

# NAFION NANOFIBER MAT IN A SINGLE FUEL CELL TEST

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**Abstract**— Proton exchange membrane, PEM, was developed and tested for potential application in fuel cell. Nafion was electrospun to nanofiber network with aid of poly(ethylene oxide), PEO, as a carrier polymer. The matrix polymer was crosslinked with Norland Optical Adhesive 63 under UV after compaction and annealing. The welded nanofiber mat was characterized for morphology, proton conductivity, and methanol permeability then tested in a single cell test station. The results of the fabricated nanofiber membrane showed a proton conductivity of 0.10 S/cm at 25°C and higher fiber volume fraction; methanol permeability of  $3.6 \times 10^{-6}$  cm<sup>2</sup>/s and power density of 96.1 and 81.2 mW/cm<sup>2</sup> for 5 M and 1 M methanol concentration respectively.

**Keywords**— Composite Membrane, Electrospinning, Nanofiber, Fuel Cell.

## I. INTRODUCTION

Fuel cell technology is expected to become one of the key technologies of the 21st century, both for stationary and vehicular applications [1-2].

Proton exchange membrane fuel cells (PEMFC) with hydrogen as a fuel attracted the most attention due to the high electrochemical reactivity, achievable efficiency (in power plants or internal combustion engines), and practically zero pollution level. However, issues regarding the appropriate safe transportation and storage of hydrogen were strong impediments for the hydrogen fuel cells commercialization [3-4].

Direct methanol fuel cell (DMFC) using liquid methanol has several advantages including high efficiency, very low emission, lower weight and volume compared with indirect fuel cells [5-7].

Proton conducting membrane is the key component of a fuel cell system. A membrane with high proton conductivity (typically  $\geq 10^{-2}$  S/cm), high chemical, thermal stability and mechanical strength is required. Perfluorosulfonated membranes are widely used as proton conductors, including Nafion series, with Nafion 117 as preferred membrane for DMFC.

Studies have shown that Nafion loses water at temperature above 80 °C, suffers fuel crossover across membrane, becomes very unstable and mechanically fails at high operating temperature. This called for modification of Nafion in several studies to curb one or two of these limitations [8-11].

## II. MATERIALS AND METHODS

### A. Materials

Nafion 5 wt% solution, Nafion117 membrane, poly(ethylene oxide), 2-propanol, sulfuric acid, and methanol were purchased from Sigma Aldrich Industries. Platinum-ruthenium alloy, (3.0 mg/cm<sup>2</sup> 1:1) from AlfaAesar.

### B. Nanofiber Fabrication

Nafion solution of 5wt% was purchased from Sigma Aldrich and the 2-propanol/water solvent (3/1 v/v) in

the Nafion solution was removed by evaporation. The Nafion powder was re-dissolved in a 2-propanol/water (2/1 wt/wt) mixture, to give a total Nafion solution concentration of 30 wt%. The carrier polymer, PEO, was dissolved in the same mixed solvents (2-propanol/water) at a concentration of 10wt%. The weight ratio of Nafion to carrier polymer was 99/1 for PFSA/PEO, while the total polymer, (Nafion + PEO), concentration in actual electrospinning Nafion/PEO solution ranged from 5wt% to 25wt%.

Nafion (1100 EW)/PEO (300,000 MW) (99/1 wt/wt) solutions with 5wt% to 25wt% polymer concentrations were electrospun using a home-made, static collector electrospinning apparatus. The applied voltage between the aluminum collector and the spinneret was 6.0–8 kV, the spinneret-to-collector distance was 8cm, and the solution flow rate was 0.20 mL/hr.

The fiber mats were annealed at 150 °C for 30 minutes under vacuum. The annealed plus welded mats of Nafion were compacted between Kapton films, to increase fiber volume fraction, under applied pressure of 10,000 psi for 5 seconds.

Annealed, welded and compacted Nafion nanofiber mats were filled with an inert and hydrophobic prepolymer, Norland Optical Adhesive (NOA) 63. The NOA – filled mats were exposed to UV light (365nm) for a period of 1 hour for each side to crosslink the NOA 63.

### C. Proton Conductivity and Methanol Permeability

Proton conductivity of water equilibrated nanofiber composite membrane and Nafion 117 film were measured at room temperature by an AC impedance technique (Agilent 4338 milliohm-meter, with all measurements made at 1kHz), using an open-frame two-electrode conductivity cell. While the methanol permeability in Nafion nanofiber composite was measured at 60 °C using a two-compartment glass diffusion cell.

### D. Characterization of Fiber Mat and Composite Membrane

The fiber morphology and fiber diameter distribution

of electrospun nanofiber mats, densified mats, and densified and welded mats were determined using high resolution scanning electron microscopy (HRSEM).

### E. Membrane Electrode Assembly

The electrode of anode and cathode had a catalyst load of  $4.0\text{mg}/\text{cm}^2$ . The first anode catalyst layer contained  $3.0\text{mg}/\text{cm}^2$  platinum-ruthenium alloy with 6 wt% dry Nafion ionomer and was painted onto a carbon cloth. Pt-Ru of  $1\text{mg}/\text{cm}^2$  with 25 wt% dry Nafion ionomer was coated on the initial layer, making it the second, after drying the electrodes at  $75\text{ }^\circ\text{C}$  for 30 minutes. Platinum black with same catalyst loading for first and second layers was used as the cathode in place of Pt-Ru alloy. Annealing of both electrodes was done at  $150\text{ }^\circ\text{C}$  for 5 minutes and hot pressed at  $130\text{ }^\circ\text{C}$  on the membrane, at 400 psi for 5 minutes. The resulting MEAs were soaked in 1.0 M sulphuric acid for 24 hours and washed with deionized water before performing a single cell fuel cell test. The MEA contained a single membrane.

### F. Single cell test

FuelCon Evaluator-C 70239 was used to collect voltage-current density data. The fuel cell ( $5\times 5\text{ cm}$  area) operating temperature was set at  $60\text{ }^\circ\text{C}$  and 500 sccm ambient pressure humidified air, while anode feed was 1 M methanol. The cell operating condition and methanol feed concentration was fixed while fuel cell performance data were collected for 30 minutes at a constant voltage of 0.4V. At scan rate of 0.05 V/min, the data for voltage vs. current density plot was recorded as well as the steady-state current.

## III. RESULTS AND DISCUSSION

### A. Fiber Morphology

Associated scanning electron micrographs and fiber diameter histograms are shown in Fig. 3.1. The 5 wt% solution resulted in electrospun droplets rather than electrospun fibers, indicating an insufficient number of polymer chain entanglements for the creation of a stabilized Taylor cone. At 10 wt% concentration, beaded fibers were generated. At a low polymer solution viscosity, just as found in literature, it is common to find beads along the fibers deposited on the collector [14]. Fiber mats without beads were fabricated with average fiber diameter of 255nm ( $C = 15\text{ wt}\%$ ), 405nm ( $C = 20\text{ wt}\%$ ), and 750nm ( $C = 25\text{ wt}\%$ ), when the polymer concentration is greater than or equal to 15wt%. Furthermore, at the 25 wt% concentration, the nanofibers were flattened.

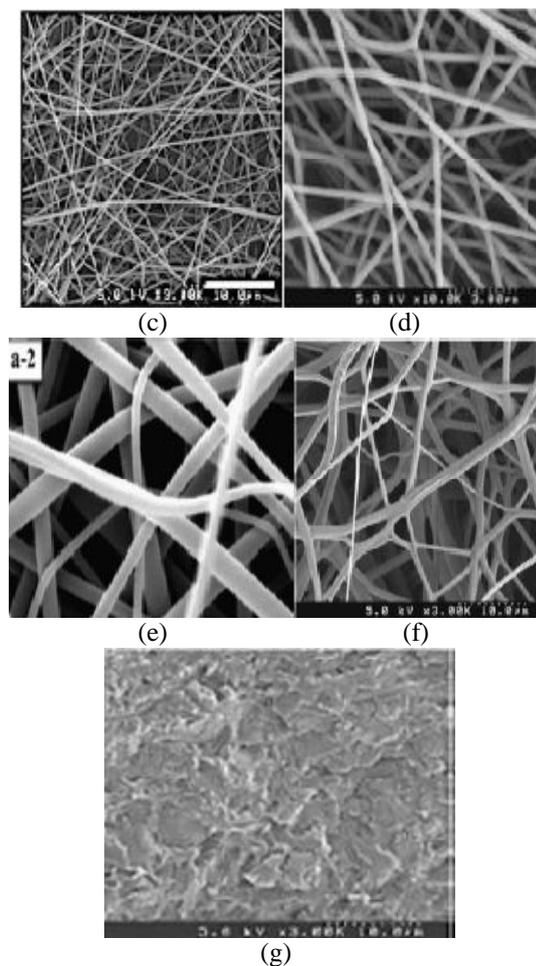
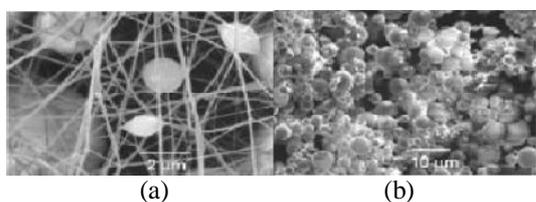


Fig. 3.1 SEM images of electrospun fiber mat surfaces (a) electrospun droplets at 5 wt% solution (b) fibers with beads at 10 wt% solution (c) & (d) smooth fibers at 15 and 20 wt% solution (e) flattened fibers at 25 wt% solution (f) annealed fiber mat surface. (g) Nafion nanofiber composite membrane.

Pawlowski and co-workers [12] stipulated that solvent evaporation is slowed for a high polymer concentration of the electrospinning solution with high solution viscosity, in which case wet fibers strike the collector of the electrospinning apparatus and are flattened on impact. It is imperative to note in this study, that the PEO concentration needed for Nafion electrospinning (1 wt%) is much lower than that reported in prior literature studies (17 wt% of PEO, as reported by Laforgue co-workers [13]).

### B. Proton Conductivity and Methanol Permeability

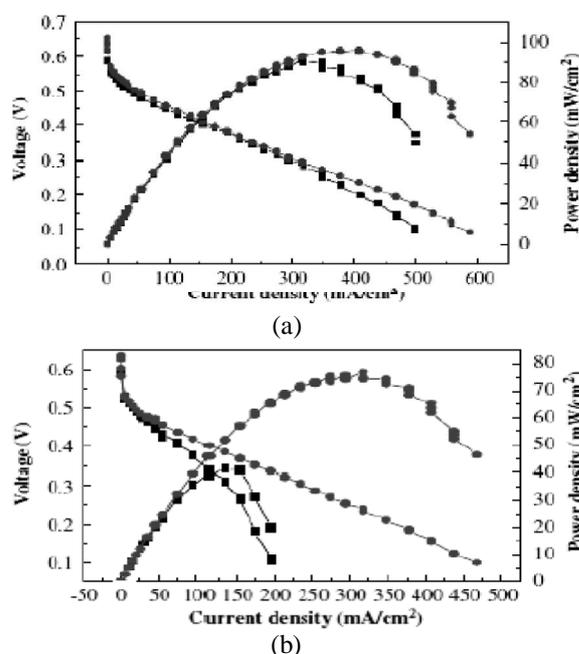
Results of proton conductivity showed same range for nanofiber composite (at higher fiber volume fraction) and Nafion 117 film. See Table 3.1. The methanol permeability of the nanofiber composite decreased substantially without accompanied loss of proton, where nanofiber volume fraction was higher. It was not clear if the difference in methanol permeability was as a result of difference in morphology obtained through electrospinning, and curing of Nafion nanofiber composite impregnated with NOA.

**Table 3.1.** Proton conductivity and Methanol permeability

Sample	Fiber volume fraction	Conductivity (S/cm)	Methanol Permeability (cm <sup>2</sup> /s)
Nafion nanofiber composite	0.50	0.057	2.8 × 10 <sup>-6</sup>
	0.75	0.075	3.0 × 10 <sup>-6</sup>
	0.85	0.082	3.4 × 10 <sup>-6</sup>
	1.00	0.100	3.6 × 10 <sup>-6</sup>
Nafion 117	-	0.100	2.6 × 10 <sup>-6</sup>

### C. Single Cell Performance

Single cell performance, (shown in Fig. 3.2), for the Nafion nanofiber mat membrane was done at methanol concentration of 1M and 5M respectively at 75°C. The evaluated value of the nanofiber mat membrane indicates improved mass transportation polarization than Nafion 117, for both concentrations of methanol. This could be observed from the irrespective peak power densities at respective methanol concentration.



**Fig. 3.2:** (a) The polarization curves of DMFC with 1 M methanol as feed at 75 °C. Nafion 117, Nafion nanofiber network composite membrane. (b) The polarization curve of DMFC with 5 M methanol as feed at 75°C. Nafion 117, Nafion nanofiber network composite membrane.

## CONCLUSIONS

Nafion doped solution was successfully electrospun to nanofibrous webs. The morphological investigation showed that electrospinning solution concentration of 15 and 20 wt% gave nanofibers with better diameter and distribution. Nanofiber composite membranes were prepared from the nanofiber mat. The proton conductivity of the fabricated nanofiber composite membrane was in same range with Nafion 117, while the nanofiber composite membrane showed reduced methanol permeability as well as improved power densities.

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## REFERENCES

- [1] K. B. Prater, *J. Power Sources*, 51 (1994) 129.
- [2] J.A. Kerres, *J. Membrane Sci.*, 185 (2001) 3.
- [3] K. Scott, W.M. Taama, P. Argyropoulos, *J. Power Sources*, 79 (1999) 43.
- [4] S.P. Nunes, B. Ruffmann, E. Rikowski, S. Vetter, K. Richau, *J. Membrane Sci.* 203 (2002) 215.
- [5] Surampudi et al., *J. Power Sources*, 47 (1994) 377.
- [6] K. Scott, W.M. Taama, J. Cruickshank, *J. Applied Electrochem.* 28 (1998) 289.
- [7] Z. Qi, A. Kaufman, *J. Power Sources*, 96 (2002) 411.
- [8] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, A.B. Bocarsly, *J. Power Sources* 103 (2001) 1.
- [9] T. Mokrani, *Organic / Inorganic Nanocomposite Membranes Development for Low Temperature Fuel Cell Applications*, Chapter 20 in *Advances in Chemical Engineering*, Z. Nawaz and S Naveed (Eds), InTech, 2012, pp 505-542 (ISBN 978-953-51-0392-9).
- [10] Q. Li, R. He, J. Jensen, and N. J. Bjerrum, *Chem. Mater.*, 15 (2003) 4896.
- [11] Z. Lu, G. Polizos, E. Manias, and D.D. Macdonald, *ECS Transactions*, 28 (2010) 81.
- [12] K. J. Belvin, H. L. Raney, D. L. Su, J. Harrison, J. S. Siochi, E. J. Pawlowski, *Polymer*, 44 (2003) 1309.
- [13] A. Robitaille, L. Mokri, A. Aji, A. Laforgue, *Macromolecule Material Engineering*, 292 (12) (2007) 1229.
- [14] C. Nithitanakul, M. Supaphol, P. Mit-uppatham, *Macromolecules. Chem. Physics*

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