization curve. This test will be done at 20% - 80 % RH and 25°C – 120 °C.

A single membrane PEM fuel cell has been designed. This fuel cell has an active area of 25cm^2, so commercially available membrane electrode assembles can be used for testing. The flow paths in the fuel cell were designed to allow flexibility with the monopolar plate flow patterns. They can accommodate any flow pattern without changing the location of the ports or sizes. The bipolar plates can also be stacked without changing anything to analyze a stacked system. Testing will be done with this prototype on a commercially available membrane electrode assembly (MEA) to achieve a standardized system. From that point we will create our own MEA using a new membrane. If that test is a success we are then going to move onto the monopolar plates by changing the flow patterns, coating, and material type. The goal of these experiments is to find the highest power density possible. While looking at the plate designs and flow patterns we will look at the gas diffusion layer (GDL) and catalyst layer to find the correct amounts to use with the new membrane.

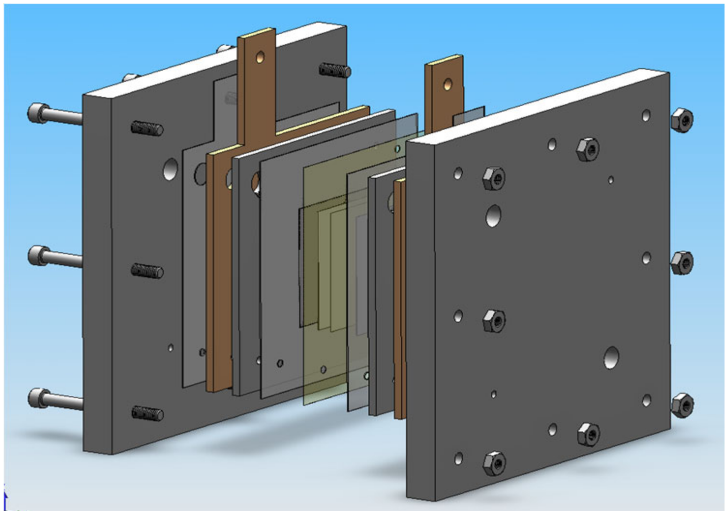

Figure 4 – Representation of MEA.

The Computational Fluid Dynamics (CFD) modeling of the existing fuel cell is being developed using commercial code FLUENT. The two-dimensional geometry of the flow field for a homogeneous single phase fluid, either hydrogen or oxygen is created, meshing and its optimization for the flow conditions is currently in progress. Meshing is one of the most important steps of CFD modeling. It should capture the details of the flow field at locations with high gradient such as boundary layer and corners using small enough elements while minimizing the number of elements used in order to keep computational time at a reasonable level. GAMBIT, the preprocessor to FLUENT, is used for construction of main flow field geometry, mesh generation and optimization. Once flow through this main 2-D geometry is successfully simulated it will be expanded to 3-D model and generalized to multi phase flow.

Overall operation of the fuel cell requires simulation of electrochemical reactions, modeling MEA and prediction of the power generation. The representation of the MEA is shown in Figure 4. For this purpose FLUENT add-on module, PEMC is being evaluated. The predictions of the completed model will be compared with the experimental measurements using the existing fuel in our laboratory. Initial model and testing will use a well studied and characterized commercially available Nafion®

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