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Nafion$^{®}$/Poly(vinyl alcohol) Blends: Effect of Composition and Annealing Temperature on Transport Properties

Nicholas W. DeLuca and Yossef A. Elabd[*]

Drexel University

Department of Chemical and Biological Engineering

Philadelphia, Pennsylvania 19104

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[*] To whom correspondence should be addressed
Phone: 215.895.0986, Fax: 215.895.5837, E-mail: elabd@drexel.edu

Abstract

In this study, the transport properties (proton conductivity and methanol permeability) of Nafion® 117, solution-cast Nafion®, poly(vinyl alcohol) (PVA), and Nafion®/PVA blend membranes were measured as a function of annealing temperature (60-250°C) and blend composition for application to the direct methanol fuel cell (DMFC). A Nafion®/PVA blend membrane at 5 wt% PVA (annealed at 230°C) resulted in similar proton conductivity, but 3 times lower methanol permeability compared to Nafion® 117. In addition, an unusual trend was observed in Nafion®/PVA (50 wt% PVA) blend membranes, where proton conductivity remained relatively constant, but methanol permeability decreased by approximately one order of magnitude with increasing annealing temperature. Infrared spectroscopy reveals a band shift in the hydroxyl peak to higher wavenumbers in Nafion®/PVA blends (25-90 wt% PVA) with increasing annealing temperature suggesting an increase in the interaction between the hydroxyl groups in PVA and the sulfonic acid groups in Nafion®. For Nafion® alone, proton and methanol transport rates increased and then decreased with increasing annealing temperature with a maximum at 210°C for both solution-cast and as-received (extruded) Nafion®. This trend coincides with two transition temperatures observed by other investigators using differential scanning calorimetry, suggesting that transport properties are affected by morphological changes in Nafion®.

Keywords: fuel cell; polymer electrolyte membranes; polymer blends; barrier membranes; electrochemistry; pervaporation

1. Introduction

Ion conducting polymers containing strong acidic groups (e.g., sulfonic acid) are of interest for a broad range of applications, such as biosensors, chemical sensors, catalysts, actuators, ion-exchange membranes, and polymer electrolyte membrane (PEM) fuel cells [1-6]. PEM fuel cells, in particular, are being investigated as replacements to current power sources used in transportation and portable electronics [6]. In this application, the ion conducting polymer or PEM serves as both a cell separator, separating the anode from the cathode, and an electrolyte, conducting protons from the anode to the cathode. Although there are a number of advantages to PEM fuel cells (e.g., renewable fuels, environmentally benign, high efficiencies), there are also a number of key shortcomings with current PEMs that hinder fuel cell efficiency. These shortcomings include low proton conductivity at higher temperatures, poor water management, and high fuel crossover. Fuel crossover is a main concern as it applies to the methanol fuel-based PEM fuel cell (also known as the direct methanol fuel cell (DMFC)). When methanol permeates across the PEM (methanol crossover) at high rates, fuel cell efficiency is reduced by a loss in fuel, cathode voltage, and overall fuel cell lifetime [7].

Nafion® (DuPont), a perfluorosulfonic acid polymer, is the most frequently used PEM in fuel cells. Nafion® exhibits sufficient proton conductivity at optimal water contents and is thermally, chemically, and oxidatively stable; however, it suffers from low conductivity at high temperatures and high methanol crossover. Current research is focused on developing Nafion® replacements that are durable, lower in cost, higher in proton conductivity at higher temperatures, maintain an adequate water balance, and are resistant to methanol [8]. More specifically, for the DMFC, researchers are synthesizing new polymers with non-fluorinated backbones as Nafion® replacements [9-14]. In addition to these studies, other investigators have focused on composites of Nafion® with a variety of fillers, such as montmorillonite, titanium dioxide, silica, hydroxyapatite, and polyfurfuryl alcohol [15-20]. Many of these investigations present results with lower methanol permeabilities; however this is commonly coupled with lower proton conductivities. For the DMFC, a polymer membrane with a high conductivity (similar to or higher than Nafion®) and low methanol permeability (less than Nafion®) is desired.

Usually, general trends observed in Nafion® and other sulfonic acid containing PEMs reveal that proton conductivity and methanol permeability simultaneously increase or decrease with changes in ion content, water content, temperature, or morphology [12,21-24]. In other words, sulfonic acid containing polymers are not selective for the DMFC application. An alternative approach is to examine polymers that are selective for protons (or water) over methanol. Pivovar and coworkers [25] investigated polymers commonly used in pervaporation, which have a higher affinity for water compared to alcohols. However, even though polymers such as polyvinyl alcohol (PVA) are selective for water over alcohols, they are also poor proton conductors. Recent work by Shao and coworkers [26,27] examines composite membranes of Nafion® and PVA, where Nafion®/PVA blends were coated on each side of a commercially extruded Nafion® film. The composite was subsequently chemically crosslinked and sulfonated. These membranes exhibited a 48% decrease in methanol permeability compared to Nafion®. Others have also combined PVA with other sulfonic acid containing polymers and have observed reduced methanol permeabilities [28-30]. These investigations warrant further study of combining conductive polymers with barrier polymers. In this study, the transport properties of Nafion®/PVA blend membranes were examined as a function of PVA content and annealing temperature as it applies to the DMFC.

2. Experimental

2.1 Materials

Nafion® (1100 EW, 5 wt% in a mixture of water and alcohols) was purchased from Ion Power, Inc. (Liquion®). Poly(vinyl alcohol) (99% hydrolyzed, average molecular weight = 86,000 g/mol) was purchased from Scientific Polymer Products, Inc. Both Nafion® and PVA were used as received. Nafion® 117, (1100 EW, 0.007 in. thickness, commercially extruded film) was purchased from Aldrich and used as received without any further purification. Other chemicals used include methanol (Aldrich, 99.8+% purity, A.C.S. reagent) and reverse osmosis (RO) water (resistivity ~ 16 MΩ cm).

2.2 Membrane Preparation

Cast membranes of Nafion® were prepared by solution casting Nafion® solution in partially covered Teflon® Petri dishes at ambient conditions for 24-36 hours. PVA membranes were prepared by solution casting 5% (w/v) PVA/water solutions in open Teflon® Petri dishes in an oven at 50-60°C under a low air flow rate. After solution casting, both Nafion® and PVA membranes were annealed under vacuum at 60°C for 4-6 hours.

Blends of Nafion® and PVA were prepared by mixing a 5% (w/v) PVA/water solution with a 5 wt% solution of Nafion® in water and alcohols. Nafion® solution was heated to approximately 80°C for 20-30 minutes. Subsequently, the PVA solution was added dropwise. Sometimes 10-30 mL of deionized water was added to the solution mixture to enhance solubility. The blend solutions were then solution cast in open Teflon® Petri dishes at ambient conditions for 24-36 hours. Membranes were then annealed under vacuum at 60°C for 4-6 hours. **Membrane thicknesses ranged from 200-500 μm and there was no visual evidence of macrophase segregation.** Blends were prepared in weight ratios of 95/5, 90/10, 85/15, 75/25, 50/50, and 10/90 of Nafion® and PVA, respectively, listed in Table 1. Increasing PVA content in a blend corresponds to decreasing ion exchange capacity (IEC), where IEC is defined as the milli-equivalent of sulfonic acid per gram of polymer (meq/g). Blend membranes were annealed at various temperatures: 120, 150, 180, 210, 230, or 250°C. Membranes were annealed at 120 and 150 °C for one hour, while all others were annealed at 180, 210, 230 and 250 °C for 10 minutes.

2.3 Proton Conductivity

Proton conductivity of each membrane was measured using AC impedance spectroscopy. Measurements were taken between 0.10 kHz and 1 MHz using a Solartron AC Impedance system (1260 impedance analyzer, 1287 electrochemical interface, Zplot software). Proton conductivity was measured normal to the plane of the membrane with a two-electrode cell comprised of 1.22 cm^2 stainless steel blocking electrodes. All membranes were prehydrated in RO water for at least 24 hours and then quickly enclosed in a sealable cell to maintain hydration during impedance measurements. The real impedance was determined from the x-intercept of the regression of the imaginary versus real impedance data over a high frequency range (10 kHz – 1 MHz) [23]. Conductivity values for each sample reported in this study are an average of multiple (at least three) experiments, where the average standard deviation was 17% of those values. **A schematic diagram of the apparatus and more details regarding the procedures have been documented elsewhere [23].**

2.4 Methanol Permeability

The methanol permeability of each membrane was measured using a temperature-controlled side-by-side glass diffusion cell (PermeGear, Inc.) with a real-time in-line Fourier transform infrared, attenuated total reflectance (FTIR-ATR) spectrometer for detection. Prior to each experiment, membranes were prehydrated for at least 24 hours and then were clamped between donor and receptor (each 3.4 ml) compartments with an exposed membrane cross-sectional area of 0.636 cm^2. Rubber and silicon gaskets were used between the donor and receptor sides to ensure a tight seal. Once tightly secured, each experiment was conducted at 25°C with a 2.0M methanol feed concentration. The FTIR spectrometer (Nicolet 6700 Series) was equipped with a temperature-controlled flow-through horizontal ATR cell (Specac, Inc.). A multi-bounce zinc selenide ATR crystal (Specac, Inc.) with a refractive index of 2.4 was used. Infrared spectra were continuously recorded throughout each experiment at 32 second intervals using 32 scans and 4 cm^{-1} resolution for each collected spectrum. In this experiment, the infrared spectrometer measures the downstream methanol concentration as a function of time, where permeability is determined from the slope of this early time data. The permeability values for each sample reported in this study are an average of multiple (at least three) experiments, where the average standard deviation was 14% of those values. This technique was developed in previous work **and a schematic diagram of the apparatus** and more details regarding the procedures have been documented elsewhere [12].

2.5 Sorption

Sorption (uptake) experiments were performed in both water and methanol. Membranes weighing approximately 100 mg were first dried in a vacuum oven at 50^{o}C for 4-8 hours before the dry weight of the membrane was measured. After 24-hour immersion in RO water or methanol, membranes were removed from solution, carefully patted to remove residual surface solvent, and immediately weighed. The percent uptake was determined by:

$$\%uptake = \frac{wt_{dry} - wt_{wet}}{wt_{dry}} x100 \tag{1}$$

where wt_{dry} is the weight of the dry polymer and wt_{wet} is the weight of the wet polymer. A balance with 0.1 mg accuracy was used. A minimum of three experiments were conducted on each sample and the values reported are the average of these experiments. The average standard deviation was 10% of these averaged values.

2.6 FTIR-ATR Spectroscopy

Infrared spectroscopy experiments were conducted using a FTIR spectrometer (Nicolet 6700 Series) equipped with a single-reflection diamond ATR attachment (Specac, Inc., MKII Golden Gate™). The diamond ATR has a ~0.5 mm^2 sampling area, where a consistent reproducible pressure is applied to every sample. Infrared spectra were collected at 4 cm^{-1} resolution and 32 scans.

3. Results and Discussion

3.1. Transport

In this study, Nafion®/PVA blend membranes were prepared at various compositions (see Table 1) by solution casting followed by annealing at various temperatures. Annealed blend membranes produced durable, flexible membranes similar to Nafion® 117 and were insoluble in water. Figure 1 shows the measured proton conductivities for annealed Nafion®/PVA blends as a function of IEC at two different annealing temperatures, 120 and 250°C. As expected, proton conductivity decreases with decreasing IEC (increasing PVA content). The conductivities at **85-100 wt%** and **0-10 wt%** PVA contents are similar for both annealing temperatures, however, at other PVA contents (10-85 wt%) the conductivity differs by as much as an order of magnitude between the two annealing temperatures. The membrane at the highest IEC (0.91 meq/g) in Figure 1 corresponds to solution-cast Nafion® with a conductivity of 0.019 S/cm when annealed at 120°C. **This result compares with conductivity obtained by Silva and coworkers [43] on solution-cast Nafion® membranes although direct comparisons cannot be made due to the use of different solvents and annealing temperatures.**

Proton conductivity and methanol permeability as a function of annealing temperature for Nafion® 117, solution-cast Nafion® and two Nafion®/PVA blends (5 and 50 wt% PVA) are shown in Figures **2a, 2b, 2c, and 2d**, respectively. Figure 2**a** shows that both proton conductivity and methanol permeability increase and then decrease with increasing annealing temperature with a maximum at 210^{o}C (0.022 S/cm; 8.07 x 10^{-6} cm^2/s). In this study, the conductivity and permeability of Nafion® 117 without an annealing treatment are 0.025 S/cm and 2.00 x 10^{-6} cm^2/s, respectively. These values are similar to values reported in the literature using similar experimental techniques [23,25,31-33].

Transport properties of unannealed Nafion® 117 are often used as a benchmark for fuel cell applications. The dashed line in Figure 2 is a guide line to help distinguish between these properties. Conductivities above the line and permeabilities below the line represent membranes with higher selectivities compared to unannealed Nafion® 117. All of the annealed Nafion® 117 membranes in Figure 2**a** are lower in selectivity **(proton conductivity/methanol permeability)** compared to unannealed Nafion® 117. In fact, methanol permeabilities are actually higher in most of the annealed samples.

Figure **2b** shows that the transport properties of solution-cast Nafion® as a function of annealing temperature exhibit a similar trend compared to Nafion® 117 with a maximum at 210^{o}C (0.039 S/cm; 3.26 x 10^{-6} cm^2/s). However, at all annealing temperatures, solution-cast Nafion® exhibits higher conductivities and lower methanol permeabilities compared to Nafion® 117. Specifically at 150^{o}C, solution-cast Nafion® has a similar conductivity and a slightly lower permeability (0.024 S/cm; 1.47 x 10^{-6} cm^2/s) compared to unannealed Nafion® 117. **Other researchers [35,40] have documented differences between commercially extruded and solution-cast Nafion®.**

Several researchers have explored thermal transitions in Nafion® using differential scanning calorimetry (DSC) [34-37]. Two thermal transitions (endothermic peaks) have been observed at 120-150°C and 230-260°C (a range of temperatures are reported here, where the exact location of these peaks vary between investigations). There are various opinions associated with the exact meaning of these transitions. Eisenberg et al. [34] and Moore and Martin [35] suggest that the lower and higher temperature transitions are associated with the matrix and ionic domain glass transitions, respectively. Almeida and Kawano [36] suggest an order-disorder transition inside the ionic clusters and melting of the crystallites in Nafion® for the lower and higher temperature transitions. Recent work by Page et al. [37] suggest melting of small, imperfect crystallites for the lower temperature transition and melting of PTFE-like crystallites for the higher temperature transition. Although there are differing opinions regarding the meaning of these thermal transitions, the location of these transitions coincide with the transport property trends observed in Figures 2**a** and **2b**. It appears that the lower temperature transition may reorient the percolated ionic structure in Nafion® leading to enhanced transport (120-210°C), while the higher temperature transition may negatively impact this ionic network resulting in lower transport rates (>210°C).

The transport properties of Nafion®/PVA blend membranes (5 wt% PVA) as a function of annealing temperature are shown in Figure **2c**. The data differs from Nafion® in that it does not appear to follow a clear trend. The measured proton conductivities are similar to annealed Nafion® 117, but the methanol permeabilities are lower than unannealed Nafion® 117. At 230°C, the Nafion®/PVA blend has a similar conductivity and a lower permeability (0.020 S/cm; 6.5 x 10^{-7} cm^2/s) compared to unannealed Nafion® 117. However, blends at other annealing temperatures do not have higher selectivities.

Figure **2d** shows the conductivity and permeability of Nafion®/PVA blend membranes (50 wt% PVA) as a function of annealing temperature. The conductivity varies slightly (with the exception of the sample annealed at 250°C), while the permeability decreases (by almost an order of magnitude) with increasing annealing temperature. More specifically, conductivities and permeabilities ranged from 0.001 to 0.002 S/cm and 2.4 x 10^{-7} to 4 x 10^{-8} cm^2/s, respectively. Even though all of the conductivities in Figure **2d** are lower than unannealed Nafion® 117, it is interesting to note that the trends observed here are not commonly observed in PEMs. In other words, proton conductivity and methanol permeability usually increase or decrease simultaneously in sulfonic acid containing PEMs with changes in polymer properties (e.g., ion content, water content, temperature, morphology). For the case of Nafion®/PVA blend membranes with a 50 wt% PVA content, the conductivity and permeability trends appear to be decoupled.

Selectivity **(proton conductivity/methanol permeability)** versus proton conductivity of unannealed Nafion® 117 and Nafion® 117, solution-cast Nafion®, and several Nafion®/PVA blends (5, 25, and 50 wt% PVA) at various annealing temperatures are shown together in Figure **3**. This is a common way to represent the gas separation properties of polymer membranes (i.e., selectivity or permeability of the desired/undesired gas versus the permeability of the desired gas) [38]. Typically, membranes used for gas separation follow a tradeoff relation, where more selective membranes are less permeable to the desired gas or more permeable membranes are less selective. Similarly, membranes for the DMFC application follow a similar tradeoff relation, where more selective membranes are usually less conductive and more conductive membranes are usually less selective. In Figure **3**, membranes that do not follow this tradeoff relation will lie in the upper right hand of the graph or to the upper right of the standard membrane (unannealed Nafion® 117). In this study, membranes of interest are solution-cast Nafion® (annealed at 180°C) with a conductivity 1.4 times higher and a similar methanol permeability compared to unannealed Nafion® 117 and Nafion®/PVA (5 wt% PVA; 230°C) with a permeability 3 times lower and a similar proton conductivity compared to unannealed Nafion® 117. Additionally, Nafion®/PVA (50 wt% PVA; 230°C) is ~3.5 times higher in selectivity compared to unannealed Nafion® 117. However, this membrane is also approximately one order of magnitude lower in proton conductivity. In this study, all Nafion®/PVA blend membranes (at all annealing temperatures) with higher than 5 wt% PVA had lower conductivities compared to unannealed Nafion® 117 (Figure 1).

3.2. Sorption

Table 2 and 3 lists the water and methanol uptake, respectively, of selected Nafion®/PVA blends. The water and methanol uptake of Nafion® 117 (0.91 meq/g; 0 wt% PVA), without annealing, is 29 and 61 wt%, respectively. These results compare well with literature values [21,39]. For solution-cast Nafion® (annealed at 60°C), the water uptake is 34 wt%, however, the membrane dissolves when placed in methanol. Grot [40] has also observed the dissolution of low-temperature solution-cast Nafion® in methanol. It is important to note that both forms of Nafion® reveal a higher affinity for methanol compared to water. In contrast, annealed PVA membranes have a higher affinity for water compared to methanol (e.g., 83 and 1 wt%, respectively, when annealed at 120°C). These sorption values for Nafion® and PVA provide motivation for this investigation.

The water uptake for Nafion® 117 (annealed at 120°C) is 20 wt%, which is lower than its measured value without an annealing treatment (29 wt%). At higher annealing temperatures, there is no clear trend in water uptake for Nafion® or Nafion®/PVA blends as a function of annealing temperature or ion content (PVA content). Interestingly, Nafion® 117 dissolves in methanol after being annealed at 120°C, where it is insoluble in methanol without an annealing treatment (61 wt% methanol uptake). In this study, all blends with low PVA content dissolved in methanol after an annealing treatment at 120°C. As annealing temperature increases, Nafion® and blends with low PVA contents become insoluble in methanol. **Other researchers observed that solution-cast films of Nafion® were insoluble after heating at 140°C for at least 40 minutes [42]. In this study, Nafion® and blends at low PVA contents were soluble when annealed at 120°C for one hour, but insoluble when annealed at 150°C for one hour (Table 3). Membranes at higher annealing temperatures only required 10 minutes of annealing time for insolubility.**

Nafion® and blends with low PVA contents all have high methanol uptakes with an overall trend of decreasing methanol uptake with increasing annealing temperature. Furthermore, Nafion® 117 has a higher methanol uptake at all annealing temperatures compared to its unannealed form (e.g., 235 wt% when annealed at 150°C). The results in Tables 2 and 3 do not match the trends observed in transport properties shown in Figure 2. This suggests that the results observed in Figures 2**a** and **2b** (transport property changes with changes in annealing temperature) are a product of changes in the polymer morphology and not differences in water content.

3.3. FTIR-ATR spectroscopy

To further understand the transport and selectivity trends, the membranes in this study were characterized by FTIR-ATR spectroscopy. Figure **4** shows the infrared spectra of the hydroxyl (O-H) band for solution-cast Nafion®, PVA, and Nafion®/PVA blends (5 and 50 wt% PVA) annealed at 60°C. The infrared band for PVA located at 3269 cm^{-1} represents hydrogen-bound hydroxyl groups between polymer chains. For Nafion®, several investigators have measured 2-14 molecules of water per sulfonate at water vapor activities of 0.15-1.0 [21,41]. The infrared band located at 3439 cm^{-1} for solution-cast Nafion® corresponds to the hydroxyl groups in water and hydronium ions that interact with the sulfonic groups on the side chains of the polymer at <100 %RH [41]. As PVA content increases in the Nafion®/PVA blend, the location of the hydroxyl band shifts, representing a distribution of interactions (e.g., 3314 cm^{-1} for Nafion®/PVA at 50 wt% PVA). This distribution may be a combination of the interactions observed in both PVA and Nafion® and also hydrogen bonding between the hydroxyl groups in PVA and the sulfonic acid groups in Nafion®, illustrated in Figure **5 as (a), (b), and (c), respectively**.

Table 4 lists the location of the infrared hydroxyl band for all membranes in this study as a function of annealing temperature. There is no significant change in the location of this band for Nafion® or PVA membranes as a function of annealing temperature. However, this band shifts significantly for Nafion®/PVA blend membranes (25 to 90 wt% PVA) with increasing annealing temperature. The infrared band shifts over 100 cm^{-1} in some cases. Figure **6** shows this band shift more clearly, where Nafion®/PVA at 50 wt% PVA shifts from 3314 to 3459 cm^{-1} with increasing annealing temperature. These results suggest a change in the distribution of interactions that occur in Nafion®/PVA blend membranes when the annealing temperature is increased. This may provide insight into the unusual selectivity trend observed in Figure **2d**, where proton conductivity remains relatively constant, but methanol permeability decreases with increasing annealing temperature in Nafion®/PVA (50 wt% PVA). Annealing at higher temperatures may encourage less interaction among hydroxyl groups in PVA and more interactions between the hydroxyl groups in PVA with the sulfonic acid groups in Nafion® **(see Figure 5c)**, resulting in an infrared band shift to higher wavenumbers observed in Figure **6**. Annealing may facilitate more hydroxyl groups from PVA into the percolated sulfonic acid cluster network (pathway for proton, water, and methanol transport), which therefore improves selectivity. In this study, the entire mid-IR spectra was inspected for solution-cast Nafion®, PVA, and Nafion®/PVA blends (at all compositions) and no evidence of covalent bond formation was observed with annealing.

4. Conclusions

In this study, the transport properties of polymer blend membranes of Nafion® (proton conductive) and PVA (selective for water over alcohols) were measured as a function of composition and annealing temperature for application to the DMFC. One key result observed was the trends in proton and methanol transport in the Nafion®/PVA blend membrane at 50 wt% PVA. As annealing temperature increased, proton conductivity remained relatively constant, while methanol permeability decreased by almost an order of magnitude. These trends differ from most investigations, where proton and methanol transport usually increase or decrease simultaneously in sulfonic acid containing PEMs with changes in polymer properties. Infrared spectroscopy supports these results in which the hydroxyl infrared band increases in wavenumber with increasing annealing temperature suggesting more interaction between the hydroxyl groups in PVA and the sulfonic acid groups in Nafion®.

In addition, annealing Nafion® alone results in a maximum in transport rates at an annealing temperature of 210°C. These trends coincide with two thermal transitions observed **by other researchers using** DSC, suggesting that the changes in transport properties are a result of changes in Nafion® morphology. Also, the Nafion®/PVA blend membrane at 5wt% PVA and 230°C annealing temperature had a similar proton conductivity, but 3 lower methanol permeability compared to unannealed Nafion® 117 (benchmark in PEM fuel cells). This increased selectivity was not observed in Nafion®/PVA blend membranes (5wt% PVA) at other annealing temperatures. This result may be a product of both morphology and chemistry. Polymer blends are intriguing in that they have the ability to impact selectivity for application to the DMFC; however there are a number of parameters in addition to composition (e.g., morphology, chemical interactions, etc.) that play a significant role in the final transport properties of the membrane.

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Table 1. Nafion®/PVA blends

PVA content (wt%)	IEC (meq/g)	Polymer Concentration (w/v%)
0	0.91	5.0
5	0.87	2.5
10	0.82	3.1
15	0.77	2.9
25	0.68	5.0
50	0.46	5.0
90	0.09	5.0
100	0	5.0

Table 2. Water Uptake of Nafion®/PVA Blends

PVA Content (wt%)	Water Uptake (wt%)					
	Annealing Temperature (^{o}C)					
	120	150	180	210	230	250
0[a]	20	60	48	21	24	48
0[b]	25	33	28	27	32	31
5	20	22	20	43	36	40
50	35	17	24	39	13	14
100	83	93	34	52	55	162

[a] Nafion® 117

[b] solution-cast Nafion®

Table 3. Methanol Uptake of Nafion® /PVA Blends

PVA Content (wt%)	**Methanol** Uptake (wt%)					
	Annealing Temperature (°C)					
	120	150	180	210	230	250
0[a]	soluble	235	141	75	73	132
0[b]	soluble	204	94	83	97	75
5	soluble	164	121	91	79	76
50	49	39	39	37	36	40
100	1	14	1	9	10	98

[a] Nafion® 117

[b] solution-cast Nafion®

Table 4. Location of Hydroxyl Infrared Band Maximum in Nafion®/PVA Blends

PVA Content (wt %)	Infrared Peak Maximum Location (cm^{-1})						
	Annealing Temperature (°C)						
	60	120	150	180	210	230	250
0[a]	3436[c]	3429	3435	3380	3416	3410	3288
0[b]	3439	3424	3434	3409	3436	3433	3420
5	3422	3430	3430	3443	3431	3461	3432
10	3388	3438	3391	3418	3381	3416	3417
15	3388	3394	3414	3408	3446	3410	3418
25	3381	3443	3410	3428	3376	3429	3464
50	3314	3391	3392	3405	3430	3436	3459
90	3276	3288	3287	3286	3294	3310	3395
100	3269	3272	3290	3285	3284	3322	3330

[a] Nafion® 117

[b] solution-cast Nafion®

[c] unannealed

Figure Captions

Figure 1. Proton conductivity vs. IEC (or PVA content) for Nafion®/PVA blends at annealing temperatures of 120 (○) and 250 °C (□), where Nafion®/PVA at 0 wt% PVA content corresponds to solution-cast Nafion®.

Figure 2. Proton conductivity (○) and methanol permeability (◇) vs. annealing temperature for **(a)** Nafion® 117**, (b) solution-cast Nafion®, (c) Nafion®/PVA (5 wt% PVA), and (d) Nafion®/PVA (50 wt% PVA).** The dashed line corresponds to the approximate proton conductivity and methanol permeability of Nafion® 117 without an annealing treatment.

Figure 3. Selectivity vs. proton conductivity for unannealed Nafion® 117 (●) and Nafion® 117 (○), solution-cast Nafion® (□), and Nafion®/PVA (5 (◇), 25 (△), and 50 (▽) wt% PVA contents) at various annealing temperatures.

Figure 4. Infrared spectra of Nafion®/PVA blend membranes as a function of PVA content annealed at 60°C. The bands shown here depict the hydroxyl (O-H) infrared stretching vibration.

Figure 5. Schematic of chemical structures illustrating interactions that occur between functional groups in **(a)** PVA, **(b)** Nafion®, and **(c)** Nafion®/PVA blend membranes.

Figure 6. Location of the hydroxyl (O-H) infrared band maximum for solution-cast Nafion® (○) and Nafion®/PVA blends (5 (□), 50 (◇), and 100 (△) wt% PVA contents) as a function of annealing temperature.

Figure 1

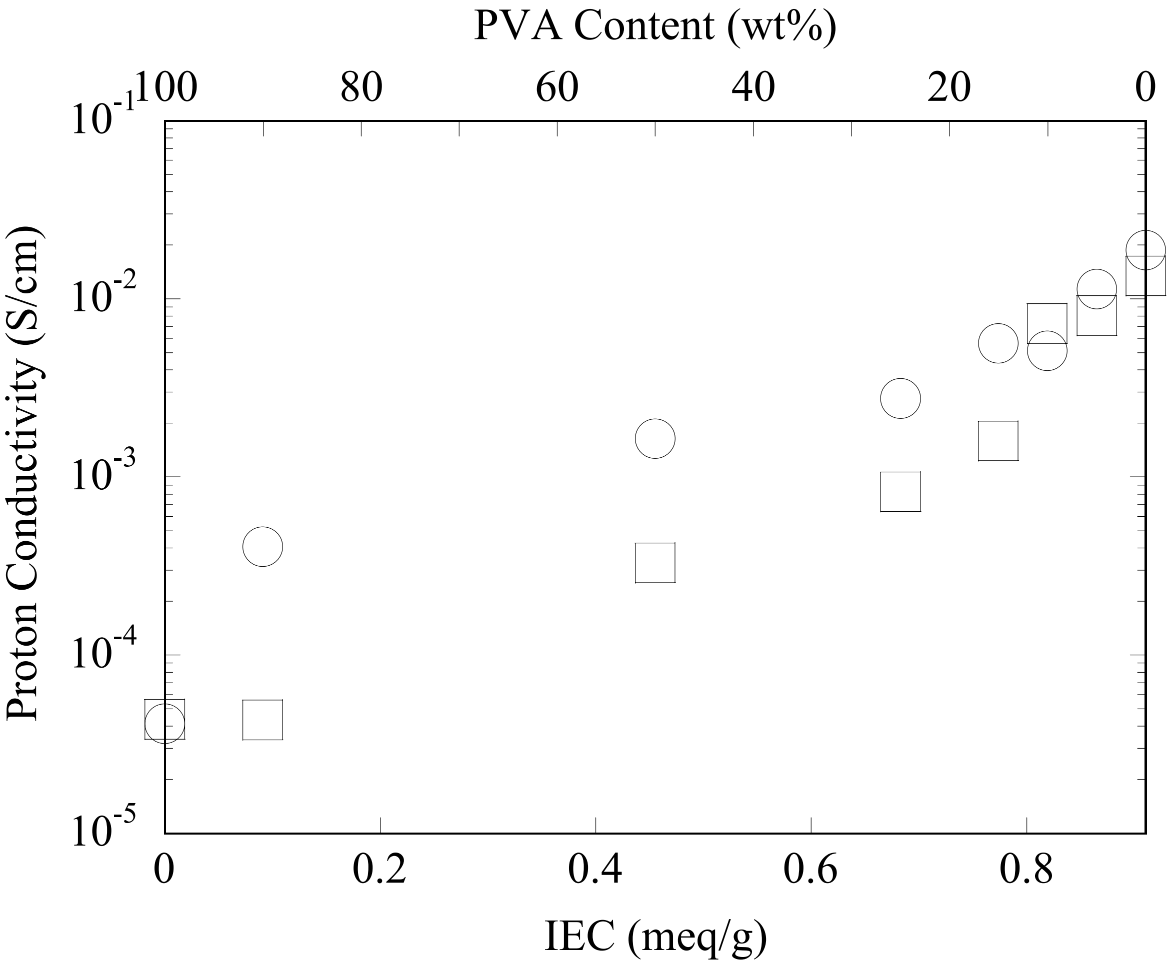
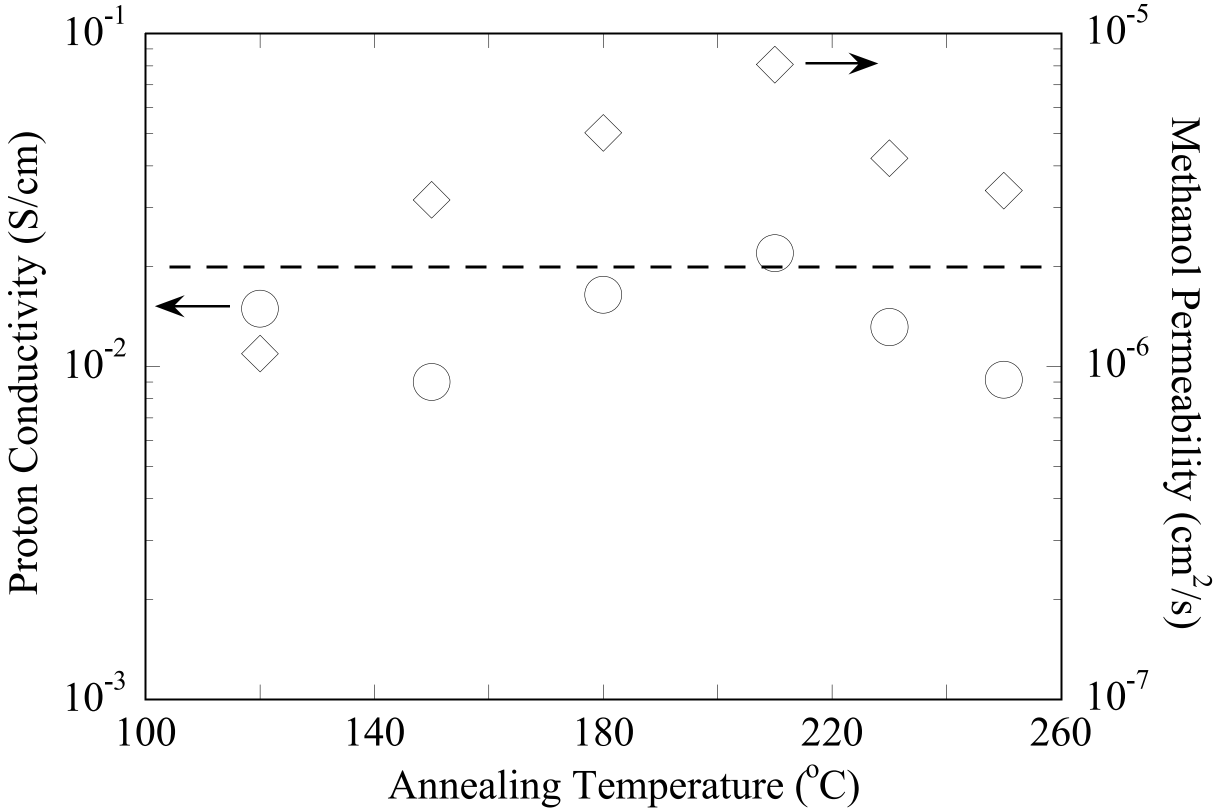
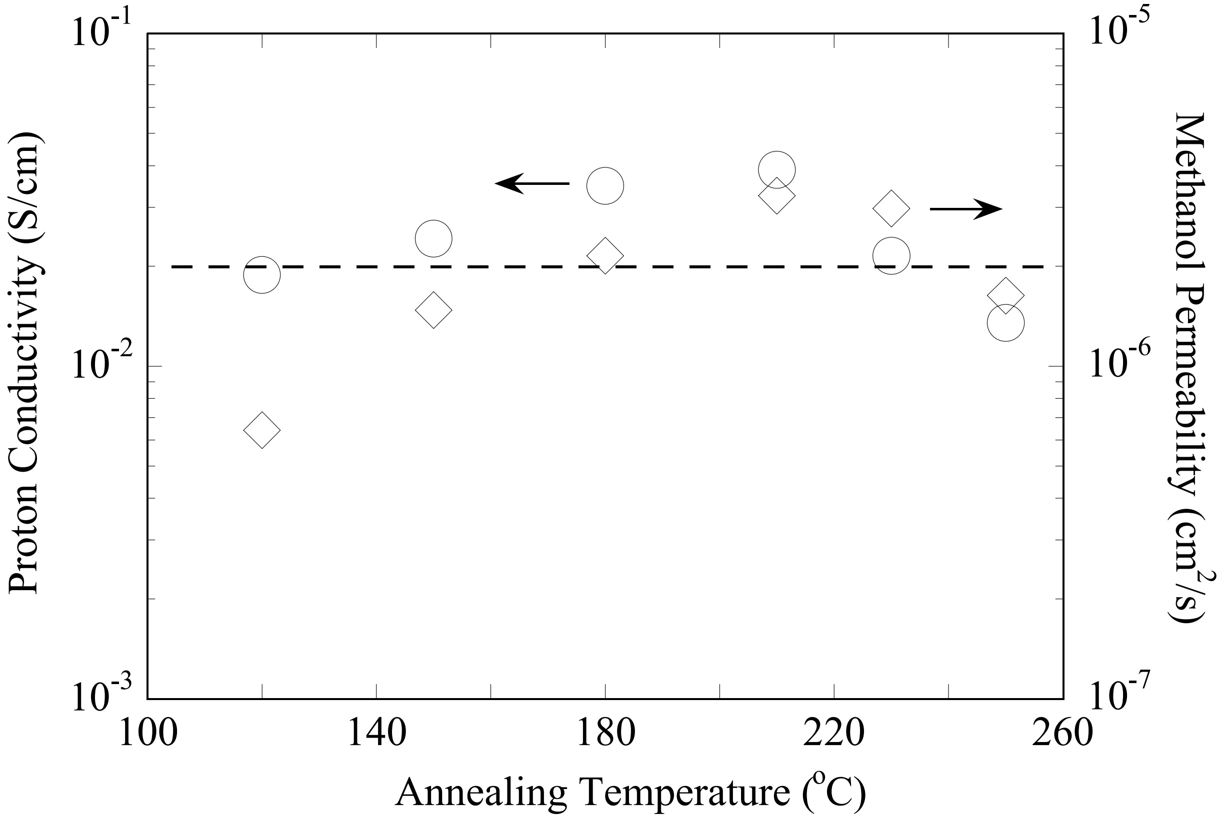

PVA Content (wt%)
100
80
60
40
20
0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Proton Conductivity (S/cm)
0
0.2
0.4
0.6
0.8
IEC (meq/g)

Figure 2a



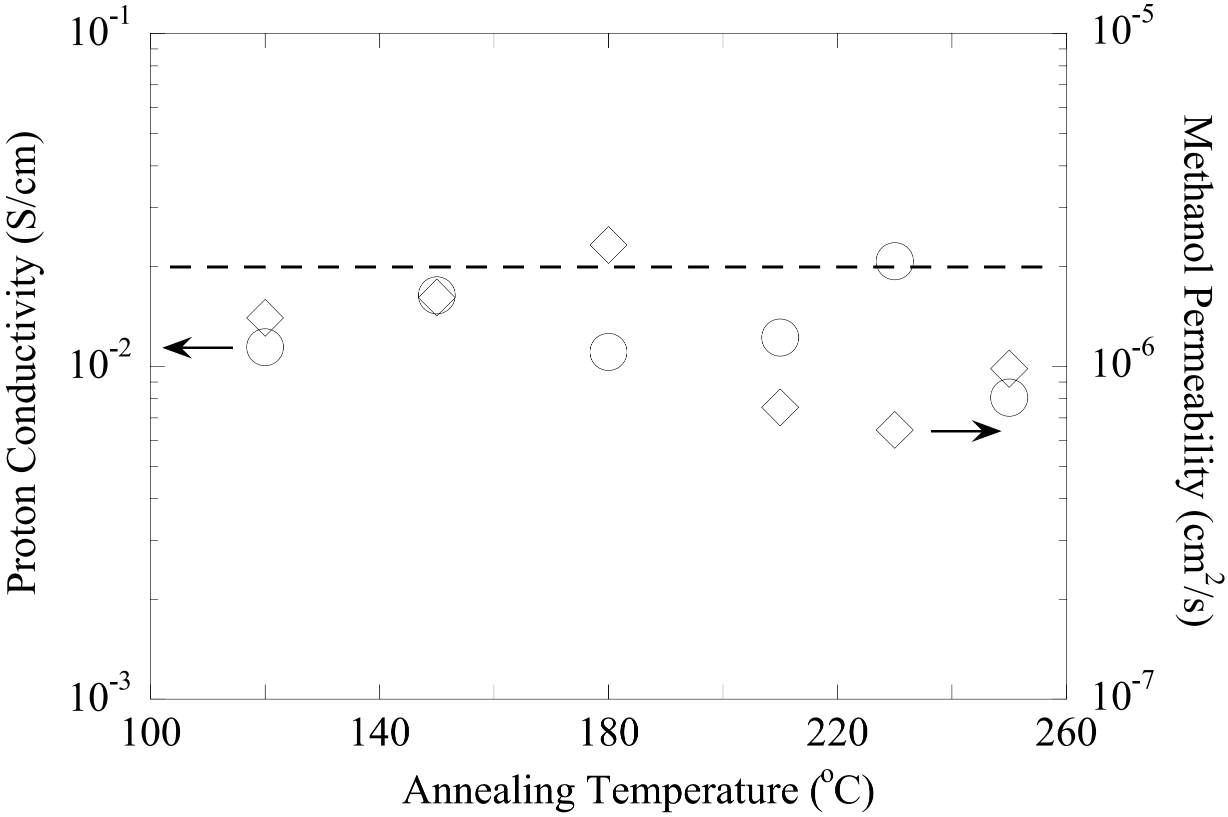
10^-1
10^-2
10^-3
10^-5
10^-6
10^-7
100
140
180
220
260
Proton Conductivity (S/cm)
Methanol Permeability (cm^2/s)
Annealing Temperature (°C)

Figure 2b



10^-1
10^-2
10^-3
10^-5
10^-6
10^-7
100
140
180
220
260
Proton Conductivity (S/cm)
Methanol Permeability (cm²/s)
Annealing Temperature (°C)

Figure 2c



10^{-1}
10^{-2}
10^{-3}
10^{-5}
10^{-6}
10^{-7}
100
140
180
220
260
Proton Conductivity (S/cm)
Methanol Permeability (cm^2/s)
Annealing Temperature (^{o}C)

Figure 2d

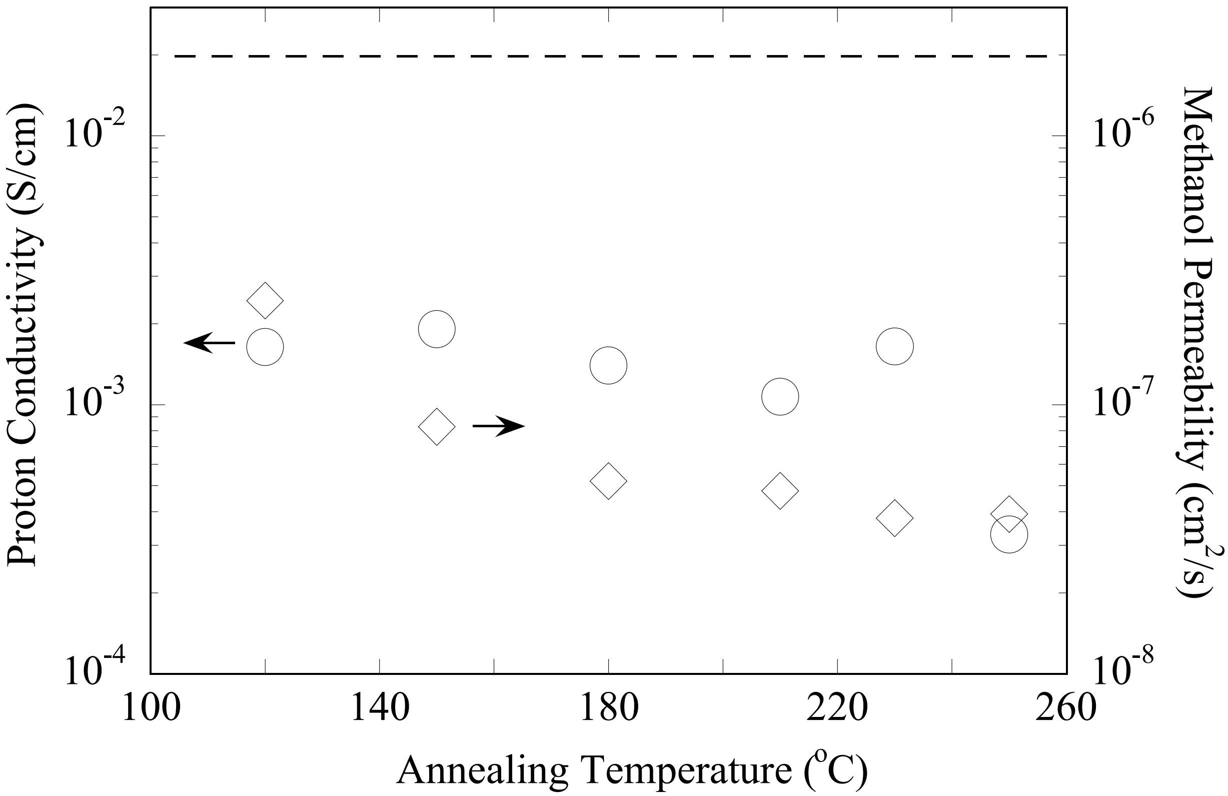
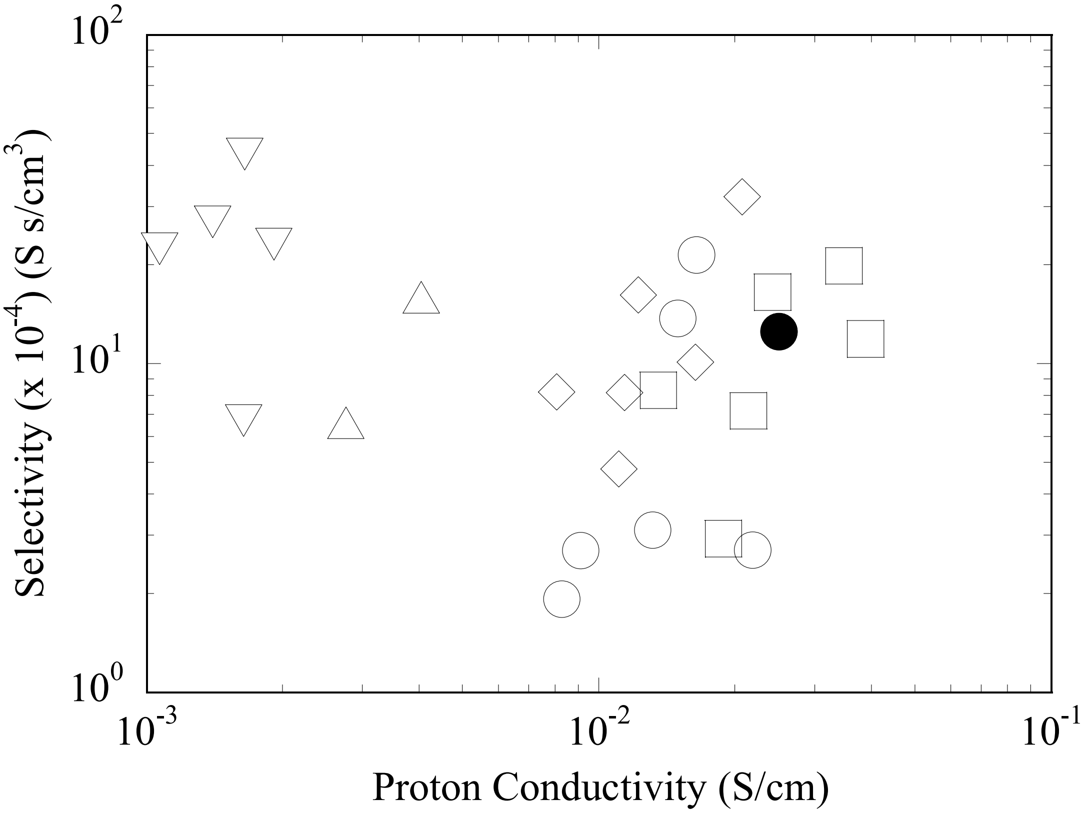

Proton Conductivity (S/cm)
10-2
10-3
10-4
Methanol Permeability (cm2/s)
10-6
10-7
10-8
100
140
180
220
260
Annealing Temperature (oC)

Figure 3



10^2
10^1
10^0
Selectivity (x 10^{-4}) (S s/cm^3)
10^{-3}
10^{-2}
10^{-1}
Proton Conductivity (S/cm)

Figure 4

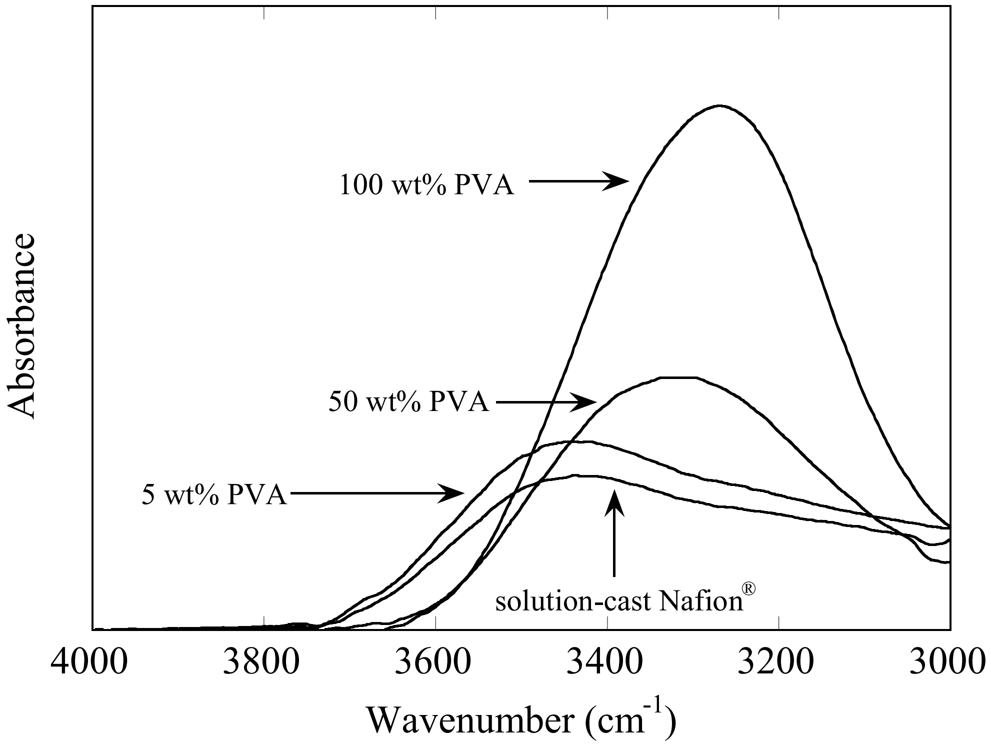

100 wt% PVA
50 wt% PVA
5 wt% PVA
solution-cast Nafion®
Absorbance
4000
3800
3600
3400
3200
3000
Wavenumber (cm^{-1})

Figure 5

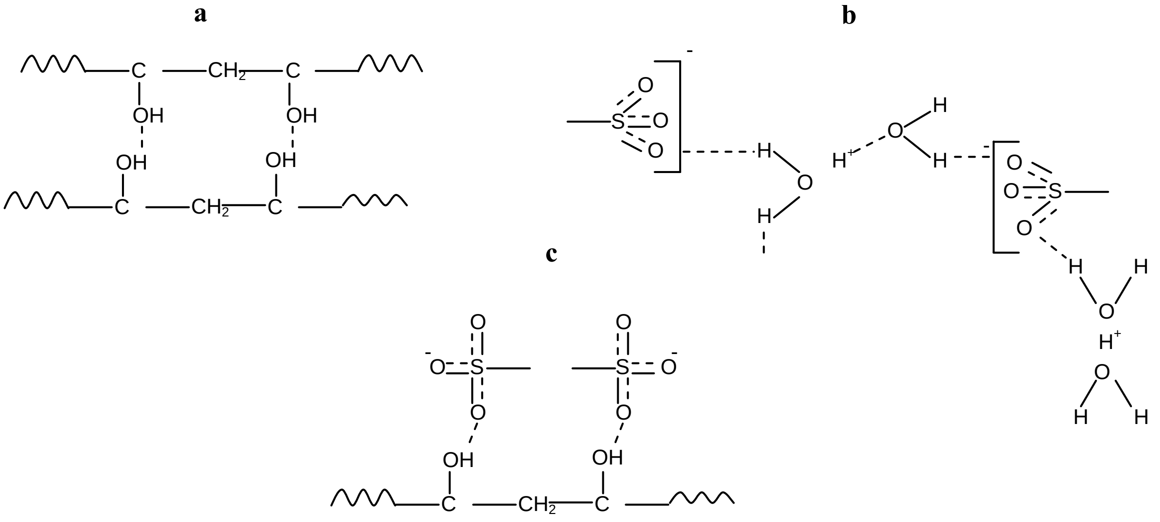
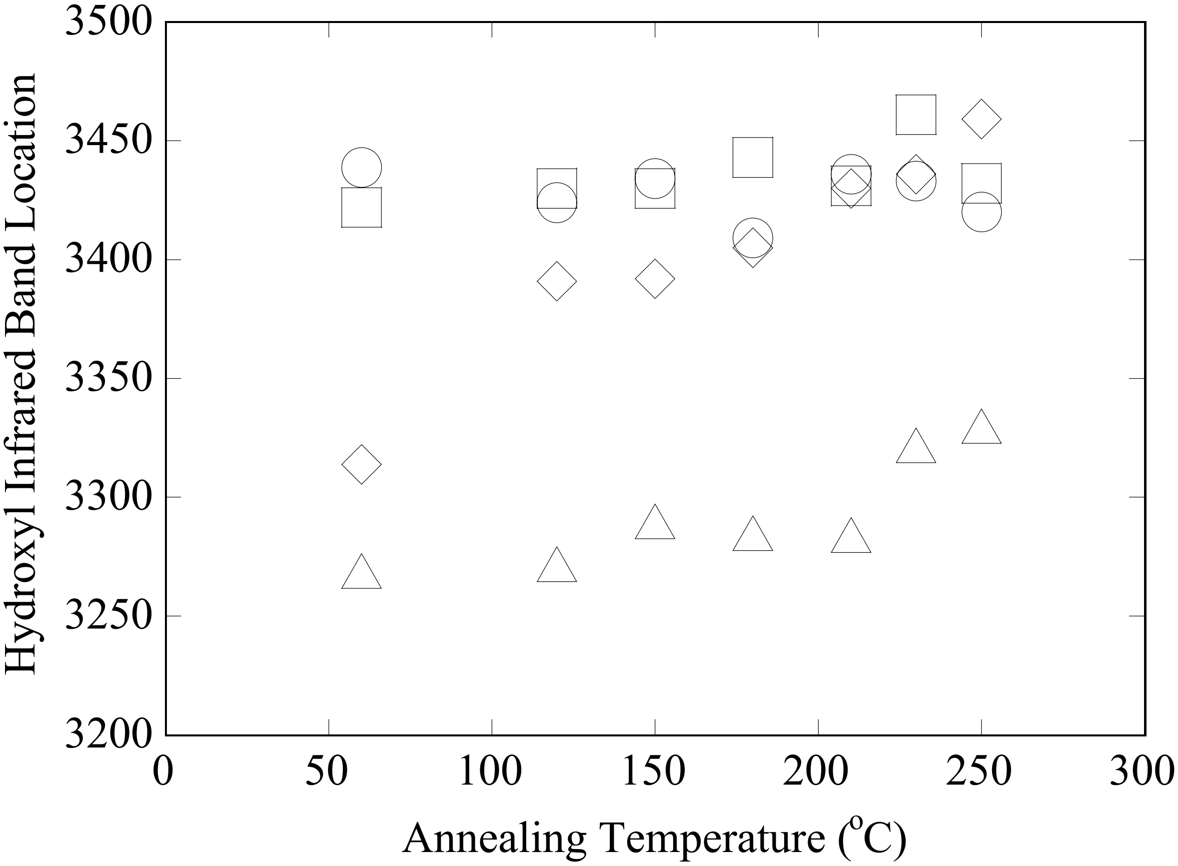


Figure 6


3500
3450
3400
3350
3300
3250
3200
0
50
100
150
200
250
300
Hydroxyl Infrared Band Location
Annealing Temperature (°C)