Electrospun Nafion® Nanofibers for Proton Exchange Membranes

Michael W. Cason Literature Seminar September 23, 2010

Electrospinning has gained significant attention in the past two decades as a method for fabricating long continuous fibers with nanoscale diameters. The generalized electrospinning process begins by pumping a polymer solution (or melt) through a conductive nozzle.[1] When the applied voltage is large enough to overcome the surface tension of the material being spun, the solution exiting the tip will taper forming a Taylor cone leading to a jet.[2] The stream narrows in width and elongates as a result of the whipping motion that occurs as surface charges interact unevenly with the electric field, and is driven at high velocities toward the substrate. Many factors influence the resulting fiber diameter, including increased distance from the nozzle, dissipating surface charge, solvent evaporation, cooling, and Rayleigh instability.[3] A schematic illustration of a representative electrospinning experiment is presented in Figure 1.

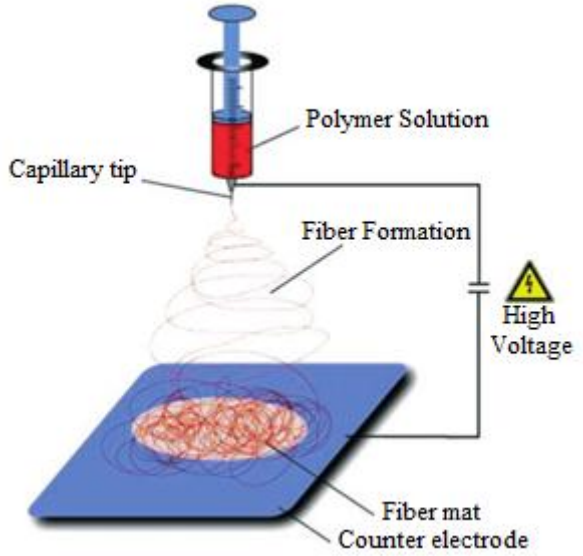

Figure 1: Cartoon schematic of an electrospinning experiment.[1]

A diverse collection of materials, such as metals, ceramics, polymers with embedded chromophores or nanoparticles, and even core-shell fibers, have been successfully electrospun.[1,4] By far, however, polymer solutions and melts have been the most thoroughly studied in the literature. In order to produce fibers with the desired properties, many experimental parameters must be precisely controlled, including molecular weight, solubility, viscosity, surface tension, electrical conductivity, solvent vapor pressure, relative humidity, electric field, and feed rate of the solution.[5,6] By tuning these conditions, a wide range of polymers can be processed using the electrospinning technique.

Polymer electrolyte membrane (PEM) fuel cells operate by oxidizing a fuel, such as hydrogen, on the surface of an anode. Electrons generated in this process are conducted along a catalyst support through the external circuit, while the generated protons travel through an electrically insulating separator, to the cathode where they

combine with oxygen, as it is reduced, forming water.[7,8] The insulating PEM must demonstrate high proton conductivity and low fuel/oxygen crossover, in addition to being mechanically robust and chemically resistant. Additionally, because the membrane must remain well hydrated to maintain good conductivity, performance at temperatures above 100 °C is compromised.[9]

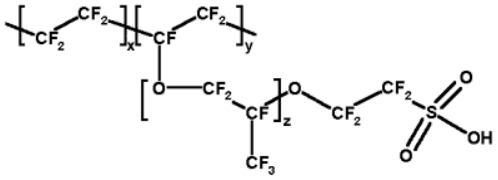

Figure 2: General chemical structure of Nafion ionomers.

Nafion, a commercially available fluoropolymer developed by DuPont, is the most commonly used proton exchange membrane in PEM fuel cells. Nafion is a "comb" copolymer, containing a tetrafluoroethylene backbone and sulfonic acid terminated perfluorinated vinyl ether "teeth".[10] The chemical structure is given in Figure 2. The proton conductivity of Nafion is due to the sulfonic acid groups present on the side chains. More specifically, these groups have been thought to organize into clusters of ~4 nm, connected by channels of ~1 nm diameter.[10,11] This segregation results in distinct hydrophobic and hydrophilic regions within the membrane. Water present in the hydrophilic regions solvates the protons of the sulfonic acid groups, allowing the protons to "hop" through the channels, from anode to cathode.[12] Typical proton conductivities of Nafion membranes are on the order of 0.1 S/cm.[9]

Recent literature demonstrates successful electrospinning of Nafion nanofibers with improved proton transport properties relative to the traditional extruded membrane topology currently utilized in devices.[9] The fiber mat generated can potentially be used "as is" after minor post-processing such as compression, or by embedding an uncharged, inert polymer matrix to obtain a phase-separated composite.[13] Nafion is challenging to process via electrospinning, as it is not soluble in most common solvents. This insolubility results in formation of micelles that cause a decrease in chain entanglement and an inability to electrospin fibers without the addition of a high molecular weight carrier.[13] A collection of reports suggest that it is difficult to produce Nafion fibers without utilizing a solution containing large amounts of carrier polymer relative to Nafion.[14-16]

Using very high molecular weight polyethylene oxide (8,000 kg/mol), Dong *et al.* fabricated very high purity Nafion fibers with diameters in this study ranged from 125 nm (98 wt %) to 400 nm (99.9 wt %).[17] Individual fibers of various diameters were collected and tested. Interestingly, the conductivity of fibers with diameters >2 μm were comparable to that of a bulk film, but as fiber diameters decreased to the nanoscale (400 nm), conductivity reached as high as 1.5 S/cm. This spike is attributed to an apparent elongation of the ionic domains due to the shear forces present when the fibers are produced; this is corroborated by X-ray scattering data.

The successful implementation of electrospinning to fabricate nanoscale Nafion fibers with improved conductivity, in combination with continued studies of fibers of other polymer types[13,18], represent an avenue toward significantly improving the performance of current membrane materials.

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