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Development of a Hyperbranched Fuel Cell Membrane Material for Improved Proton Conductivity

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Abstract: A new material for proton conducting membrane with a higher proton transport but reduced water transport is being developed. The new material optimizes proton channel formation, this reducing water transport at the same time. Different proton transporting groups along with different gas flowing channels are examined as well. To meet the goals we design, synthesize, and simulate various proton transporting groups using MD techniques for faster optimization, which in turn helps to synthesize and test only promising structures in the laboratory. At the same time, computer modeling is used to improve the fuel cell system at various operating conditions, specifically by changing a variety of membrane parameters (properties) in the design units. This is compared to the results obtained with the newly-synthesized PEM membrane. A schematic of the synthesis of the hyperbranched, fluorinated polymer is described as well.

Keywords: fuel cell, proton exchange membrane, molecular dynamics modeling, proton transport, water transport, hyperbranched fluorinated polymers, proton conducting groups

Nomenclature

r_i	Radius of the ithparticle
D_at	Diffusion coefficient time
T	Temperature of the system, K
N	Number of particles
V	Volume
RT	Room temperature
TGA	Thermogravic Analysis

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Tg	Glass transition temperature
P	Pressure
fs	femtoseconds

Greek Symbols

θ	Mass density, gm/cc

Subscripts

0	Reference value

Notations

d/dt	Derivative

1 Introduction

In the 20^{th} century, the human population quadrupled and the primary power consumption increased 16-fold (McNeill J.R., 2000; Giner J. L. et al., 1989; Node M et. al., 1980; Modena S. et al., 1988). In order to solve the global energy crisis and alleviate environmental concerns, clean, sustainable, and renewable sources are needed to replace fossil fuels for use as automotive power supplies and for stationary as well as portable applications. Several properties make fuel cells attractive for electricity production, the major advantages being high efficiency and energy density (energy per unit weight of the power source), which makes them superior to batteries in portable equipment. To make them a practical source of energy for most applications, though, breakthroughs are needed to improve their performance and reduce their costs. One of the main distinctions between batteries and fuel cells is that in batteries energy is stored as chemical energy, but in fuel cells electricity is produced on demand.

One promising fuel cell is the hydrogen fuel cell (HFC) or proton exchange membrane fuel cell (PEMFC) (Gorte R.J, 2005). A fuel cell converts hydrogen (the fuel) into electricity using oxygen and catalysts without fossil fuels, combustion, or environment-harming emissions. A basic PEMFC device (Figure 1 Guvelioglu, Galip, 2006) consists of a thin polymer exchange membrane (PEM), which is sandwiched between two active catalyst layers and are backed by porous gas-distribution electrodes (carbon cloth). This entire assembly is called the membrane electrode assembly (MEA), and its typical thickness is roughly 0.5 - 0.8 mm. The PEM allows protons to pass through; electrons from hydrogen transit via an external circuit, creating direct current. At the cathode, the electrons combine with oxygen and protons, generating heat and water as the only products. Multiple fuel

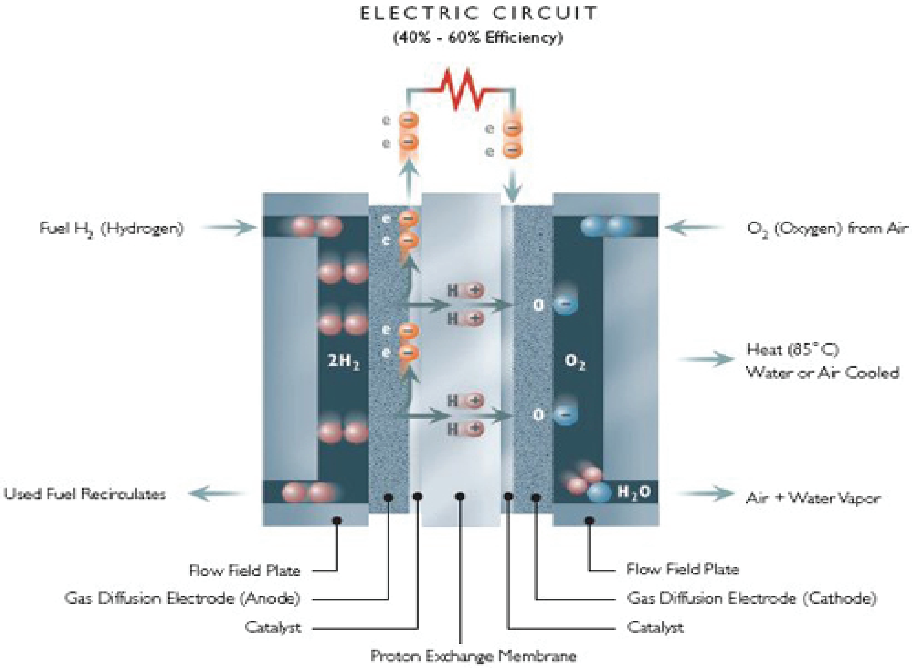


Figure 1: Internal operation of a PEMFC.

cell units are often combined into a fuel cell stack to provide enough energy for most applications.

There are several well-recognized limitations preventing PEMFC's from reaching their maximum capabilities (McNeill J.R., 2000; Hermann A., 2005). For instance, for DuPont's Nafion® membranes (sulfonated fluorocarbons), the standard PEM for fuel cell membranes (Sebastian P. J., 2005), high backpressure and relative humidity is required for operation above 80 ˚C, because efficient proton transport across the membrane only occurs in the present of water molecules (Kreuer Klaus-Dieter; Paddison Stephen J., 2004). The water, though, results in cathode flooding and thermal instability (Paddison S.J.; Elliott J.A., 2006), and flooding of the cathode destroys the catalyst needed for energy generation. Adding selective hygroscopic inorganic compounds has modestly extended the upper temperature limit (Eisenberg A , 1977), but a novel, high performance fuel cell membrane is yet to emerge due in part to the incomplete understanding of how polymer molecular chemistry and morphology determine the proton and water transport.

In our laboratories we started synthesizing an improved membrane, with particular emphasis on increased proton transport, decreased water transport, and improved incorporation of the catalyst layer into the PEM. The process begins with modeling studies conducted by the Molecular Modeling Center at CMU to identify fundamental parameters needed in a polymer membrane for lower-cost materials that offer the potential of improved performance. Hence, the route to such an effective membrane will be aided by a multiscale modeling that connects local chemical information, such as protogenic groups, side chains, and backbone structure, to proton and water transport. The new material is a hyperbranched, fluorinated polymer. The branching increases flexibility of the polymer chains and thus will allow for more effective phase separation between the proton transporting groups and the bulk of the membrane. This will lead to a more efficient formation of proton channels and reduces the amount of proton transporting groups located in the polymer matrix, instead of the channels. Because of that, less protogenic groups will be needed, which decreases the amount of water that will be conducted. The hyperbranched polymer will be strengthened by crosslinking, which allows for the control of the proton channel size at the same time. Additionally, crosslinking can be performed in the presence of either catalyst, thus the problem of catalyst loss due to non-adhesion of the membrane can be reduced.

1.1 Computer Modeling of Fuel Cell Membrane Materials and Fuel Cell Membranes

One of our goals is to contribute validated computational models that provide a nano- to microstructure-based description of the properties of fuel cell membrane materials, which helps to understand their behavior in various applications. A combination of modeling and experimentation has reduced the cost and accelerated the pace of building and understanding prototype systems. Here the fuel cell processes are described at the micro level: molecules of membrane materials and an unit cell consisting of membrane, water, and ions. In order to design the best performing fuel cell membrane, we employed, molecular dynamics (MD) simulation using Accelrys Corp's Material Studio software (1) will be used to study the polyelectrolyte membrane design modeling (PEM), under standard pressure and temperature conditions for various levels of hydration. After polymer structure is built it will be minimized. The energy minimized structure will be used to study how it behaves in the presence of water molecules to understand its hydration and proton transportability.

A variety of simulation and analysis tools will be used to identify critical design issues for fuel cells and various components into the systems to avoid enormous experimental difficulties and higher cost (Schmitz A., 2003). Despite its importance, the molecular level understanding of the problem appears to be limited. Only a few molecular simulations techniques have been reported especially in the design of high temperature polyelectrolyte membrane (Yan Liuming, 2007).The most modern fuel cells have either solid oxide or polymer electrolytes. For PEMFCs, the most commonly studied electrolytes are based on polyethylene oxide (PEO) derivatives (Ennari J., 2000).

The improved membrane design will be carried out in conjunction with experimental results. The most promising structure will be synthesized and the results of the characterization will be fed back to improve the model. This cycle will continue until the thermal stability and proton transport of the membrane are optimal. Proper combination of experimentation and modeling will potentially allow rapid prototyping, shortening of design cycles in all levels of components, and rigorous examination of design component alternatives, which are all critical to the commercial success of fuel cell technology. The optimized membrane model parameters will also be fed into the PEMFC computational model to better understand transport limitations at the electrode and membrane interfaces of the fuel cell.

Coarse-grained representations of polymers, oil-water/surfactant, proteins, and biomolecular aggregates combined with enhanced computer power currently allow the simulation of systems of large polymeric and biologically relevant size (sub-micrometric) and timescale (micro or millisecond) (Groot, R,D, Warren P.B.,1997). Although these techniques still cannot be considered as predictive as all-atom simulations, noticeable advances have recently been accomplished mainly concerning the use of more rigorous parameterization techniques and novel algorithms for sampling configurational space (Vanessa O., 2006). For example, ten- or hundred-nanosecond simulations of proteins and large polymeric systems in aqueous or other solvents are currently feasible. In these processes, the number of degrees of freedom is at least one order of magnitude and the timescale four to six orders of magnitude larger than what is currently feasible with all-atom simulations or atomistic dynamics (Vrbka L, 2006). Furthermore, in some cases, atomistically detailed simulations might not be the most appropriate, as an increasing number of polymers and biomolecular aggregates are being studied experimentally using larger scale techniques such as cryo-EM, small-angle X-ray scattering, advanced spectroscopic and NMR techniques, thus making it possible to directly compare simulation and experiment (Allahyarov E., Taylor P.,2009; Elliott, J. A., Hanna, S, 2000).

Therefore, the idea of using simplified descriptions through the ‘integration’ of a large number of degrees of freedom into a few ‘coarse grained assemblies’ arises spontaneously. With respect to earlier studies, a larger variety of different simplified descriptions and more rigorous methodologies for the parameterization are currently being proposed (Vanessa O., 2006). This review provides a classification of currently used coarse-grained models for macromolecular systems. The bead models, that is, models based on a united-atom representation of the polymeric and biopolymeric system have been studied (Flock D. et. al., 2004). In general, as the number of beads decreases, the simulation is less expensive and larger systems can be simulated. However, parameterizing force-fields that are both accurate and transferable, that is, capable of describing the general dynamics of systems with different compositions and different configurations, becomes increasingly difficult as the graining becomes ‘coarser’, because more specific interactions must effectively be included in fewer parameters and functional forms. For this reason, most currently popular coarse-grained models are parameterized based on a single reference configuration and dynamics (Kissa E., 1994). Different models represent different compromises between accuracy and transferability, with different degrees of independence from the reference configuration. Recent methodologies for ‘extreme’ coarse graining have also been reported, based on different mathematical approaches for the integration of the degrees of freedom. In this research, the model will be built by combining specific functional groups into one bead (e.g. fluorinated hydrocarbons, ester group, fluorinated group etc) (Fig. 2). The decision which atoms will be combined into beads is essential in this technique. In this research the composition and the beads and the interaction between beads will be optimized according to the accuracy of the simulated results in comparison with the experimental results.

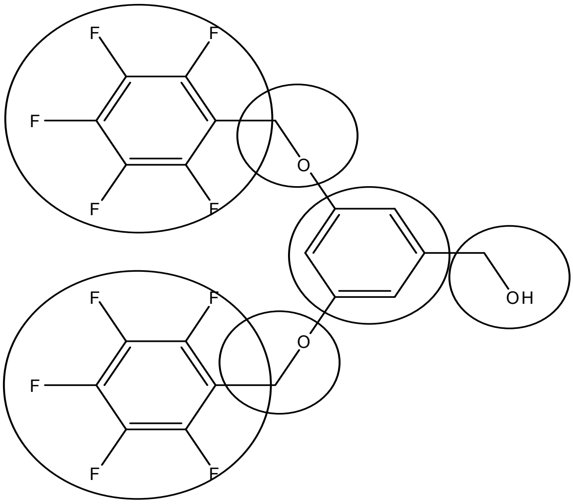


Figure 2: Coarsening of HBFP monomer by bead technique.

1.2 Synthesis methodology of Fuel Cell Membranes

1.2.1 Fluorinated Polymers

PEMs in hydrogen fuel cells have to fulfill a number of requirements: thermal and chemical stability, high proton conductivity, and low water conductivity (Barbir, F., 2005). For high thermal and chemical stability fluoropolymers are commonly used. Fluorocarbon polymers exhibit increased thermal stability, hydrophobicity, lipophobicity, improved chemical resistance, and decreased intermolecular attractive forces, in comparison to their hydrocarbon analogs (Chambers, R. D., 1973) because of the fundamental atomic properties of fluorine: high ionization potential, low polarizability, and high electronegativity. Due to the very high electronegativity, C-F bonds are always strongly polarized resulting in a highly ionic character, which is the reason for the thermal stability of perfluorocarbons. The high ionization potential combined with the low polarizability leads to weak intermolecular interactions, which leads to low surface energy for perfluorocarbons. Therefore, perfluorocarbons have been used to create non-interactive and non-wettable surfaces with low surface energies. These properties reduce water transport and thus are excellent materials for PEM membranes if coupled with specific proton transporting groups.

1.2.2 Proton Conductivity of Membranes

Proton conductivity in these materials results from hydrophilic functional groups with acidic protons, such as sulfonate, phosphonates, and phosphates. Due to the difference in hydrophilicity these groups will phase separate from the rest of the polymer, if the rigidity of the polymer chain allows for that movement. Phase-separated hydrophilic functional groups will form channels across the membrane for the hydrophilic, charged protons. Depending on the size of the channel different amounts of water will be transported with the protons, in fact so far proton transport seems to be dependent on concurrent water transport (Barbir, F., 2005).

The human body also contains membranes with selective ion transport: These membranes sustain the potential needed for information transport in neurons and ensure osmotic stability in all cells. These membranes contain channels that transport ions selectively across the membranes, i.e. channels for larger ions do not let smaller ions pass, even ions from the same column in the periodic table. This indicates that in this case ion transport is not dependent on a shell of water molecules around the ion, as it is currently in the channels of PEM's. The functional groups responsible for the ion transport in those channels are mostly imidazoles and carboxylic acids, therefore these will be tested here for building more effective proton channels across PEM's.

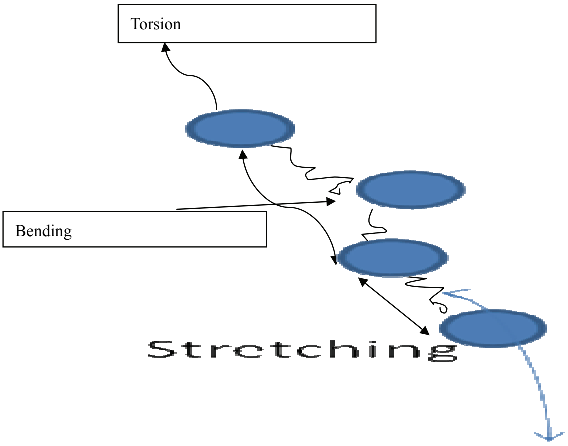


Figure 3: Bead- spring forces during motion

The size of the channel and the mechanical properties in this system will be determined by the type and amount of crosslinker used. An additional advantage of this system is that crosslinking will also be used to fix the two catalysts on each side of the membrane to form the catalyst layers. Because the polymer will cross-linked around them the catalyst particles will not be able to leak out of the system.

2 The Novel Idea

This article presented the preliminary results from a new hyperbranched polymer to investigate solutions to several of the current problems of fuel cell membranes: more effective proton transporting groups, proton channel formation, reduced water transport, and better retention of catalysts. But, the majority of the possible polymer structures will be investigated computationally; only computationally promising ones are expected to be synthesized and characterized. The characterization results will then also be used to refine the computational model, further increasing the effectiveness of this approach. Structure-activity relationships for novel polymeric materials for PEMs can be identified to predict properties of the materials, faster and easier by computational methods than synthesizing various polymers with a large variety of proton transporting groups. All the combinatorial functionalization and various % of branching would take up an enormous amount of computational and respective synthesis time and effort. Therefore, for the preliminary investigation, we built few structures of the HBFP with 20% and 25% branching , in order to optimize the material selection and key property predictions such as proton transfer, diffusivity, mechanical behavior, and temperature susceptibility at extreme operating conditions. Such information is difficult, time consuming, and expensive to acquire by classical experimental techniques, but is fundamental to the design of new compounds and formulations.

3 Research Design and Methods

3.1 Molecular Modeling and coarse- graining methods of PEM and Proton Transport

PEM, the proton conducting polymer membrane, the critical component of the next generation fuel cell systems, is examined by atomic-scale molecular dynamics (MD) simulation using Material Studio (Accelrys Inc.). Using this model, the specific PEM polymer structures discussed in the synthesis section is examined. How the water molecules distribute in or cluster around the substituted HBFP molecules, and what pathways for transferring protons (H^+) exist in the water-swollen PEM will be studied. This is analyzed using the radial distribution function between polar/polar and polar/non-polar functional groups. Proton diffusion in the PEM is also investigated in the presence of varying water uptake and temperature.

Initially, the polymer structure is built and the energy is minimized by appropriate numerical optimization procedures and force fields given in the Discover module. The minimized structure is then be used to construct the periodic amorphous cell to develop an understanding of the molecular properties and behaviors of the liquids and amorphous polymers at various operating conditions. Amorphous systems consisting of the two different kinds of polymers with various proton transporting groups with and without anions, hydronium ions, and protons and varying amounts of water are constructed and analyzed. The PCFF force field using Discover/Forcite Modules of Material Studio (Accelrys, 2005) is used to parameterize to generate a new force field to simulate these ions and the protons as accurately as possible in an atomistic model. The vibrational spectra will be calculated and compared to experimental IR spectra; this data will be fed back into the simulation to improve its accuracy. To optimize the duration of the simulation, different methods of calculating the non-bonding interactions are tested. The trajectory data files generated by the dynamic simulations, the dynamics of the polymer chains and proton transporting groups, the polymers' chemical resistance, hydrophobicity, crosslinking density, glass transition temperature, phase separation, and proton channel formation are analyzed. This information is used to guide experimental synthesis.

The primary aim of the molecular modeling work is to study the structures and dynamics of the polymer with hydronium ions, water, and protons. The mechanism of water self-diffusion is analyzed. In addition, molecular dynamics simulation is applied to calculate the polymer density at various levels of substitution as well as

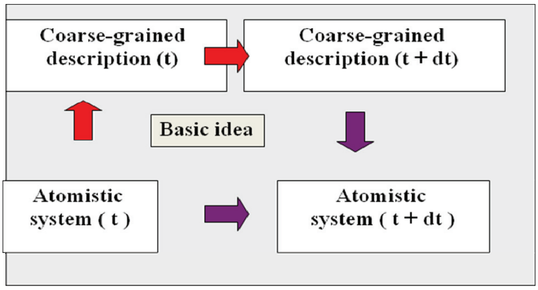


Figure 4: Derivation of physically consistent particle-particle interaction potentials.

the conformation in the periodic cell. From the simulation trajectories the Einstein diffusion coefficients are calculated. The ion conductivities of the whole system and of the ions are estimated and compared with experimental values. For computer simulation verification and validation the same properties of DuPont's Nafion under the above simulation conditions will be tested (Zhou X., 2007). If the correlation between the experimental and simulation results is in good agreement, then the simulation model will be used to evaluate several different proton transporting groups, including biomimetic ones as suggested in the synthesis section.

Then new polymer materials will be synthesized and their mechanical strength and durability will be determined in the future. Towards this end, a series of molecular dynamics simulation is used to parameterize a coarse-grained model of the novel polymers and performed a series of dissipative particle dynamics (DPD) simulations (Accelrys Inc.) of micro phase segregation in hydrated membranes with different water content. Such simulation should provide an indication of the hydrophilic activities associated with the network. If successful the fuel cell will be fabricated for further testing purposes.

3.2 Coarse Graining

The current description of beads for the phosphate-substituted HBFP and their names are described in Fig. 5. Both the hydrophilicity of each functional group and its size is distinguished. In order to compute the bead interaction parameters, the solubility parameters and molar volume were computed by MS studio software. From this we can compute the Flory-Huggins interaction parameters, which can be estimated from Hildebrand solubility parameters of the solvent and polymer using the equation $\chi_{ij} = V/(RT)(\delta_i - \delta_j)^2$, where i and j are the i^{th} and j^{th} beads, V the solvent molar volume, δ_i and δj are the respective solubility parameter, which is determined either experimentally by intrinsic viscosity or by Synthia, a mod-

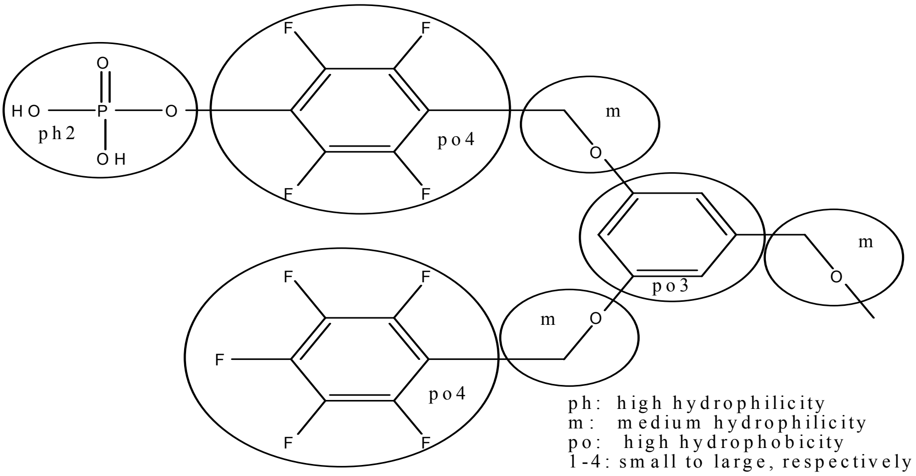


Figure 5: Description of beads of current phosphate-substituted HBFP.

ule supported by Material Studio (MS) or by molecular modeling. Currently, we used molecular modeling method explained in the above section by Forcite module. Flory-Huggins theory is a mathematical model of the thermodynamics of polymer solutions that takes account of the great dissimilarity in molecular sizes by adapting the expression for the entropy of mixing (Flory Paul J, 1942). The Flory-Huggins parameters were then converted into repulsion parameters (Huggins M.L., 1941) in DPD by using the formula

$$a_{ij} = 25 + 3.5\chi_{ij} \tag{1}$$

We used those values computed by the equation (1) in the DPD module of materials studio for simulation and some preliminary outcomes are presented in the results section. The ultimate goal of this section to use coarse-grained MD simulation to understand the structure-function relationship of proton transport across the electrode/electrolyte interfaces of a PEM fuel cell.

4 Preliminary Results

4.1 Fuel Cell Membrane Material Modeling

An important controlling factor in the efficiency of these fuel cell systems is the acceleration of ion migration through the electrolyte. The migration is influenced by a number of different atomistic effects, such as the size of the ions, coordination, and the nature of interaction with other chemical components within the

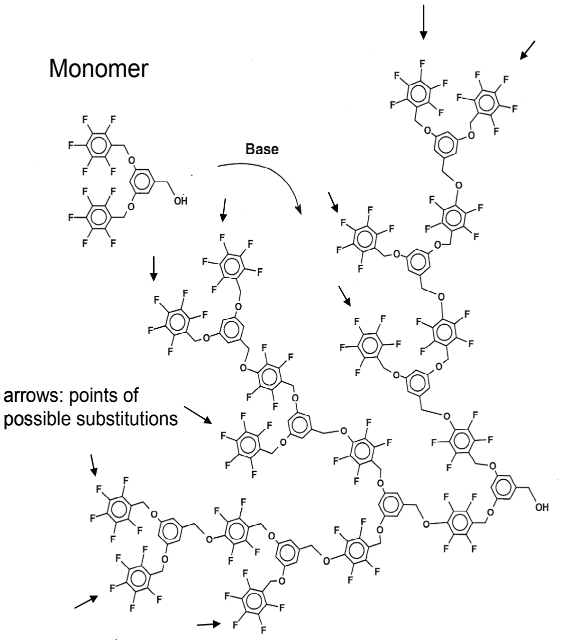


Figure 6: Chemical structure of HBFP polymer 2, synthesized from monomer 1.

system. Atomistic—molecular dynamics (MD)—simulations using Accelrys' Material Studio software can considerably contribute for understanding the conduction process, morphologies, and mechanism of proton transfer, which in turn helps to optimize fuel cell membranes.

Randomly hyperbranched polymer fragments (fragments of structure in Fig. 6) were minimized until a global minimum was reached.

The oligomer structures in the presence and absence of water were compared, and it was found that most of the water molecules moved away from the fluorinated polymer molecules. When proton transporting groups (in this case phosphate) were added to the structure, the water molecules concentrated around those groups. At the same time, all of these polar groups phase-separated from the hydrophobic fluorinated part of the structure. Preliminary results also suggest that the more phosphates were added, the more water molecules concentrated around each phosphate after a certain amount of branching was reached. This phenomenon will be investigated in more detail.

The analysis of the preliminary simulation results revealed that the protons are strongly coordinated to the water molecules and weakly coordinated to the anions. When the concentration of water in the system was lower the protons showed a

Table 1: Diffusion Coefficients of Ions

Component	Diffusion Coefficient ($10^{-9}m^2s^{-1}$)
H^+	11.8
H_3O^+	2.8
H_2O	3.3
Acid Anion	1.1

greater coordination to the anions. Various experimental studies (Yunusov A. et. al, 1983) showed that lower water concentration systems leads to lower proton conductivity, implying that reduction of proton-anion coordination and increasing proton-water coordination are important factors in improving the performance of membrane transport in those cases.

Another important factor that can be learned using computer simulation is the self-diffusion coefficient for proton transfer through the PEM fuel cell membrane, which can be determined from the mean square displacement (MSD) of the proton. The self-diffusion coefficient of an atom undergoing random Brownian motion in three dimensions can be evaluated from the limiting slope of the mean square displacement as a function of time, as described by the following Einstein diffusion equation:

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{n_\alpha} \left\langle [r_i(t) - r_i(0)]^2 \right\rangle$$

In a realistic calculation the log (MSD against time) can be plotted; then, if the calculation has converged, a straight line should be obtained. Figure 7 clearly shows that proton transport has not been reached at 800ps dynamic simulation time. Therefore, a longer dynamic simulation time is probably required. It is also possible that convergence does not occur because a polymer structure with only 20% branching is too rigid to permit reorganization of polar substituent's in short time period.

In the atomistic molecular dynamics simulations, the model for the membrane material, different HBFP were built with different amount of branching, which results in different density and diffusion coefficients. The HBFP (without proton transporting groups) is shown in Figure 8. The energy-minimized structure for the phosphate-substituted HBFP is shown in Figure 9. Typical energy-minimized structures of HBFP with 5 % and 10% branching are shown in Figure 10 and 11, respectively. Figure 12 shows the theoretical and experimental results for the dependence of the glass transition temperatures (Tg's) on the molecular weight (MW) at 50% branching. This initial study, using the "amorphous periodic cell" in the

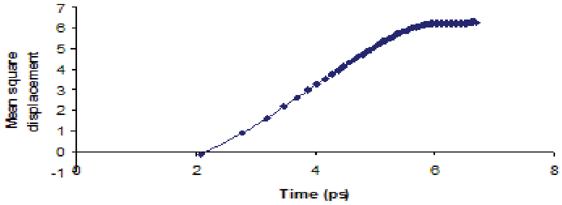


Figure 7: Mean-Square Displacement vs. time of 20% branching HBFP (log-log plot).

Discover Module in the Materials Studio software, shows good agreement between the computer simulation and experimental results, indicating that the basic model is appropriate for prediction of the effect of different amounts of branching on the Tg.

Typically, the electrolytes in these materials contain protons, hydronium ions, water, polymers, and the anions of the acid. Figure 13 shows a typical model that includes the phosphate-substituted HBFP with H_3O^+, H^+, and water. Several cells of these mixtures have been constructed using the Material Studio-Amorphous Cell polymer chain construction. The structure was then refined by a process of minimization and dynamics procedure by Discover Module. With the help of these data, a simulation model of phosphate substituted HBFP has been obtained and the structural properties of this polymer material are being investigated. The mechanism of proton conductivity and its relationship to the structural properties are evaluated along with the diffusion coefficient, radius of gyration, end–to-end distance, and the coordination of ions. These chemical properties play a key role in overall fuel cell efficiency and design.

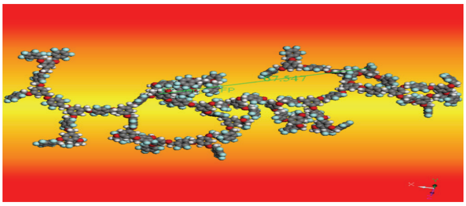


Figure 8: Ball-stick Model of HBFP.

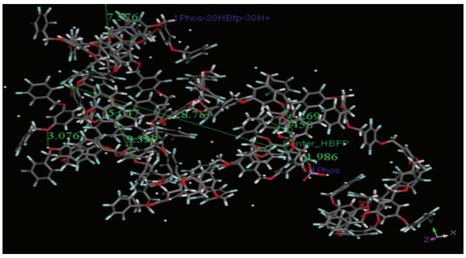


Figure 9: Phosphate-Substituted HBFP.

Using coarse-grained MD simulation techniques, we have simulated a coarse–grained model of solvated HBFP in the aqueous environment, with the following

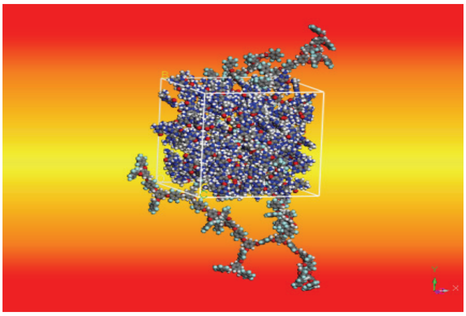


Figure 10: HBFP with 5 % branching.

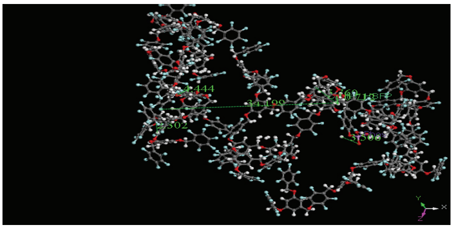


Figure 11: HBFP with 10% branching.

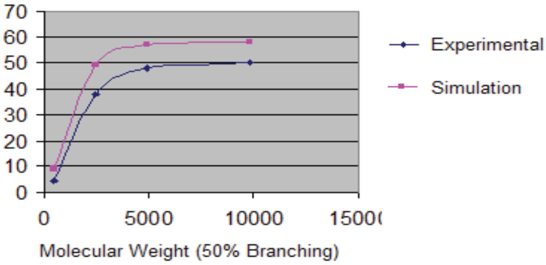


Figure 12: Molecular weight vs Tg of HBFP.

three main objectives: (i) to obtain details on the local environment of the aqueous polymer and to assess the solvent effect on binding, (ii) to investigate the translational and rotational motion of solvent molecules absorbed in the polymer matrix, and (iii) to elucidate details of the proton transport though the hydrophilic regions of the membrane. A property which is of central importance for understanding the functional features of randomly phosphate-substituted HBFP is proton conductivity and water crossover. It was found that the conductivity parameter is strongly dependent on the amount of water. Also, the spatial distribution of polar phosphate groups in proton conductive channels was characterized.

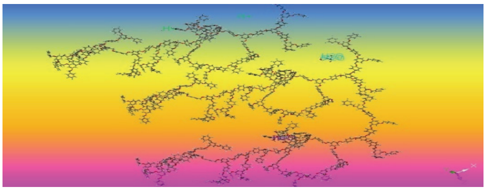


Figure 13: Substituted HBFP with Electrolytes.

It is known that not all of the protons transporting groups are located inside the channels; some are randomly distributed throughout the matrix. These groups conduct water across the membrane, but not protons. The additional water transport via these groups results in flooding of the electrodes, which is currently one of the major problems reducing the effectiveness of fuel cells. In this study a dynamic self-consistent mean field theory has been applied to obtain the morphologies of hydrated phosphate-substituted HBFP (25%) as a model for PEM at different amounts of water as shown in figure 14. A coarse-grained mesoscale model was developed by dividing the polymer structure into five components/beads: hydrophilic phosphate group, hydrophobic fluorinated aromatic ring, methylene glycol group, tri-substituted aromatic ring (branching group), and water. A 25% branching is employed during the coarse- graining. The interaction parameters for this model were generated using classical MD via Material Studio. In the wet state the phosphate group dissociates and delivers protons as charge carriers. Hydrophilic phosphate groups and water molecules organize into hydrophilic nano-domains inside the chemically stable HBFP matrix. This gives rise to hydrophilic and hydrophobic regions and results in unique permeability characteristics of the membrane that forms proton channels. The matrix, on the other hand, forms an effective barrier towards hydrophilic compounds such as water, oxygen, and protons.

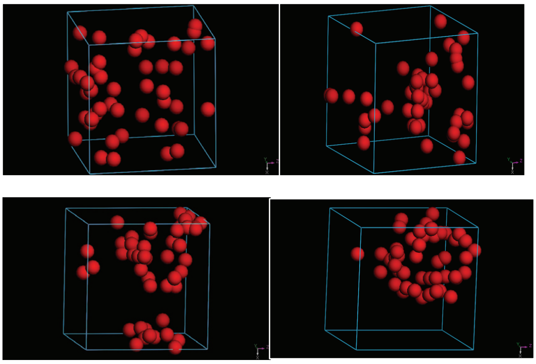


Figure 14: Typical phosphate groups forming the channel: 80 % water, 20% HBFP (water not shown for clarity) during a dynamics simulation of 1, 10 , 50, & 200 ps, respectively.

The following results show how hydrophilic groups are being organized in the aqueous environment (Fig. 14). The beads for coarsening need to be further refined to more accurately describe its effect on proton conductivity. Figure 15 shows the clustering of phosphate groups along the periodic box dimension (20X20X20) as simulation time progresses. This can be seen for all other simulation conditions. This also confirms our conclusion that phosphate groups in the HBFP gives rise to channel formation in the aqueous environment. But as the water content decreases the formation of straight channels is reduced. Straight channels peak at 50% water at the 25% HBFP branching (Fig. 16).

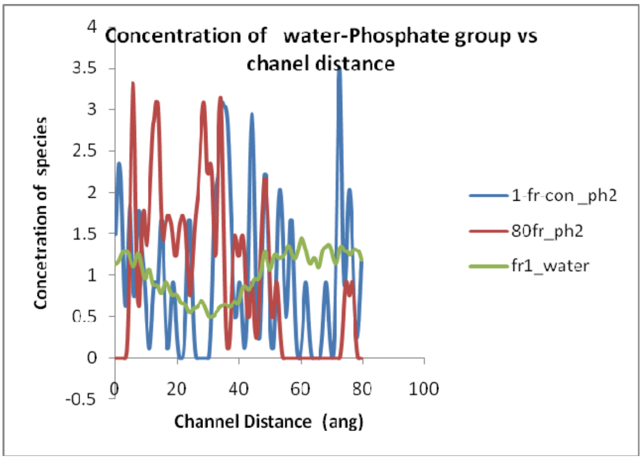


Figure 15: Concentration of water and phosphate groups vs distance (blue: initial distance, red: distance after 80 ps, green: water).

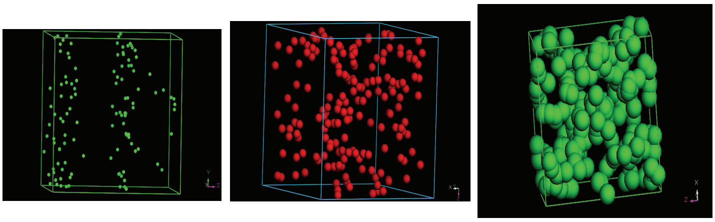
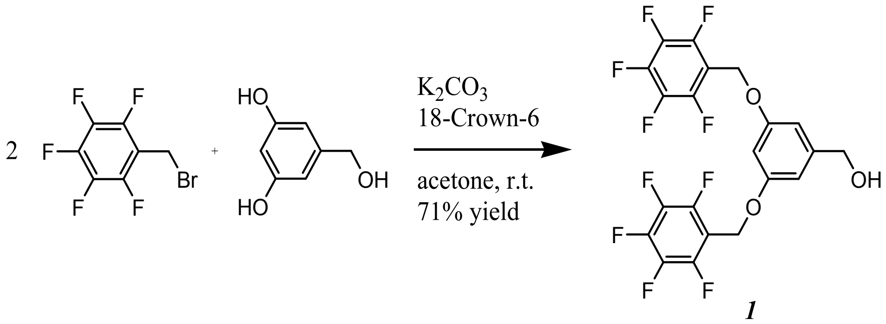


Figure 16: (a) 50% water), (b) 40% (c) <1%, for 20% (left to right) phosphate substitution on HBFP (water not shown for clarity).

The present simple coarse–grained simulated morphology shows somewhat phase separated micelles filled with water (water not shown for clarity) surrounded by side chains containing phosphate groups, embedded in the fluorocarbon matrix (80% water, 20%, phosphate substituted HBFP). When the amount of water is reduced to almost 1% and the amount of substitution is kept the same, the location of the phosphate groups changes from spherical to phase separated cylindrical column to randomly coiled to somewhat oblong. Fig. 16 (a) clearly shows that 50% water is necessary to have the 25% branching HBFP for a well organized straight channel to pass the proton. This may or may not change depending upon the coarse–graining functional group beads chosen, which in turn changes the interaction parameter. We will investigate such coarse-graining (CG) methodology during the course of this research to optimize the model by always comparing the results with experimental data.

4.2 Synthesis of Hyperbranched Fluorinated Polymers

Hyperbranched polymers were used because the hydrophilic proton transporting groups phase-separate more efficiently with this flexible material than with rigid, linear polymers. This then leads to more proton channels with less proton transporting groups, reducing the amount of water transport across the membrane in the process. Presently, we synthesized the hyperbranched fluorinated polymer from the AB_2 monomer 3,5-di(pentafluorobenzyloxy)benzyl alcohol with sodium metal as the catalyst (Fig. 2) (Mueller A, et. al., 1998). Different nucleophilic substitution reactions at the p-fluorine of the leftover pentafluorophenyl groups with hydrophobic groups have already performed on this polymer (Mueller, A., 1998).



Scheme 1: Synthesis of monomer 1

To synthesize a hyperbranched polymer, a monomer with two different functionalities, in this case F and OH, is used. The A_2B monomer 1 is synthesized by treating 3, 5-dihydroxybenzyl alcohol with pentafluorobenzyl bromide, in the presence of

K_2CO_3 and 18-crown-6, in acetone at room temperature for 6 days (Scheme 1) (Mueller A. et. al., 1998). The product was purified by column chromatography and obtained in a 78% yield. The polymer 2 has been synthesized by reacting monomer 1 with sodium potassium alloy in THF (Figure 3) (Mueller A.,1998). Care was taken in neutralizing Na/K potassium alloy with sterically hindered alcohols to reduce the amount of substitution of alcohols at the p-fluorine site of the end groups (arrows in Fig. 3).

The substitution with imidazole was performed by reacting the polymer with excess imidazole in chloroform at 50 °C. Excess imidazole was removed during rotary evaporation and extraction with water. It was found that substitution mostly occurred at the internal, non-fluorinated ring, not the p-F position as expected. The maximum yield obtained from the substitution reaction was 58%.

Cross-linking of the substituted HBFP was done to form a strong, thermally-stable membrane. As the polymer is cross-linked, it becomes insoluble in the solvent and precipitates. The polymer solution was placed into the petri dish, with the base 4-dimethylamino pyridine being added last. The dish was lightly swirled inside the hood and then set aside. After 20 minutes, light heat was applied to the dish to ensure that all the THF was evaporated from the dish. After less than 5 minutes and before heat was added, a membrane was formed in the dish. The membrane appeared to be a glassy solid.

We are currently increasing the amount of imidazoles in the reaction. We are also currently substituting the polymer with phosphate and sulphate. On aliphatic polymers usually phosphonate and sulfonate groups are used, because they are more stable than phosphate and sulfate groups. In this case the aromatic ring stabilizes the phosphate and sulfate group. The stability of the polymer will be determined by TGA, and if it is found that, in spite of the aromatic ring, phosphate and sulfate groups are not sufficiently stable, sulfonate and phosphonate will be used instead in the future.

The polymer was substituted with phosphates in a two-phase reaction, the polymer in the chloroform phase and the phosphate in the water phase. 18-Crown-6 was used as the phase transfer catalyst to increase the reaction yield. Initial results show substitution, but full characterization and optimization of the reaction and the respective molecular modeling and coarse-graining techniques are underway, which will be published in the near future.

5 Conclusions

The effects of FC design parameters on the performance of the system have been studied by models. Preliminary results are very encouraging from the atomistic

MD and coarse graining methods. A MD method has been developed to compute the diffusion coefficient of water, hydronium, protons, and other acid anions in the HBP, which is used for the computer simulation models. From the coarse graining method we were able to obtain a phase separated proton channels even at 25% branching. We hope that at least 45-60 % branching will be able to produce much better results in the near future. At this level both modeling techniques, MD and CG can be simultaneously used for predicting diffusivity and the percentage of protonation, which can be acquired by variety of random branching and by different functionalization procedure. Also, an atomistic MD method has been developed for determining molecular weight vs Tg of hyperbranched fluorinated polymer at various degrees of branching for future 3D FC system optimization. A HBP for PEMFCs with more efficient proton transport is being developed by protonating different amount of branching. We are hoping that, more effective membrane FCs, that is more durable, efficient, and operable over a broader range of temperature than those currently available can be prepared by these techniques. In the very near future, array of polymer will be synthesized, characterized using variety of techniques, such as dynamic mechanical analysis and porosimeter, and utilized in the construction of membranes. The membranes will be evaluated over a range of conditions, such as temperature, humidity, and acidity. Using experimental results and predictions from molecular simulation, polymer structure will be modified to optimize membrane properties. Much will be learned about the requirements for proton transport. We will also investigate short and long time scale of proton hopping in relation to HBP- water loading and its sensitivity to the level of hydration and hydrogen bond switching with the rate of proton hopping for bulk water and over all water loadings of the polymer. A long term goal is the generation of membrane materials that will greatly enhance the operational characteristics of hydrogen FCs and can be tested using computer simulation model of the system in the future.

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