

Electrospun Nanofiber Membranes and Electrodes for Fuel Cells

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ABSTRACT

Nanofiber electrospinning is a proven technique for fabrication of high performance hydrogen/air fuel cell membranes and electrodes. Herein, recent work is summarized on electrospun proton and hydroxide conducting polymeric membranes and low-Pt loading nanofibrous fuel cell cathodes.

A dual-fiber electrospinning was utilized for fabrication of membranes from ionomers and reinforcing polymers. An electrospun membrane from polyphenylsulfone (PPSU) and a 3M ionomer (72 vol% 3M 660EW) showed a proton conductivity of 93 mS/cm at 120°C and 50%RH. An MEA with this membrane gave high power output which was insensitive to hydrogen and air humidity in the 50-95%RH range. In a complimentary project, nanofiber cathodes composed of Pt/C powder embedded in a proton conducting binder were prepared. Very high power density, 906 mW/cm² at 80°C, was produced from MEAs with a Nafion 212 and a cathode electrospun from HiSpec™ 4000 catalyst, at a Pt loading of only 0.055 mg/cm².

Keywords: fuel cell, electrospinning, membrane-electrode assembly

1 INTRODUCTION

Electrospinning is gaining popularity as a convenient and cost-effective technique for the fabrication of sub-micron diameter polymer fibers. During electrospinning, an electrostatic field causes a necking down of the polymer solution or melt that is ejected from a spinnerette and then an acceleration of the extruded polymer jet as it travels towards a grounded collecting surface. During exposure to air, solvent is evaporated from the jet or the polymer melt cools and solid fibers are deposited on the collecting surface.

Electrospinning was invented in the early 1900s, but little interest was seen until the work of Reneker and co-workers in the 1990s [1]. In 2008, Pintauro and co-workers [2] proposed utilization of electrospinning for the fabrication of nanocomposite fuel cell membranes as alternative to traditional membranes based on polymer blends and copolymers. These early membranes were fabricated by electrospinning an ionomer fiber mat followed by the impregnation of an uncharged, reinforcing polymer into the inter-fiber voids. Post-electrospinning processing steps were usually required to convert an electrospun mat into a dense and defect-free fuel cell

membrane. These steps included mat compression, fiber welding, ionomer annealing, inert polymer impregnation, and a final hot acid/water treatment. The resultant nanofiber composite membrane morphology decoupled the proton conduction function of the ionomeric nanofibers from the mechanical support and swelling control functions of the uncharged polymer.

Dual-fiber electrospinning was recently introduced to avoid a separate interfiber void-filling impregnation step during nanofiber composite membrane fabrication [3]. Now, the ionomer and the uncharged polymers are simultaneously electrospun as separate fibers that mix into a single mat. Subsequent processing, via hotpressing and either annealing or solvent vapor exposure, induces flow of one of the polymer components into the interfiber void space while retaining the nanofiber morphology of the second polymer.

Another interesting application of polymer electrospinning is the fabrication of low Pt-loaded fuel cell electrodes for use in proton-exchange membrane (PEM) hydrogen/air fuel cells. This process was introduced by Zhang and Pintauro in 2011 [4] and its development is continuing. Very high power outputs are possible with the nanofiber morphology, due to high Pt cathode utilization, low oxygen mass transport resistance, and good water removal rates.

Our recent work on electrospun fuel cell membranes and Pt electrodes will be discussed below.

2 DUAL-FIBER COMPOSITE MEMBRANES

2.1 Proton Conducting Membranes Fabrication and Characterization

Two types of perfluorosulfonic acid polymers (PFSAs) were employed in the study: Nafion® (EW 1100 g/eq.) and 3M660 (EW 660 g/eq.). PFSA's micellar dispersions can not be electrospun directly and therefore a carrier polymer must be added to allow for spinnability. For example, a 400kDa MW polyethylene oxide (PEO) at a loading of 1wt% was used as the carrier for Nafion and a 1000kDa PEO was used as the carrier for 3M660 at 0.3wt%. A 2:1 n-propanol/water mixture was used as the solvent for the ionomer/PEO mixtures. Polyphenylsulfone (PPSU) served as the uncharged, reinforcing polymer which was electrospun from a separate spinnerette but simultaneously with the PFSA/PEO mixture. An NMP-acetone mixture (20

wt% acetone) was used as the solvent for the PPSU. The ionomer and the uncharged polymer solutions were simultaneously electrospun from two spinnerettes onto a rotating drum that oscillated laterally to generate a dual nanofiber mat of uniform composition and thickness.

Two basic morphologies were prepared from the electrospun, porous Nafion-PPSU mats. Scanning electron microscope (SEM) micrographs of a representative samples are shown in Fig.1.

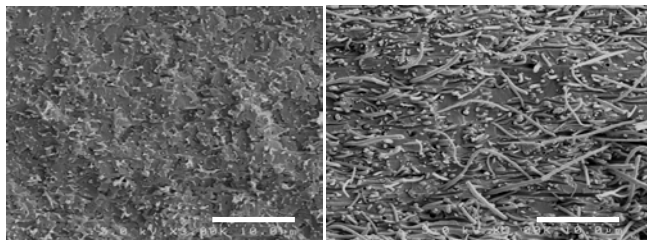


Figure 1. SEM micrographs of the cross-sections of an electrospun membrane with Nafion fibers encapsulated in PPSU (left) and an electrospun membrane with a Nafion film being reinforced by PPSU fibers (right). Each membrane is ~70 wt% Nafion. Cross-sections were obtained by freeze-fracturing. Scale bars are 10 μm .

In one realization, (Fig. 1 left micrograph), the PPSU component was softened and allowed to flow by exposure to chloroform vapor. During this processing step the PPSU filled the voids between the Nafion nanofibers without affecting the ionomer fibers. The resultant structure was that of an interconnected Nafion nanofiber mat encapsulated in a continuous PPSU matrix. The inverted structure (Fig. 1 right micrograph), where a continuous Nafion matrix is reinforced by PPSU nanofibers, was obtained through thermal fusion of the Nafion fibers by hotpressing a mat at 127°C and 24000 lb for 10 minutes. Under these conditions, the Nafion nanofibers softened and flowed to fill the void space between PPSU nanofibers. The final step in the both variants was thermal annealing of Nafion at 150°C for 2 hrs under vacuum.

The basic properties of the PPSU-reinforced Nafion composite membrane and the commercial Nafion 212 membranes are presented in Tab.1. It can be observed that both membranes have equivalent area specific resistances (due to a lower thickness of the nanofiber composite film), but their swelling characteristics are quite different. The in-plane swelling, is very low for the nanofiber composite membrane. This is a desirable membrane property for hydrogen/air fuel cell applications in that it improves MEA durability.

Membrane durability was evaluated by recording the fuel cell open circuit (OCV) during repeated exposure of hydrogen and air at different levels of humidification at 80°C (2 min at 100% RH and then 2 min at 0% RH). During this cycling protocol, the membrane swells and shrinks, thus undergoing mechanical stresses which lead to

microcracking and hydrogen gas crossover which causes the OCV to decrease.

Membrane	Conductivity (S/cm)	Area-Specific Resistance (Ohm-cm ²)	In-Plane Swelling (%)	Volumetric Swelling (%)
Nanofiber Composite	0.066	45 (36 μm)	6	42
Nafion 212	0.095	45 (51 μm)	37	75

Table 1: Properties of a Nafion-PPSU nanofiber membrane and a commercial Nafion 212 referenced. Proton conductivity was measured at 23°C with the samples equilibrated in liquid water; the area-specific resistance (membrane thickness divided by conductivity) was recorded for membranes equilibrated in water vapor at 80°C and 90%RH. Equilibrium swelling was measured in liquid water at 100°C.

The changes in OCV for the MEAs fabricated with Nafion 212 and with the Nafion/PPSU nanofiber composite membrane are shown in Fig. 2 [3]. Here, MEA failure is defined as a drop in OCV below 0.8 V. It can be seen that the nanofiber composite membrane failed after 842 h as compared to 546 h for Nafion 212 which is a 54% improvement in durability. The superiority of the MEA fabricated with the nanofiber composite membrane is evident.

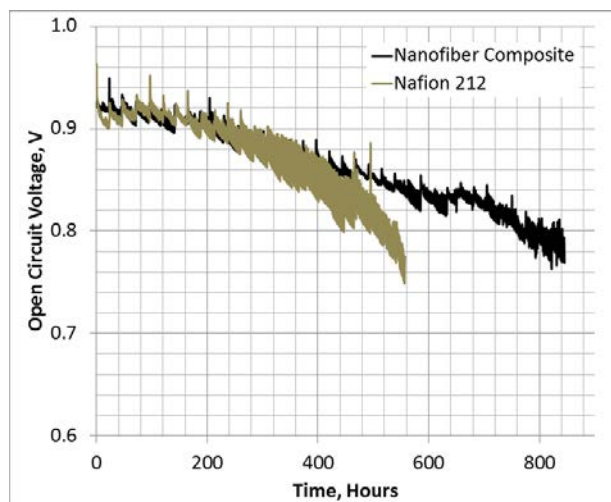


Figure 2. Accelerated durability tests with commercial Nafion 212 and a composite Nafion-PPSU nanofiber membrane (65vol% Nafion with PPSU nanofibers, 31 μm).

Another exciting demonstration of the great capabilities of electrospun composite membranes involves the use of low EW PFSA polymers. Such highly charged polymers swell excessively in room temperature water and lose mechanical strength, thus requiring some kind of

mechanical reinforcement. A dual fiber electrospun composite membrane, composed of 72 vol% 660 EW PFSA, from 3M Company, and 28 vol% PPSU was fabricated, where the PFSA surrounded the PPSU fibers [5]. The membranes exhibited a very high proton conductivity under semi-dry conditions, e.g., 93 mS/cm at 120°C and 50% RH, as compared to 37 mS/cm for commercial Nafion. The dimensional stability of the membrane upon liquid water equilibration was excellent, with an in-plane swelling at room temperature of only 5%, as compared to 84% for a neat 660EW solution cast film. A MEA containing the nanofiber composite membrane had significantly higher power output in a hydrogen/air fuel cell, as compared a a MEA with a Nafion 211 membrane (Fig. 3), especially under low relative humidity fuel cell operation. The power output of the nanofiber composite membrane MEA was relatively insensitive to changes in feed gas humidity, between 50% and 93% RH for temperatures of 80°C and 100°C. Such insensitivity to RH is highly desirable in automotive fuel cells.

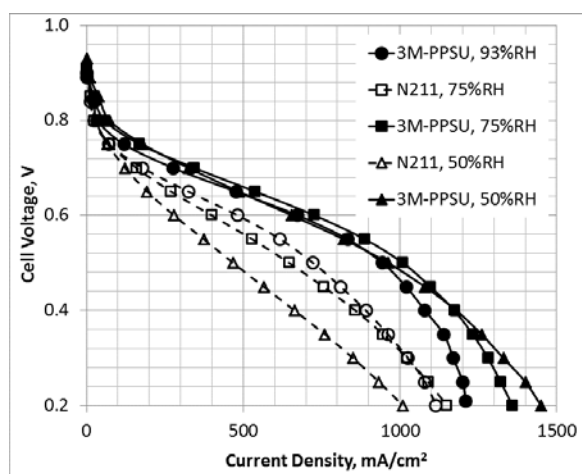


Figure 3. Fuel cell performance comparison of Nafion and electrospun 3M-PPSU membranes at relative humidity of 93, 75 and 50%.

2.2 Alkaline Membranes Fabrication and Characterization

During the last decade, there has been a revival of interest in alkaline fuel cells (AFCs), where a solid hydroxide ion conducting polymeric membrane is used instead of a liquid electrolyte. One important advantage of AFCs over proton conducting membrane fuel cells is the possibility of AFC operation with less expensive non-noble metal electrodes, e.g. Ni or Ag.

The most popular type of alkaline fuel cell membrane contain quaternary ammonium ion exchange sites which can be conveniently obtained using many aromatic polymers via chloromethylation and subsequent amination. Our group has utilized dual-fiber electrospinning for the preparation of composite alkaline membranes with controlled water uptake, excellent dimensional stability and good

mechanical properties [6]. To prepare a nanofiber composite anion exchange membrane, a highly chloromethylated polysulfone and PPSU were electrospun simultaneously to obtain a dual nanofiber mat with uniform intermixing of the two polymers. Subsequent compaction, pore closure through exposure to chloroform vapor, and amination, converted the mat into a dense and defect-free film where an interconnected network of tetramethylammonium-substituted polysulfone nanofibers was embedded in a polyphenylsulfone matrix. While the membranes cast from the neat ammonium polymers swelled significantly in water, e.g. 170 vol% at IEC of 2.47 mmol/g, the composite membranes swelled significantly less, because their water uptake was controlled by the inert PPSU matrix that surrounded the charged fiber network. This effect had a very surprising consequence that is exemplified in Fig. 4. Here the inter-relationship between the effective ion-exchange capacity (IEC) and the OH⁻ ion conductivity is shown for neat quaternary ammonium polymer films and for a series of nanofiber composite membranes. At low IEC, the neat film's conductivity surpasses that of the composite due to the presence of PPSU which dilutes the ionomer component, but at the highest values of IEC, the situation is reversed. This unusual behavior can be associated with the significant increase in the concentration of fixed charge sites and OH⁻ ions when PPSU-restricts the water swelling of the quaternary ammonium fibers.

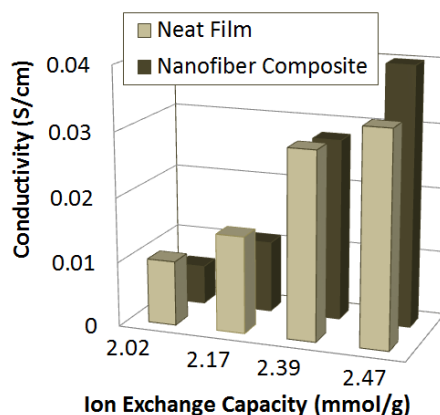


Figure 4. Hydroxy-ion conductivity of the neat homogeneous cast film (light gray bars) and of the composite QAPSF-PPSU membrane (dark gray bars; 63% QAPSF and 37% PPSU).

As a result, the nanofiber composite membrane containing 63 wt% of ammonium polymer fibers (with a fiber IEC of 2.47 mmol/g), exhibited a OH⁻ conductivity in water at room temperature of 0.040 S/cm vs. 0.033 S/cm for the neat ammonium film. Also, the mechanical properties of the composite membranes were better than those of the homogeneous films. For example, the composite membrane with 63 wt% ammonium polymer nanofiber had tensile strength of 25 MPa and an elongation at break of 7%. In contrast, a dry film of the neat ammonium

polymer of the same IEC shattered on handling or became a highly swollen gel, unsuitable for tensile testing, when exposed to liquid water at room temperature.

3 ELECTROSPUN FUEL-CELL ELECTRODES

3.1 Low-Pt Electrodes Fabrication and Characterization

There is a concerted effort by researchers around the world to lower the Pt catalyst electrode loading in a proton exchange membrane hydrogen/air fuel cells for automotive applications to decrease the overall fuel cell cost. Thus, a Pt loading target would be ~9g of Pt for a 50kW hydrogen/air fuel cell stack. There is also a need to improve the durability of Pt/C-based fuel cell electrodes.

Electrospinning appears to be well suited for the preparation of nanofibrous fuel cell electrodes with low Pt content. Our group has already fabricated a nanofiber electrodes by electrospinning an ink composed of Pt/C catalyst particles in a solution of Nafion and poly(acrylic acid) [4]. Exceptionally high power densities and high platinum mass activity were achieved when using the mats as cathodes in H₂/air and H₂/O₂ fuel cell membrane-electrode assemblies. The nanofiber cathodes also exhibited outstanding stability in accelerated durability tests.

In Fig. 5, micrographs of a standard decal transfer fuel cell cathode and an electrospun nanofiber electrode are shown. The nanofibrous morphology of the electrospun electrode is evident with a mean fiber diameter of 600 nm. This structure is maintained during MEA fabrication and fuel cell operation.

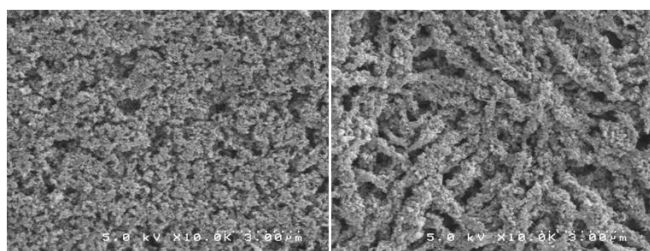


Figure 5. SEM micrographs of a standard decal fuel cell cathode (left) and an electrospun nanofiber cathode (right); magnification 10,000 times.

Membrane-electrode-assemblies (MEAs) were fabricated with electrospun nanofiber electrodes containing Johnson-Matthey (JM) HiSpec™ 4000 catalyst and a Nafion® 212 membrane. MEA performance was evaluated in a hydrogen/air fuel cell, where power output was correlated with cathode Pt loading (0.029-0.107 mg_{Pt}/cm²), changes in fuel cell temperature (60°C and 80°C), backpressure (up to 3.0 atm), and feed gas flow rates. In all experiments, the nanofiber anode had a fixed Pt loading of 0.10 mg/cm². Experimental results showed that the mass activity (0.1 A/mg_{Pt} at 0.9 V) and electrochemical surface

area (~41 m²/g) of nanofiber cathodes were very high and more power was generated from nanofiber electrode MEAs than a conventional MEA with decal electrodes. For example, as shown in Fig. 6, the maximum power density for H₂/air fuel cell operation at 80°C, 1 atm (ambient) pressure, 125 sccm H₂, and 500 sccm air was 513 mW/cm² for a nanofiber cathode at 0.107 mg_{Pt}/cm² vs. 386 mW/cm² for a conventional decal MEA with cathode/anode Pt loadings of 0.104/0.40 mg/cm². Similarly, an electrospun cathode with a Pt loading of 0.055 mg/cm² produced a maximum power density of 906 mW/cm² at 80°C and 3 atm pressure with 2000 sccm fully humidified air and 500 sccm H₂.

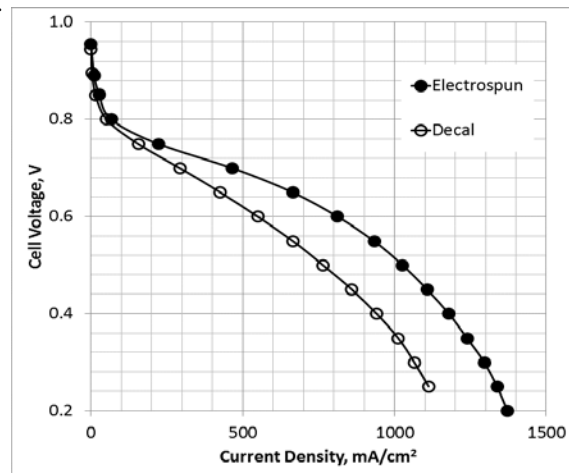


Figure 6. Hydrogen/air fuel cell polarization curves for 5 cm² MEAs with a Nafion 212 and HiSpec™ 4000 catalyst electrospun cathodes and anodes. The Pt/C: Nafion:PAA weight ratio was 65:23:12. The anode Pt loading was 0.10 mg/cm² and the cathode Pt loading was 0.107 mg/cm² (closed circles). Also shown is a standard decal MEA with cathode and anode Pt loadings of 0.104 mg/cm² and 0.40 mg/cm², respectively (open circles). Operating conditions: 80°C, 125 sccm H₂ and 500 sccm air at 100%RH.

These results demonstrate that electrospinning is a powerful, robust, and effective technique for the fabrication of low-Pt high-performance hydrogen/air fuel cell electrodes.

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