Properties and Morphology of Stretched Recast Nafion Membranes

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PROPERTIES AND MORPHOLOGY OF STRETCHED RECAST NAFION® MEMBFRANES

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Introduction

We recently reported on the fabrication and use of stretched recast Nafion® in a direct methanol fuel cell, where uniaxial film elongation was carried out prior to polymer annealing (1). Uniaxial stretching had no effect on proton conductivity but it did cause the methanol permeability to decrease. After annealing, morphological changes in recast/stretched Nafion were permanent. Stretched Nafion films work very well in a direct methanol fuel cell at 1.0 M methanol, with a lower methanol crossover as compared to Nafion 117 and a power density at 0.4 V of 76 mW/cm^2 at 60^{o}C and 160 mW/cm^2 at 80^{o}C (1.0 atm. air and anode/cathode catalyst loadings of 4 mg/cm^2). The use of stretched recast Nafion in H_2/air fuel cells is currently under investigation.

In the present paper, more detailed analyses of the properties and morphology of stretched recast Nafion membranes will be presented.

Experimental

Membranes were prepared from Nafion polymer that was recovered after evaporating the solvent from a commercial Liquion 1100 Nafion solution (Ion Power, Inc.). Membranes were cast into a Teflon dish from a solution of 5 wt% Nafion in DMAC solvent. After partial evaporation of the solvent at 60^{o}C, the membrane was removed from the casting dish, placed in the stretching frame, heated to 125^{o}C and then uniaxially stretched to a given draw ratio ranging from 2.0 to 7.0. The membrane was kept in the stretching frame and further heated (at 125^{o}C) for 1 hour to fully evaporate DMAc, followed by an annealing step at 150^{o}C for 2 hours. The membrane was removed from the stretching apparatus, boiled in 1.0 M H_2SO_4 for one hour, and then soaked in deionized water until further use. The stretched recast membranes had a final wet thickness of 50-60 µm.

A series of experiments were performed to characterize the properties and morphology of stretched recast Nafion membranes, including proton conductivity (in-plane and through-plane AC impedance), equilibrium water sorption (% weight gain), wide-angle x-ray diffraction (of dry membranes), differential scanning calorimetry, DSC (to determine the fraction of freezable water in the membrane), methanol permeability (a two-compartment diffusion cell), transmission electron microscopy (TEM), water self diffusion (pulsed field gradient NMR), and small-angle x-ray scattering (SAXS).

Results and Discussion

A portion of the experimental data collected on stretched recast Nafion are presented in Table 1 (effect of draw ratio on equilibrium water uptake), Figure 1 (the effect of draw ratio on through-plane proton conductivity for membranes in 25^{o}C water and methanol permeability for 1.0 M methanol at 60^{o}C), and Figure 2 (effect of draw ratio on the fraction of freezable water). Of primary importance for fuel cell operation, the proton conductivity is independent of draw ratio, but the methanol permeability decreases with membrane elongation, up to a draw ratio of about 4. The total membrane water content is independent of draw ratio and is similar to water uptake in Nafion 117, but the fraction of freezable water in stretched recast Nafion is much less than that in commercial Nafion.

Table 1 – Equilibrium Water Swelling of Stretched Recast Nafion (dry weight basis)

Draw Ratio	Water Swelling at 25^{o}C (wt%)	
	Recast Nafion	Nafion 117
1	32	35
2	31	
3	29	
3.5	30	
4	31	
7	30	

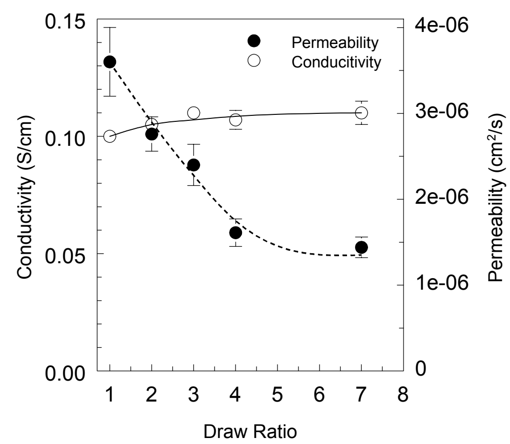

Figure 1 – Proton conductivity (through-plane for membranes equilibrated in water at 25^{o}C) and methanol permeability (1.0 M methanol at 60^{o}C) as a function of draw ratio for stretched recast Nafion.

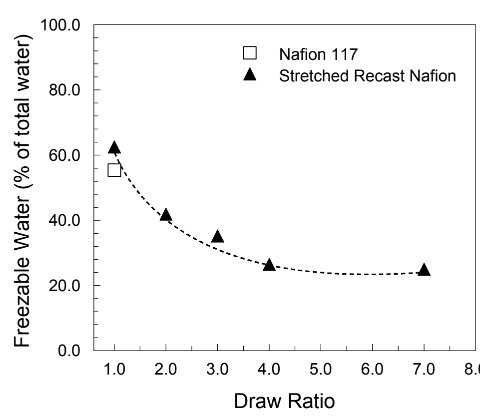

Figure 2 – Percentage freezable water in stretched recast Nafion as a function of draw ratio (from DSC experiments).

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).