Pre-Stretched Recast PFSA Films for PEM Fuel Cells

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Introduction

Perfluorosulfonic acids (PFSAs) are a family of polymers with a $–CF_2$-CF_{2-} backbone and side chains that terminate in hydrophilic sulfonic acid ion-exchange sites. The most commonly used PFSA membrane in proton-exchange membrane (PEM) fuel cells is DuPont's 1100 EW (0.91 mmol/g ion-exchange capacity) Nafion®. Unfortunately, methanol crossover in these membranes is unacceptably high for efficient use in a direct methanol fuel cell and the mechanical resilience of Nafion under humidity/temperature cycling in a hydrogen/air fuel cell is less than satisfactory. Similarly, membranes made from 3M Company 733 EW PFSA (1.36 mmol/g ion-exchange capacity) suffer from excessive water swelling and poor mechanical properties.

We have found that uniaxial stretching of solution cast PFSA membranes prior to polymer annealing improves membrane mechanical properties and durability in a fuel cell and lowers methanol crossover, without adversely altering the membrane's ionic conductivity.

Experimental

Uniaxial stretching was carried out with three PFSA polymers: DuPont's Nafion® (with a long and branched side chains of $-O–CF_2CFCF_3–O–(CF_2)_2–SO_3H$), 3M Company PFSA (a short-side-chain version of Nafion with $–O–(CF_2)_4–SO_3H$ pendant groups), and Aquivion® from Solvay Solexis (with very short side chains of $–O–(CF_2)_2–SO_3H$).

PFSA membranes were cast into a Teflon dish from a dimethylacetamide (DMAc) solution. After evaporating ~85% of the DMAC solvent, the resulting films were uniaxially stretched at a temperature at/above the polymer's α-transition temperature to a draw ratio between 2 and 7 (where the draw ratio is defined as the final membrane length divided by its initial length.). After stretching, the films were heated to remove residual solvent and then fully annealed while in the stretching frame. For example, Nafion membranes were stretched at 125^{o}C and annealed for 2 hours at 150-180^{o}C. Membrane samples were removed from the stretching apparatus after annealing, boiled in 1.0 M H_2SO_4 for one hour, and then soaked in deionized water until further use. Stretched recast membranes had a final wet thickness of 40-190 μm., depending on the draw ratio and initial membrane thickness.

Membrane were characterized in terms of transport properties (in-plane proton conductivity and methanol permeability), polymer/membrane structure properties (e.g., wide angle x-ray diffraction), mechanical properties (stress-strain experiments), and fuel cell tests (hydrogen/air and direct liquid methanol). For all PFSA polymers, structure and physical property changes that occurred as a consequence of elongation were made permanent by annealing after stretching.

Results

Films prepared with Nafion 1100EW, 3M 1000 EW and 825EW, and Aquivion 830EW PFSA show an increase in crystallinity upon uniaxial stretching, with a decrease in methanol permeability and no change in proton conductivity. A direct methanol fuel cell employing a stretched 3M 825 EW PFSA membrane with a draw ratio of 4, for example, exhibits a 31% improvement in power density at 0.4V, as compared to a fuel cell with a Nafion 117 (1100 EW) membrane. The higher power output was associated with the combined effects of low methanol crossover and low membrane sheet resistance.

Un-stretched 733 EW PFSA from 3M Co. has no crystallinity before or after stretching. The nanostructure of ionic domains, however, varied with draw ratio. From wide-angle x-ray diffraction, ionomer peaks of a stretched membrane shift to higher values of 2θ and a new ionomer peak appears when the draw ratio is greater than 4. For a stretched 733 EW membrane (DR=4), there is a significant increase in storage modulus with a proton conductivity equal to that of an un-stretched film. This combination of properties makes stretched 3M 733 EW PFSA a promising PEM material for hydrogen/air fuel cells. In a humidity cycling open circuit voltage fuel cell test at 80°C, the lifetime of a stretched 3M 733 EW PFSA membrane (DR=4) was extended by a factor of 3.5, as compared to that of an un-stretched membrane.

In this presentation, an overview of pre-stretched recast PFSA films will be presented, in terms of the method for creating the films, the properties of stretched ionomers as a function of draw ratio, and the use of stretched films in fuel cell membrane-electrode-assemblies [1-4].

References

1. J. Lin, R. Wycisk, P. N. Pintauro, and M. Kellner, "Stretched Recast Nafion for Direct Methanol Fuel Cells," Electrochem. Solid- State Lett., **10**, B19-B22 (2007).
2. J. Lin, P.-H. Wu, R. Wycisk, A. Trivisonno, and P. N. Pintauro, "Direct Methanol Fuel Cell Operation with Pre-Stretched Recast Nafion®," J. Power Sources, **183**, 491–497 (2008).
3. J. Lin, P.-H. Wu, R. Wycisk, P. N. Pintauro, and Z. Shi, "The Properties of Water in Pre-Stretched Recast Nafion," Macromolecules, **41**, 4284-4289 (2008).
4. W. Zhang, D. L. Kish, and P. Pintauro, "Morphology and Performance of Stretched PFSA for Direct Methanol Fuel Cells, " Electrochemical Society Transactions, **33(1)**, 635-645 (2010).