Fabrication and Properties of Electrospun Fuel Cell Membranes

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Introduction

High performance polymeric ion-exchange membranes are used in many types of fuel cells. Such membranes must possess the requisite transport properties (a high ionic conductivity and low gas/fuel permeability) and have outstanding durability (i.e., mechanical, chemical, and thermal stability in both the wet and dry states). Past strategies for fabricating fuel cell membranes have included: (1) The use of new polymers with a high ion-exchange capacity, (2) The use of block copolymers which self assemble into nano or micro domains, where one block provides ion transport pathways and the second imparts mechanical strength to the membrane, (3) Combining the desirable properties of two different polymers in a single membrane by blending the polymers prior to membrane casting, (4) Impregnating a charged polymer into a microporous inert support, where the support provides the mechanical properties that the ion-exchange polymer lacks, and (5) Crosslinking the polymer to limit/control solvent swelling and improve mechanical properties. While these approaches have resulted in some successes, there are inherent difficulties and drawbacks in all of the schemes. For example, the use of block copolymers is limited by polymer chemistry (it is difficult to covalently link blocks with very different chemistries and properties) and by the availability of a suitable solvent for solution casting membranes from the resulting block material. Also, there is no guarantee of long range organization of phase-separated domains in a block copolymer after membrane casting.

An alternate approach is to use polymer nanofiber electrospinning as a forced assembly technique to generate a phase separated bicontinuous composite membrane nanomorphology [1-3]. Two different membrane structures are possible: (1) An interconnected 3D web of ion-exchange polymer nanofibers surrounded by an inert (uncharged) polymer matrix or (2) Inert (uncharged) polymer nanofibers surrounded by the charged polymer.

Nanofiber Electrospinning

Electrospinning is a convenient method for producing nano- and micro-fibers from a variety of different polymers. The most common commercial electrospinning units utilize an array of many spinnerets. A polymer solution or melt is pumped to the spinnerets which are polarized to a high voltage, usually 1-20 kV. The resulting electric field causes the emerging polymer liquid filament to initially deform and finally eject from the spinneret tip as a charged jet which elongates dramatically and dries/solidifies on its way to a grounded target (collector) surface. At the collector, a nonwoven fiber mat forms that is composed of continuous fibers of controlled diameter. Nanofiber electrospinning is cost-effective for a number of commercial products (see, for example, the webpage for eSpin Technologies, Inc. at www.espintechnologies.com) and has found diverse application in composites, filtration media, medical and pharmacological products, textiles, and sensors.

Dual Fiber Electrospinning

A dual fiber electrospinning process has been developed by Ballengee and Pintauro [2] for ion-exchange membrane fabrication. In this approach, two different polymers (an ionomer and an uncharged reinforcing polymer) are electrospun simultaneously to produce a mixed nanofiber mat. One of the polymers is then melted around the fibers of the other to fill the mat voids thereby producing a dense and defect-free membrane. Advantages of the dual fiber method include: (1) The choice of materials for the ion-exchange and uncharged polymers is very broad (much broader than block copolymer self-assembly systems and blended solution cast membranes), (2) The physical structure of the nanofiber network (the diameter and number density of nanofibers) is independent of the choice of polymer constituent(s), (3) The nanofiber structure (e.g., solid fibers, porous fibers, flat ribbons, or core-shell composite fibers) is controlled via the electrospinning conditions, thus providing a high degree of flexibility regarding the final membrane product, and (4) There is no need for a separate polymer impregnation step during membrane fabrication (impregnation of a polymer solution into a porous mat is difficult; repeated impregnations are often needed to eliminate defect voids and pin-holes).

Membrane Fabrication and Characterization

In this tutorial, nanofiber composite membranes for three fuel cell systems will be described: (1) Hydrogen/air proton conducting fuel cell membranes composed of low equivalent weight perfluorosulfonic acid polymer for ion transport and uncharged polyphenylsulfone for mechanical support and swelling control; the goal here is to improve hydrogen/air fuel cell membrane durability and fuel cell operation at high temperatures and low relative humidities, (2) OH^- ion conducting alkaline fuel cell membranes containing ionomer fibers (polysulfone with quaternary ammonium fixed-charge groups) that are embedded in an uncharged polyphenylsulfone matrix; such membranes must have high conductivity, good mechanical properties, and moderate water swelling, and (3) Hydrogen/bromine regenerative fuel cell membranes with low bromine crossover and low sheet resistance, where Nafion® perfluorosulfonic acid polymer nanofibers are surrounded by an uncharged/inert matrix of polyvinylidene fluoride. For each system, methods for membrane preparation will be presented, along with membrane characterization results and fuel cell data.

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