COATED AND LAMINATED FABRICS FOR FUEL CELLS

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Goal  
This project deals with the development and characterization of the polymer electrolyte membrane based fuel cell (PEMFC) components with the aim to increase efficiency, reduce cost and further develop and optimize the substrates, recipes and process technology.

Abstract  
The electrical characterization of the air/hydrogen polymer electrolyte membrane fuel cell is done. The effect of hydrogen flow rate on voltage, resistance and current is investigated at standard conditions. There is an optimum flow rate that gives the maximum voltage and current. The effect of load on thickness and resistivity of various gas diffusion layers (GDL) is measured. Loading reduces the thickness and resistivity of the GDLs. New GDL structures are being made with wet-lay process.

A low cost composite polymer electrolyte membrane was developed. It can increase the fuel cell durability when operated at below 80°C. The polymer electrolyte membrane was prepared from Nafion®/polypropylene composite (70:30 weight ratio). The addition of polypropylene to the composite membrane showed a decrease in the flow rate of back diffused water from cathode to anode giving rise to a steadier water content (water molecules per sulfonic acid group) at the anode required for the efficient distribution of proton concentration. The polypropylene used in the membrane decreases the cost of the membrane. However the low performance of the composite membrane should be addressed.

The effect of adding (i) sulfonated phenethyltrimethoxysilane (s-PETMS) and (ii)charged meltblown polypropylene (MBPP) to Liquion® on the performance of composite polymer electrolyte membrane (CPEM) was investigated. The COMSOL multiphysics software was used to model the water concentration inside the membrane based on Fick’s second law. The conductive media equation was applied to show the current density distribution inside the membrane.

Experimentally, a composite membrane LPMn, having ratio of s-PETMS:charged meltblown polypropylene (C-MBPP):Liquion® as 4.5:40:55.5, showed a 15-20% decrease in the current density compared to the Nafion® membrane. The decrease in current density after 90 minutes was 10-12% for Nafion® membrane and 3-6% for the LPMn polymer electrolyte membranes. Along with time, the percentage increase in water concentration was 2.5-4.0% for the composite membranes and 8-8.5% for the Nafion® membrane.

The modeling results were consistent with the experimental data for the operational temperatures and showed that the presence of charged meltblown polypropylene helped maintain a steady water concentration at the anode surface. The s-PETMS likely increased the ion exchange capacity of the membrane and thus increased the current density.

PROJECT ACTIVITIES

I. Characterization of Gas Diffusion Layers

In order to understand the mechanism of PEMFC, a single PEMFC was manufactured. The end plates, which are made of PVC, are used for cell mechanical stability in compression. For flow field plates, graphite was used due to its good electronic conductivity and non-corrosive features. Commercial membrane electrode assembly (MEA) which has Nafion® 112, with a thickness of 51μm and basis weight of 100g/m², was placed between the graphite flow plates. The single air/hydrogen (99.99%) PEMFC has been tested in room temperature (22°C) to obtain optimum flow rate. The test apparatus is shown in Figure 1.
The other focus of the study is fuel cell compression. In fuel cell stack, the cell components are held together under high compressive loads mainly to prevent gas leakage. While the GDL is compressed, mass transfer resistance of the reactants increases, and thus reduces the cell performance. On the other hand, high contact pressure can decrease the contact resistance between the cell parts, and physical compression increases GDL’s electrical conductivity. To see the compression effect on GDL’s conductivity, four point probes test device was designed and used with Instron as shown in Figure 2.

Results

![Graph 1: Voltage (V), Resistance (kOhm), Current (mA) vs. Flow Rate results of the PEMFC](image1)

The average theoretical cell voltage $E_{oc}$ is 1.23 V; however, in operation conditions, it is found that the voltage is less than this. There are many reasons for voltage drop, such as activation losses, fuel cross over and internal currents, ohmic losses, mass transport and concentration losses.

As shown in Figure 3, increasing the flow rate causes a decrease in voltage drop; this result can be explained by fuel cross over losses. In a practical fuel cell, some unused fuel will diffuse from anode through electrolyte to cathode where catalyst will react directly with the oxygen, producing no current from the cell. The crossing over of one hydrogen molecule from anode to cathode can be defined as fuel crossover; wasting two electrons is essentially equal to two electrons crossing from anode to cathode internally, rather than external current. Mass transport losses caused by reactant and product concentrations, act as an internal resistance which drains fuel cell voltage so that there is a significant drop in fuel cell performance. In the electrode layer that consists of catalyst layer and gas diffusion layer, the performance of fuel cell is affected by the reactant distribution which is maintained by gas.
diffusion layer (GDL). As a consequence, mass transport losses can be reduced by reducing gas diffusion layer thickness. Figures 4 and 5 show the change of resistivity and thickness with load, respectively, for different GDLs.

![Resistivity vs. compression load](image1)

**Fig. 4 Resistivity vs. compression load**

![Thickness vs. compression load](image2)

**Fig. 5 Thickness vs. compression load**

II. Preparation and investigation of Liquion®/polypropylene composite membrane for fuel cell

**Preparation of mixture of Liquion®/bifunctional silica sol**

Penethyltrimethoxysilane (PETMS) was sulfonated by adding chlorosulfonic acid dropwise, under nitrogen atmosphere. The s-PETMS was mixed with de-ionized water and absolute ethanol in ratio 1:3.23:9.48, and constantly stirred for 8 hours at ambient temperature, to obtain bifunctional silica sol that had 7.5 % weight solid. Liquion®, bifunctional silica sol, and denatured ethanol were mixed followed by ultrasonication at room temperature, for 15 minutes [1,2].

**Preparation of the composite polymer electrolyte membrane**

The clean and dried nonwoven polypropylene samples were given corona charge treatment. The charged samples were then impregnated with mixture of Liquion®/bifunctional silica sol (LBS). The dried composite was hot-pressed at 4.12 MPa pressure, 160°C temperature for 30 minutes. The effect of the compression temperature (200°C, 160°C and 140°C) and time of compression (from 5 to 30 minutes) on CPEM preparation was observed. The pressed composite was kept in a vacuum oven at 33.86 kPa and 130°C for 120 minutes; then cooled under vacuum to room temperature. The composite was further annealed by cooling to room temperature in 60 minutes, to relieve the internal strains. The membrane was immersed in 500 mL of 0.1M sulfuric acid solution for 4 hours.

**Table 1** 

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<tr>
<th>Composite polymer electrolyte membrane prepared</th>
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Preparation of charged nonwoven polypropylene

The nonwoven polypropylene was placed on an electrically grounded aluminum plate, and an A/C supply of 18 kV was applied to another metal plate with charged copper pins as shown in Figure 6 (tip at 2.5 cm distance from ground plate) [3].

![Figure 6 Corona charging of nonwoven polypropylene](image)

Preparation of membrane electrode assembly (MEA)

The membranes were pressed between Liquion® coated gas diffusion electrodes at 60°C and 4.12 MPa pressure for 30 minutes to form membrane electrode assembly [4].

Performance testing of the membrane electrode assembly

The fuel cell operation was carried out in the polycarbonate box shown schematically in Fig 7.

![Figure 7 Fuel cell Laboratory operational set up](image)

The MEAs were placed in a single stack fuel cell. The fuel cell assembly was placed in the humidified polycarbonate box for 2 hours and then supplied with a constant hydrogen gas feed rate, 2.35 μg/sec and oxygen gas feed rate, 19.84 μg/sec. The temperature was maintained using a controlled heating plate [5].

For quick evaluation of the membrane stability with time, the cell was operated at high current density i.e., by using a low load resistance, 3Ω. The dependence of cell performance from the current density was characterized using a current-voltage curve by plotting cell potential as a function of total current

Characterization
The scanning electron microscope analysis was conducted; water uptake, % dimensional stability, ion exchange capacity were measured for the polymer electrolyte membranes prepared.

Modeling of the polymer electrolyte membrane (PEM)

The COMSOL software was used to model the current density and water concentration profile in the fuel cell as a function of time [6,7]. The diffusion equation module was applied to understand the water concentration whereas the conductive media equation module was used to understand the effect on the current density, as a function of time and temperature. Following were the governing equations used:

i) Material conservation equation (Nernst–Planck equation)

\[
\nabla (F \cdot \sum_k z_k \cdot (-D_k \cdot \nabla c_k - z_k \cdot u_m,k \cdot F \cdot c_k \cdot \nabla F_c)) = F \cdot \sum_k z_k R_k
\]

\text{eqn. 1}

\begin{align*}
&u_m,i \quad \text{mobility of the ion species} \\
& R \quad \text{number of coulombs of charge per mole of ion species} \\
& z_i \quad \text{valence of charge}
\end{align*}

The left hand side term of the equation gives ionic flux using (i) the concentration gradient (\(\nabla c_i\)) of the ion species, and (ii) potential difference due to the change in concentration of ion species. \(D_i\) is the temperature dependent diffusion coefficient of the species. The right hand side evaluates the ionic flux from the charge generated by the ionic species. The mobility (\(u_{m,i}\)) is directly proportional to the charge and inversely proportional to the mass of the ion species.

ii) Butler-Volmer equation

\[
i \cdot n = S_{a,c} \delta \delta i_{0,c} \left( \exp \left( \frac{\alpha_{a,c} F \eta_c}{R_g T} \right) - \exp \left( \frac{\alpha_{a,c} F \eta_c}{R_g T} \right) \right) \text{ at } \partial \Omega_a \text{ eqn. 2}
\]

\[
i \cdot n = S_{a,c} \delta \delta i_{0,c} \left( \exp \left( \frac{\alpha_{a,c} F \eta_a}{R_g T} \right) - \exp \left( \frac{\alpha_{a,c} F \eta_a}{R_g T} \right) \right) \text{ at } \partial \Omega_c \text{ eqn. 3}
\]

\[
i \cdot n = 0, \quad \text{ at } \partial \Omega_\text{water} \text{ eqn. 4}
\]

where,

\(\alpha_{a,a}, \alpha_{a,c}\) anode and cathode transfer coefficients

\(F\) Faraday’s constant

Butler-Volmer equation gave the relationship between the electrical current (\(i\)) and overpotential (\(\eta\)). The source term (\(i \cdot n\)) describes the transfer current at the cathode and anode boundary of the cell.

iii) Fick’s second law

Fick’s second law for diffusion was used to understand the continually changing state of diffusion of water inside the membrane with respect to time.

\[
\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2} \text{ eqn. 5}
\]

\(\phi\) is the water concentration in membrane

\(t\) is time of the fuel cell operation

\(D\) is the water diffusivity

The water diffusivity and proton conductivity are all functions of water content inside the membrane.
iv) Ohms law

\begin{equation}
    i = -\kappa \nabla \phi
\end{equation}

The conductivity is proportional to the concentration of the ion species and its charge.

Results and discussion

Dimensional stability

The composite membranes showed a deformation around 0.98%. Nafion® membrane swells when hydrated and thus shows deformation (Figure 8). The high swelling in the N-117 membrane leads to poor mechanical strength. The swelling in the Liquion® region is suppressed in the composite membrane because of the porous nonwoven polypropylene. It was found that dimensional change on composite membrane upon hydration was isotropic, while dimensional change of the N-117 was anisotropic.

Ion exchange capacity

The addition of 7.5% by weight of s-PETMS to Liquion® showed an increase by 80% (Figure 9). The IEC results obtained for LPMc were similar to the commercial N-117. Thus, we decided to compare the voltage-current characteristics of the N-117 membrane to the LPMc membrane. The water concentration in the membrane is related to the amount of sulfonic acid groups. For a polymer electrolyte membrane carrying sulfonic acid groups, average water content for effective continuous migration of the protons at anode is 5 to 9; at the cathode ranges from 12 to 22; in the interior of the membrane is about 12 to 15 [8].

Scanning electron microscope analysis

The composite membrane prepared by hot press at 160°C for 30 minutes under 4.12 MPa pressure showed no degradation of the membrane surface. Uniform membranes were obtained when applying hot press at about 160°C.
It was determined from the images that the raw material selection and the preparation technique play an important role in preparing an effective composite polymer electrolyte membrane (Figures 10 and 11). The SEM image data for the range of hot press temperatures used for membrane preparation suggested that temperature close to the melting point of polypropylene allows a better contact between the nonwoven and the Liquion ionomer solution [4].

**Performance testing using fuel cell kit**

The voltage-current data obtained shows around 13 to 15% drop in the current density after 90 minutes for membrane electrode assemblies having 100% Nafion®. The Nafion®/PP composite membrane shows 5% drop in the current density under similar conditions. Thus, the inclusion of propylene is believed to have improved the water management in the membrane.

**Current-voltage characteristics**

N-117 membrane showed a steady value in current density for about 15 minutes and then decreased about 4%. The initial drop of the polarization was due to electrochemical activation determined by the oxygen reduction rate at the cathode surface. The experimental data showed about 10 to 12% decrease in the current density after 90 minutes for N-117 membrane (Figures 12 and 13).

![Fig 12. Current density characteristics with time for N-117](image)

![Fig 13. Current density characteristics with time for LPMc](image)

The decrease in current density after 90 minutes was 3 to 6% for LPMc membrane under same conditions. At the anode surface of the fully hydrated membrane, the water concentration increases with time due to diffusion of water formed at the cathode [9, 10]. Thus, we obtained a decrease in current density with time. In the CPEM, the nonwoven polypropylene decreases the inflow of the diffused water to the anode. Thus, the rate of increase in water concentration with time at the anode is less than that of which occurs when the N-117 membrane is used. Hence, the fast migrating of protons was constant with time in the composite samples.

**Water management**

The water concentration of LPMc was 90% that of the N-117 membrane, even after 90 minutes of fuel cell operation. The figure of the change in water concentration with time showed about 8% increase in water concentration for N-117 membrane, as compare to 2-4% increase for the composite membranes.

Zawodzinski et al [11] suggested that the number of water molecules dragged per proton is relatively independent of hydration range at which the membrane is sufficiently conductive. In the porous nonwoven region, the clusters of water molecules combine to form flexible rod like structure giving a continuous migration of protons through it. The corona charged polypropylene showed high water concentration due to better impregnation of Liquion® in polypropylene to give a continuous ionic phase.

The polypropylene controls the water concentration in the membrane by hindering the diffusion of (i) excess water molecules formed at the cathode and (ii) water molecules dragged by electro-osmotic pressure from anode to cathode.

**Modeling of PEM**

*Model for current density*
Nafion® membrane showed a steady current density initially. The model data after 90 minutes showed a maximum current density near the cathode surface next to the oxygen inlet. A lower current density was observed at the cathode surface near the oxygen outlet. The composite membranes showed a decrease in current density from the cathode to the anode. Along with time, very marginal change in the current density was observed across the membrane (Figures 14 and 15).

The electronic resistances could significantly change the current density in the membrane. Although the electron transport equation 4.9 was solved in the one-dimensional PEMFC models of Bernardi and Verbrugge [12], the equation enables direct incorporation of the contact resistance at interfaces between two components and direct implementation of the total current as a boundary condition instead of the cell voltage (Figures 16 and 17).

Nafion® membrane showed 8% increase in water concentration after 90 minutes of experimental fuel cell operation. The membranes showed an increase in the water concentration distribution with time at the anode.
boundary. The composite membranes showed a 55 to 60% less water concentration compared to the maximum value in the porous nonwoven region initially.

The flux of water from the cathode is hindered by the nonwoven region giving a higher concentration gradient across the nonwoven region. The water concentration at the anode side of the nonwoven region showed the lowest water concentration [13].

The percentage water concentration profile obtained from modeling was found to be in a good agreement with the experimental results. This is due to the continuous constant flux of diffused water given at the cathode. This helps maintain a steady water concentration at the anode surface.

Conclusions

The LPMc composite membrane showed an 80% increase in the ion exchange capacity. The percentage drop in maximum current density values in a time frame of 90 minutes was 10 to 12% of that for Nafion® membrane and 3 to 6% for the LPMc membranes. Thus, charged meltblown polypropylene acted as a barrier to the inflow of diffused water from the cathode to the anode. Also, s-PTEMs increased the density of the sulfonic acid sites in the membrane for proton transfer facilitating the current density.

The water concentration inside the membrane after 90 minutes at ambient temperature and 60°C showed an increase of 2.5 to 4.0% for the composite membranes and 8 to 8.5% for the Nafion® membrane. This suggests that the inclusion of nonwoven polypropylene in the CPEM does have a control on the distribution of water concentration. The modeling helped to understand the water concentration and current density profile across the membrane with time. The experiments conducted did provide an understanding of the efficiency of the composite membrane compared to the commercial Nafion® membrane.

References


Project Websites:
http://www.ntcresearch.org/projectapp/?project=F04-AE01

Conference Proceedings:

National Textile Center Annual Report: November 2007
**Oral Presentations:**
- Isikel, L., “Comparative Evaluation of GDL Media for PEMFCs”, Auburn University Annual Graduate Student Research Paper Competition, 9 March 2006, Foy Union, AU.

**Poster Sessions:**

**SINCE THE INCEPTION OF THE PROJECT:**
- Graduate students involved in the research: 3
- Undergraduate students involved in the research: 1
- Presentations: 5
- Publications: 1
- Poster sessions: 4
- Contacts with industry: 12
- Contacts with academic (non-NTC), including those in other disciplines in the same university: 5

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