Nafion Nanofiber Composite Membrane Fabrication for Fuel Cell Applications

C. Okafor, M. Maaza, T. Mokrani

Abstract—A proton exchange membrane has been developed for direct methanol fuel cell (DMFC). The nanofiber network composite membranes were prepared by interconnected network of Nafion (perfuorosulfonic acid) nanofibers that have been embedded in an uncharged and inert polymer matrix, by electro-spinning. The spinning solution of Nafion with a low concentration (1 wt% compared to Nafion) of high molecular weight poly(ethylene oxide), as a carrier polymer. The interconnected network of Nafion nanofibers with average fiber diameter in the range of 160-700nm, were used to make the membranes, with the nanofiber occupying up to 85% of the membrane volume. The matrix polymer was crosslinked with Norland Optical Adhesive 63 under UV. The resulting membranes showed proton conductivity of 0.10 S/cm at 25°C and 80% RH; and methanol permeability of 3.6 x 10^{-6} cm^2/s.

Keywords—Composite membrane, electrospinning, fuel cell, nanofibers.

I. INTRODUCTION

FUEL cells are becoming a very good alternative and reliable source of power in our world today, considering the impact of fossil fuel on the environment [1], [2]. Fuel cells like Direct Methanol Fuel Cells (DMFCs) are now widely used in portable electronic devices because of their advantages they possess for electronic devices and transportation applications. A very important part in direct methanol fuel cells, possibly the heart, is proton exchange membranes, (PEMs). It is very important that a good PEM transport proton as well limit fuel crossover.

Perfluorosulfonated polyelectrolytes such as Nafion, Aciplex, and Flemionhave been used as PEMs for fuel cells [3]. Major drawback they possess is the level of permeation fuel infuses through them. Research has grown over the years to develop PEMs that could limit this disadvantage. Recent studies have proposed several routes towards achievement of this purpose. Fabrication and mechanical alterations of polyelectrolytes and blending of available PEMs are used commonly by several research groups [4]. Making organic/inorganic micro- or nanocomposite membranes is another successful way for improvement of PEM performance in DMFC applications [2], [5], [6]. Fibrous membranes are another type of membranes recently applied for gas/liquid separation and hemodialysis applications due to their unique properties such as high specific surface area and good mechanical properties [7].

For several decades, electrospining has existed [8] and is one mostly used method for producing fibrous nano materials for medical and filteration purposes from both natural and synthetic materials [9]. A number of polymers with potential applications as proton conductors have been fabricated by electrospinning process. Examples are poly(ether sulfone) [9], polysulfone [10], polystyrene [11], polybenzimidazole [12], and poly(acrylic acid) [13].

In this study, Nafion nanofibers have been fabricated via electrospinning technique and membranes based on Nafion nanofiber mat have been fabricated and studied for potential application in DMFCs.

II. EXPERIMENTAL

A. Materials

Nafion 5 wt% solution, Nafion117 membrane, poly(ethylene oxide), 2-propanol,sulfuric acid, and methanol were purchased from Sigma Aldrich Industries.

B. Nanofiber Fabrication

Electrospinning solution was prepared as follows. 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%. Poly(ethylene oxide) (PEO) (MW 300,000 g/mol) used was purchased from Sigma Aldrich. The Nafion/dopant electrospinning solutions were prepared by dissolving Nafion powder in 2-propanol/water (2/1 wt/wt) to obtain 30wt% Nafion solution. The carrier polymer, PEO, was dissolved in the same mixed solvents (2-propanol/water) at a concentration of 10wt%. The Nafion solution and the 10wt% PEO were mixed together in the solvent. 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 as-spun mats fiber volume fraction was inadequate for fuel cell membrane applications. The proton-conducting phase

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in the developed membrane need to be improved with interconnectivity between proton conducting fibers, thus mat densification and fiber welding was carried out. The inter-fiber voids between fibers were filled with an inert/impermeable polymer to create a defect-free and fully dense nanofiber network composite membrane. 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 still contained inter-fiber voids, thus, these voids were filled with an inert and hydrophobic pre-polymer, 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. 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. To image a mat cross-section, dry membranes were manually fractured after cooling in liquid nitrogen. All specimens were sputter coated with palladium (5nm thickness).

D. Proton Conductivity

In-plane and through-plane proton conductivity of water equilibrated nanofiber composite membrane and Nafion 117 film were measured at room temperature by an AC impedance technique (Agilent 4338 milliohmmeter, with all measurements made at 1kHz), using an open-frame two-electrode conductivity cell. Membranes were arranged together with a thickness of 1mm, for the through-plane measurements, so as to minimize surface capacitance effects (Preliminary through-plane conductivity of stacked commercial Nafion membranes was proved successful by using such an approach [14]).

E. Methanol Permeability

Methanol permeability in Nafion® nanofiber composite was measured at 60°C using a two-compartment glass diffusion cell [15]. The membrane was clamped vertically between the two compartments, one of which was filled with 1.0M methanol solution. The other (receiving) compartment contained deionized water. Concentrations of methanol in the receiving compartment were collected in real time by continuous circulation of solution in the receiving compartment through a differential refractometer, Personal DaqView acquisition software was used for data collection. Methanol permeability (P) was found from slope of the following plot derived from Fick's first law
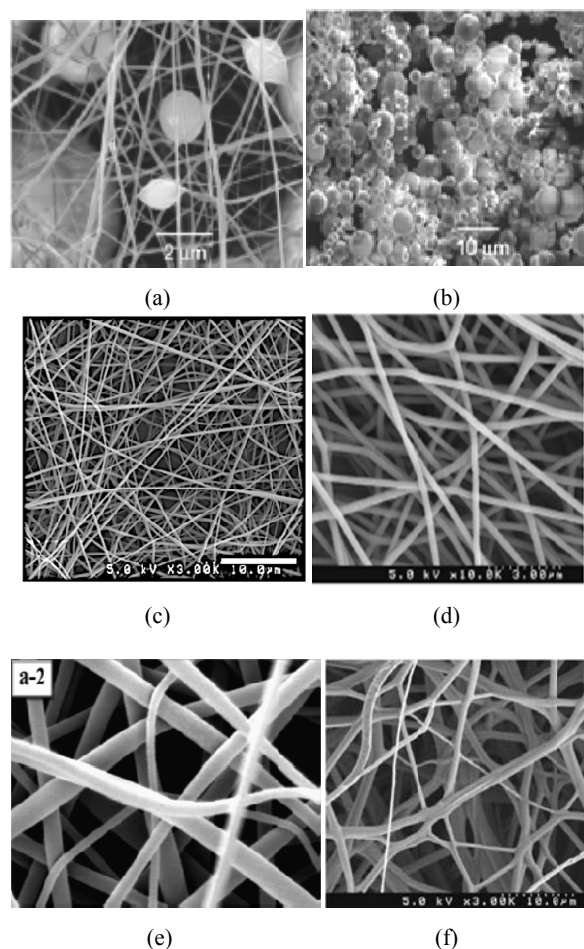
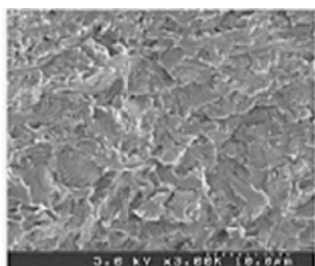$$\ln\left[\frac{1}{1-\frac{C_R(t)\left(1+\frac{V_R}{V_L}\right)}{C_L^O}}\right] \quad vs \quad t$$

where $C_R(t)$ is the methanol concentration in the receiving compartment at a given time t after the start of a permeation experiment, C_L^O is the initial methanol concentration in the feed compartment, V_L is the solution volume in the upstream methanol compartment of the permeation cell, V_R is the total volume in the downstream (receiving) compartment including the refractometer recirculation loop.

III. RESULTS AND DISCUSSION

A. Fiber Morphology

Associated scanning electron micrographs and fiber diameter histograms are shown in Fig. 1. The 5 wt% solution resulted in electrosprayed 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 [16]. Fiber mats without beads were fabricated with average fiber diameter of 255nm (C = 15 wt%), 405nm (C = 20 wt%), and 750nm (C = 25 wt%), when the polymer concentration is greater than or equal to 15wt%. Furthermore, at the 25 wt% concentration, the nanofibers were flattened.

(a)   (b)

(c)   (d)

(e)   (f)

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(g)

Fig. 1 SEM images of electrospun fiber mat surfaces (a) electrosprayed 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
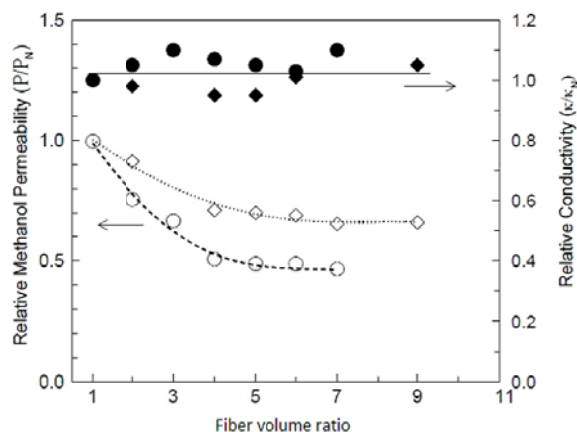

Fig. 2 Through-plane proton conductivity as a function of fiber volume ratio Nafionnanfiber composite and Nafion 117: ● proton conductivity of Nafion 117 ♦ proton conductivity of Nafionnanofiber composite; ○ Methanol permeability of Nafion 117; ◊ Methanol permeability of Nafionnanofiber composite

Pawlowski and co-workers [17] 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 [18]).

B. Proton Conductivity

Proton and methanol transport in recast and commercial Nafion films were found to be the same, as would be expected, Fig. 2. Methanol permeability decreased without accompanying proton loss in Nafion nanofiber mat, than Nafion 117, where nanofiber volume was higher. Both Nafion 117 film and Nafion nanofiber composite film exhibited credible proton conductivity and permeability within measured error analysis. It was not clear if the difference in methanol permeability was as a result of difference in morphology obtained through electrospining and annealing of the Nafion nanofiber mat. Thus giving the nanofiber mat film better alignment, polymer chain packing and crystallinity than Nafion 117film.

IV. Conclusion

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. Then the fabricated membranes were characterized and studied for potential application in DMFC. The proton conductivity of the nanofiber composite film and Nafion 117 were about same range. The results of methanol permeability indicated that the nanofiber composite film had lesser methanol permeability than Nafion 117 probably due to morphological changes as a result of poly alignment, chain packing and crystallinity from electrospining and annealing.

References

[1] Iman Shabania, b, Mohammad Mahdi Hasani-Sadrabadia, c, Vahid Haddadi-Asla, Masoud Soleimanid. Nanofiber-based polyelectrolytes as novel membranes for fuel cell applications, Journal of Membrane Science 368 (2011) 233

[2] M.M. Hasani-Sadrabadi, E. Dashtimoghadam, F. Majedi, K. Kabiri, N. Mokarram, M. Solati-Hashjin, H. Moaddel, Novel high-performance nanohybrid polyelectrolyte membranes based on bio-functionalized montmorillonite for fuel cell applications, Chem. Commun. 46 (2010) 6500.

[3] X. Du, J. Yu, B. Yi, M. Han, K. Bi, Performances of proton exchange membrane fuel cells with alternate membranes, Phys. Chem. Chem. Phys. 3 (2001) 3175.

[4] J.A. Kerres, Blended and cross-linked ionomer membranes for application in membrane fuel cells, Fuel Cells 5 (2005) 230.

[5] M.M. Hasani-Sadrabadi, E. Dashtimoghadam, S.R. Ghaffarian, M.H. Hasani Sadrabadi, M. Heidari, H. Moaddel, Novel high-performance nanocomposite proton exchange membranes based on poly (ether sulfone), Renew. Energy 35 (2010) 226.

[6] M.M. Hasani-Sadrabadi, S.H. Emami, R. Ghaffarian, H. Moaddel, Nanocomposite membranes made from sulfonatedpoly (ether etherketone) and montmorillonite clay for fuel cell applications, Energy Fuels 22 (2008) 2539.

[7] K.H. Lee, D.J. Kim, B.G. Min, S.H. Lee, Polymeric nanofiber web-based artificial renal microfluidic chip, Biomed. Microdevices 9 (2007) 435.

[8] A. Fomhals, US Patent 1,975,504 (1934).

[9] M. Soleimani, S. Nadri, I. Shabani, Neurogenic differentiation of human conjunctiva mesenchymal stem cells in nanofibrous scaffold, Int. J. Dev. Biol. 54 (2010) 1295.

[10] R. Gopal, S. Kaur, C.Y. Feng, C. Chan, S. Ramakrishna, S. Tabe, T. Matsuura, Electrospunnanofibrouspolysulfone membranes as pre-filters: particulate removal, J. Membr. Sci. 289 (2007) 210.

[11] C. Pattamaprom, W. Hongrojjanawiwat, P. Koombhongse, P. Supaphol, T. Jarusuwannapoo, R. Rangkupan, The influence of solvent properties and functionality on the electrospinnability of polystyrene nanofibers, Macromol. Mater.Eng. 291 (2006) 840.

[12] J. Kim, D. Reneker, Polybenzimidazolenanofiber produced by electrospinning, Polym. Eng. Sci. 39 (1999) 849.

[13] L. Li, Y.L. Hsieh, Ultra-fine polyelectrolyte fibers from electrospinning of poly(acrylic acid), Polymer 46 (2005) 5133.

[14] Simader, K.;Kordesch, G., Fuel Cells and Their Applications, NewYork: VCH, 1996.
[15] Kunz, R.; Fento, H.R.; Jiang, J.M., Journal of Power Sources, vol. 150, no. 120, 2005
[16] C, Nithitanakul, M. and Supaphol, P. Mit-uppatham, "Ultrafme Electrospun Polyarnide-6 Fibers: Effect of Solution Conditions on Morphology and Average Fiber Diameter," Macromolecules. Chem. Physic, vol. 205, pp. 2327-2338, 2004
[17] K. J., Belvin, H. L., Raney, D. L., Su, J., Harrison, J. S. and Siochi, E. J. Pawlowski, "Electrospinning of a micro-air vehicle wing skin.," Polymer, vol. 44, pp. 1309-1314, 2003.
[18] A., Robitaille, L., Mokrini, A., Ajji, A. Laforgue, Macromolecule Material Engineering, vol. 292, no. 1229, 2007