

# SUPRAMOLECULAR FUEL CELL MEMBRANES

A. Fuchs<sup>1</sup>, J. Sutrisno<sup>1</sup>, C. Evrensel<sup>2</sup>, F. Gordaninejad<sup>2</sup>, B. Kavlicoglu<sup>2</sup>, Y. Liu<sup>2</sup>

1) Chemical Engineering Department, University of Nevada, Reno – Nevada, USA

2) Mechanical Engineering Department, University of Nevada, Reno – Nevada, USA

## Introduction

The development of fuel cell technology depends on the availability and low cost of high quality proton exchange membranes (PEMs). The trend in PEMs research includes: high temperature operation, low humidity, and high proton conductivity. A variety of polymers are being considered to improve the performance of the membranes so that they meet the expectations of DOE's 2020 projections.

The currently available PEMs are suitable for use at maximum 80°C because of the requirement of the presence of water for proton conductivity. However, for emerging applications, a fuel cell operating at temperatures as high as 120 °C is required. This can possibly be achieved by creating novel PEMs. Supramolecular polymers are being investigated extensively and may be conjugated with heteropolyacids (HPAs) to prepare high performance PEMs. Metal coordinated polymers, such as: ruthenium or zinc bipyridine polybenzimidazole (PBI) will be synthesized during this project. Self assembled supramolecular structures are formed by the interaction of metal (Ru or Zn) and the nitrogen heterocycle from bipyridine PBI [1]. In addition, hydrophilic – hydrophobic blocks of polymer backbones also create supramolecular interactions, resulting in bi-directional proton conductivity.

Membrane characterization techniques including: differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), electrochemical impedance spectroscopy (EIS), rheology and single membrane test cell studies will be done as part of this project.

## ***Nanostructured Composite PEMs***

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 [2]. Composite membranes are prepared using polyimide (PI) and polybenzimidazole (PBI) with heteropolyacids (HPAs) [3]. Nanostructured PEMs may be prepared from supramolecular polymers and HPAs.

## ***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 [4] 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.

Surface polymerization with supramolecular polymers has been used for the fabrication of thin films with metallo-supramolecular polyelectrolytes (MEPE) for stimuli responsive layers as well as electrochromic windows. Investigation of the self-assembly of three-dimensional MEPE networks on the surface as a means to control the amount deposited were conducted by adjusting the cross-linking degree. Self assembled iron(II) and 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene (tpy-ph-tpy) on quartz slides have resulted in homogeneous thin layers. A base layer of polyethyleneimine (PEI) / poly (styrene-sulfonate) (PSS) was used for a well defined starting condition [5].

### ***Supramolecular PEMs - Polybenzimidazole***

PBI (5 wt.%) was dissolved in N,N-dimethylacetamide (DMAc) or 1-Methyl-2-pyrrolidone (NMP), and mixed together with sulfonated polymer. 3-pentadecylphenol (PDP, 1-5% of PBI-sulfonated polyamide) was added and mixed to dissolve PDP. Then, solution was evaporated and dried in a vacuum oven at 80 oC for 24 hours to form a membrane.

## **Results and Discussion**

The focus of our efforts is the development of a nanocomposite membrane with HPA and supramolecular polymers. The first report consisted of differential scanning calorimeter (DSC) results of a bipyridine PBI. The results indicated that the bipyridine PBI had a thermal transition of 357.2<sup>0</sup> C. The synthesis method of the bipyridine PBI was described in the earlier bimonthly report.

During the course of this research dissolving the bipyridine PBI was investigated using various solvents including: dimethyl acetamide (DMAc), n- methyl pyrrolidone (NMP) and dimethyl formamide (DMF). DMAc was found to be most commonly used in the literature and was the most effective, although high concentrations of PBI could not be achieved.

### ***Characterization of HPA***

The diameter of silicotungstic acid particles was measured using Nikon Eclipse LV100 microscope. Figure 2 shows that the particulate sizes ranged from 2.7 to 3.8 microns.

### ***PBI and Inorganic Proton Conductor Composite Membrane***

In order to enhance the proton conductivity, inorganic proton conductors were used to prepare composites with the supramolecular PEMs. The inorganic proton conductor also improved the mechanical strength of the composite PEM [6- 14]. In addition to the curve

shown on the left hand side, the peak on the right side represents the Warburg impedance behavior. The conductivity for this system was  $1.4 \times 10^{-5}$  S/cm which is substantially lower than the Nafion™ membrane. In addition, these membranes were very brittle.

### ***Supramolecular PEMs - Polybenzimidazole***

The synthesized polymer is supramolecular because of hydrophobic / hydrophilic interactions between the sulfonated polymer (hydrophilic) and the PBI (hydrophobic) segments. These polymers are expected to form controlled “lamellar” or layered structures by adding the amphiphile (PDP). This is anticipated to provide an additional level of hierarchical design.

There is also hydrogen bonding between the amphiphile (PDP) and the sulfonic acid group. Proton transfer occurs between the sulfonic acid group and the nitrogen heterocycle in PBI. We believe that phase separation takes place in the hydrophobic / hydrophilic system, providing the opportunity for enhanced directional proton conductivity. Mechanical shearing provides orientation of within the membrane. Channels of hydrophobic and hydrophilic regions are formed during shearing.

These regions provide different proton conductivities in the radial and tangential directions. We speculate that because of the long chained nature of the polymers that a lamellar or “onion-skin” structure of both the hydrophobic and hydrophilic regions is developed during shearing. Therefore enhanced proton conductivity results tangentially. It is more difficult for protons to cross over the hydrophobic bands formed within the membrane. The proton conductivities measured were:  $3.30 \cdot 10^{-3}$  S/cm for the tangential direction and  $1.03 \cdot 10^{-3}$  S/cm for the radial direction.

### ***Composite Membranes - Polyamic Acid and Organoclay***

Composite membranes were synthesized from polyamic acid and sulfuric acid treated organoclay. This system was investigated in order to improve the proton conductivity of the composite membrane. Organoclay was chosen as reinforcement because it is known to provide high quality composite PEM membranes [8-16]. The sample of composite membranes is shown in Figure 10. In our case, the organoclay was first treated with sulfuric acid in order to increase the conductivity. In imidization process the first step involves reaction between the dianhydride and diamine. The second step is the thermal imidization step and ring closing. This approach was used for synthesis of the composite membrane.

The proton conductivity as a function of temperature from 25 – 80 °C. The proton conductivity increases from  $1.59 \cdot 10^{-2}$  S/cm (25 °C) to  $2.56 \cdot 10^{-2}$  S/cm (80 °C). This is the highest proton conductivity achieved in our experiments to date. This approach may have applications for anhydrous operation.

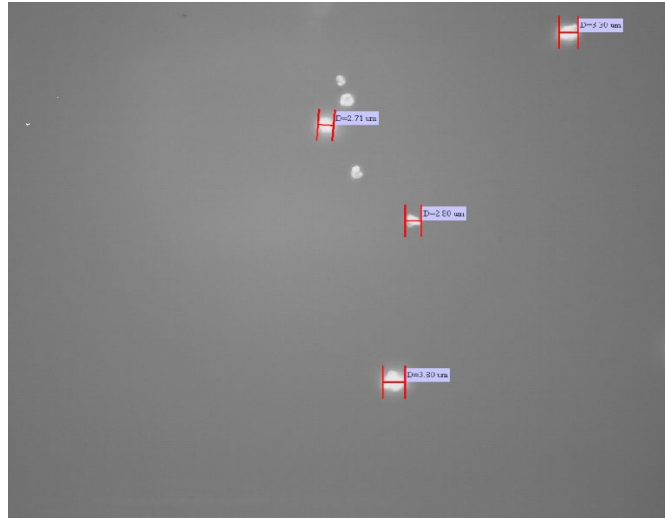


Figure1: Microscopic image of finely ground silicotungstic acid

The surface initiator will be immobilized on the HPA using silane through the formation of silanol group that is covalently bonded to the HPA surface. In the ATRP technique, copper based metal and sparteine will be used as metal catalyst and ligand respectively. The goal of this surface polymerization is to prevent the HPA from being washed out with water during fuel cell operation.

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