

Optimization of the Synthesis of Nafion–Montmorillonite Nanocomposite Membranes for Fuel Cell Applications through Statistical Design-of-Experiment

Christine Felice and Deyang Qu*

Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Blvd., Boston, Massachusetts 02125, United States

Nafion–montmorillonite nanocomposite membranes are reported to be effective for reducing fuel crossover when used as the electrolyte in fuel cells. The synthesis of a membrane involves several adjustable parameters. Using the statistical design-of-experiment method, four of the most critical parameters were studied: choice of mixer, clay percentage, curing temperature, and curing time. Fuel crossover and conductivity were measured for each of the membranes, to assess how the parameters influence the properties of the membranes. Curing time is critical for hydrogen crossover reduction. Four different two-factor interactions are critical for methanol crossover reduction: clay percentage and curing temperature; type of mixer and curing temperature; type of mixer and clay percentage; and curing temperature and time. Clay percentage and curing temperature individually influence in-plane conductivity, as does the interaction between the type of mixer and clay percentage. The factors that influence through-plane conductivity are the type of mixer and clay percentage individually and the interaction between clay percentage and curing temperature. More membranes were made by using the determined best process and varying the type of clay and the clay percentage. The same crossover and conductivity studies were performed, and the results are reported.

1. Introduction

Nafion is a polymer almost exclusively used in proton-exchange membrane (PEM) fuel cells as the solid electrolyte, because of its attractive properties, such as good conductivity and electrochemical stability. Nafion has perfluorosulfonic acid (PFSA) side chains attached to a Teflon-like backbone. The PFSA side chains form ionic clusters that form the basis of the membrane's proton conduction network when hydrated. As promising as these membranes are, there are several deficiencies that must be addressed. Fuel crossover (e.g., hydrogen or methanol) greatly decreases the efficiency of the cell, because no useful current is produced from the fuel's oxidation. How one can reduce such fuel crossover is the focus of this work. It is thought that hydrogen traverses the Nafion membrane through the interfacial area between the hydrophobic backbone and hydrophilic ionic clusters, while methanol is thought to permeate, along with water, through the hydrophilic region. To reduce fuel crossover, Nafion–clay nanocomposites have been produced, studied, and proven to be effective.^{1–8} The nanoscale clay platelets that are dispersed in the polymer act as “road blocks” in the path that the fuel takes across the membrane. Unfortunately, the addition of clay also decreases the conductivity, when compared to that of a plain Nafion membrane. Therefore, a balance must be made between decreasing fuel crossover and maintaining the good conductive properties of the membrane.

A common clay used to make the nanocomposites is montmorillonite (MMT), the ideal chemical formula of which is $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot y\text{H}_2\text{O}$. The platelets consist of an aluminum oxide octahedral layer sandwiched between two silicate tetrahedral layers. Cations (usually Na^+) are located between these platelets. MMTs are very hydrophilic and add to the water-absorbing properties of the Nafion membranes. Chen et al.⁹ and Boo et al.¹⁰ have previously shown that the degree of exfoliation of nanoparticles in the polymer increased the quality of the

nanocomposite. The co-solvents, such as DMAc or NMP, that are used for making the Nafion–clay solution have been shown to have an effect on the dispersion of the clay particles and the resulting morphology of the membranes^{11,12} and are essential additions to the process for successfully making PEMs.

Many different methods for preparing Nafion nanocomposite membranes have been studied.⁵ For the solution casting method, the polymer–clay dispersion in a suitable solvent is first casted on a substrate (e.g., a glass plate) at the desired thickness. The casted film is then air-dried on the substrate. When a membrane is made via the hot-pressed method, the clay is mixed with the melted polymer and pressed onto a glass plate. It is then heated above the glass-transition temperature. Although these two methods are successful and widely used for small-scale production, the properties of the membranes vary greatly between batches. Therefore, it is of great interest to understand the impact of the various parameters of synthesis on the performance of the Nafion–clay nanocomposite. Unfortunately, quite a few parameters are involved in the synthesis of Nafion–clay nanocomposites. Not only could those parameters have a significant impact on the performance of the synthesized membrane individually, but the interactions between those parameters also could have an effect. A good example is the curing time and temperature.

After casting a membrane, it is important to cure it at an elevated temperature, because the heat will drive off any remaining solvents, allow the Nafion molecules to rearrange, and seal any pinholes that may be present. Vengatesan et al. directly studied the effects of curing time and temperature on the performance of cast Nafion membranes.¹³ Jung et al. observed different properties and morphologies of Nafion cured at different temperatures.¹⁴ Because it is important to reduce crossover by adding clay to the Nafion, while at least maintaining a reasonable conductivity, the effects of the curing conditions must be characterized better.

The previous studies reported in the literature have focused on producing different types of membranes and/or characterizing membranes. However, to successfully scale-up PEM production

* To whom correspondence should be addressed. Tel.: +1 617-287-6025. Fax: +1 617-287-6188. E-mail: deyang.qu@umb.edu.

for commercialization, systematic process development must be performed. To date, such a study has not been done; therefore, this work was created with the intent to begin to evaluate each process variable and the interactions between them and how they affect the membrane's properties. Although the intention is not to understand the mechanisms that govern fuel crossover and conductivity in this study, hypotheses are made in an attempt to begin to identify such mechanisms.

2. Experimental Details

2.1. Materials. The DuPont DE2021 NAFION solution (referred to as 20% Nafion) was purchased from Ion Power, Inc. Cloisite 10A, which is an organically modified montmorillonite (MMT) clay powder, was obtained from Southern Clay Products, Inc. *N,N*-dimethylacetamide (DMA) and 1-methyl-2-pyrrolidinone (NMP) were purchased from Sigma-Aldrich. Dowex HCR-W2, 16–40 mesh ion-exchange resin was purchased from Acros Organics. Isopropyl alcohol and methanol were purchased from Sigma-Aldrich.

2.2. Preparation of Nafion–MMT Nanocomposite Membranes. A 9:1 ratio (by weight) DMA/NMP solution was prepared. The amount of clay powder needed to produce a membrane with 5 or 10 wt % composition, with respect to Nafion content, was mixed with a 5:1 weight ratio of 20% Nafion:DMA/NMP solution. This solution was mixed in a planetary mixer (Kurabo Mazerustar KK-50S) and then homogenized using either an IKA T-25 digital Ultra-Turrax homogenizer equipped with an S-25-N-18G dispersion tool or a Cole-Parmer CP501 ultrasonic homogenizer equipped with a 1/2 in. probe. The solution was set up under vacuum, constantly stirred, and intermittently heated, until the solution weight was reduced by ~36%–40%.

The resultant solution was cast at room temperature using the ChemInstruments EZ Coater EZ-100 data acquisition system, which was modified for use with a doctor blade. The membrane was allowed to dry overnight. It was cured in an oven at the temperature and time specified by the design-of-experiment. After cooling to room temperature, the membrane and glass casting plate were placed in an 80 °C deionized water bath for ~5 min, to facilitate the membrane's removal from the plate. The membrane was allowed to dry on filter paper overnight.

2.3. Preparation of H⁺-Modified MMT. The method described by Alonso et al. was used with slight modifications to exchange cations in the MMT with H⁺ ions.² First, a 2 wt % dispersion of MMT in deionized water was prepared by stirring the solution for 1 h. The dispersion was pulled by vacuum through the ion-exchange resin six times. It was then centrifuged at ~1400 rpm for 10 min. The deionized water was decanted, and the clay was dried in an oven overnight.

2.4. Experimental Techniques and Instrumental Details. The detailed designs of the electrochemical apparatus were reported previously.⁴ Hydrogen crossover current and impedance measurements were made using a Solartron SI 1287 potentiostat with a Solartron 1252A frequency analyzer for AC measurements. For hydrogen crossover current testing, the anode of the fuel cell was supplied with hydrogen and the cathode was supplied with an equal pressure of nitrogen (30 psi). CorrWare software was used to control the voltage sweep from 0.0 V to 0.4 V. The membrane was hydrated overnight in deionized water at 75 °C before testing.

For through-plane impedance testing, a homemade Teflon cell with two platinum foil electrodes was used. ZPlot software was used to control the potentiostat and frequency analyzer. The hydrated membrane was sandwiched between the two electrodes,

and a variable force could be applied during testing using a vertical hand wheel test stand (IMADA model HV-110S) equipped with a digital force gauge (IMADA model DS2).

In-plane impedance testing was performed with a Teflon conductivity cell purchased from BekkTech, LLC. and using the in-plane impedance technique. The cell was equipped with four platinum electrodes. The hydrated membrane was placed between two Teflon grates and pressed against the electrodes.

Methanol crossover testing was performed using a homemade cell with two equally sized compartments. The hydrated membrane was placed between the two compartments. One compartment was filled with deionized water and the other was filled with a 30% methanol solution. Samples were taken from the side with water at set intervals. The amount of sample taken was negligible, compared to the volume of liquid in the compartment. The methanol concentration was measured using an Agilent or Perkin-Elmer gas chromatograph equipped with a flame ionization detector. The internal standard used for analysis was isopropyl alcohol.

All measurements were taken at ambient temperature and relative humidity (18 ± 1 °C, $33\% \pm 5\%$). The relative humidity has a direct impact on the measurement of proton conductivity; to ensure the accurate determination, the PEM was full hydrated and the duration of the measurement was kept as short as possible (<5 min).

MINITAB software was used to design and evaluate the experiments.

2.5. Design-of-Experiment. In traditional experimental designs that aim to study the effects of different variables (factors) on an outcome, only one of these variables is changed per experiment, while the other parameters are kept constant. This allows the experimenter to properly identify which single variable influences the outcome of each experiment. A downfall to this method is that it does not allow the experimenter to study the influences of the interactions between the variables. The design-of-experiment method, which allows several factors to vary simultaneously, can be used to do this.¹⁵ The design-of-experiment method is very helpful for process development, since, in reality, individual variables as well as their interactions may affect the effectiveness of a process. For this method, the variables (called "factors") are identified. An experiment that allows for all possible combinations of factors is generated. The order in which these experiments are run is random (the order is computer-generated) so that there is no possibility of any bias. The software is capable of performing an analysis of variance on the input data (e.g., conductivity, fuel crossover). The results are then evaluated to determine which factors and interactions between factors most affect the process.

The factors are normally selected based on their significance of effects on the response. For this work, four factors were chosen: the type of mixer used to mix the Nafion and clay, the weight percentage of clay (with respect to the Nafion content), the curing temperature, and the curing time. A two-level full-factorial (2^4) design was used and 16 groups of experiments were performed. The hydrogen and methanol crossover and conductivities were measured for each membrane as responses. Table 1 summarizes the design factors. The following responses were chosen: methanol crossover, hydrogen crossover, in-plane conductivity, and through-plane conductivity.

3. Results and Discussion

The Nafion–clay nanocomposite membrane has been proven to reduce fuel crossover.^{1,4,16} This paper aims to systematically optimize the membrane synthesis parameters, to achieve maxi-

Table 1. Values of the Four Factors at Two Levels

factor	Value of Variable	
	low level (–)	high level (+)
type of mixer	ultrasonic	mechanical
clay percentage (%)	5	10
cure temperature (°C)	110	140
cure time (h)	4	12

mum reduction of fuel crossover while minimizing the sacrifice to the membrane's conductivity. Table 2 summarizes the design of each of the 16 membranes with their responses. In addition, a control membrane with no clay was also made using the same techniques and tools as the nanocomposite membranes. When needed, the membranes will be referenced by their designation in the first column.

3.1. Fuel Crossover. Fuel crossover decreases the efficiency of the cell, because the fuel is consumed without producing any useful current. Because Nafion membranes are somewhat permeable to hydrogen and methanol, it is important to design new membrane composites that will reduce this crossover while maintaining functionality. For this work, both hydrogen and methanol crossover are studied, because these membranes can be used in fuel cells that consume both of these fuels.

The mass-transfer limiting current was measured in situ, to determine the amount of hydrogen crossover. This was done by maintaining an equal pressure of hydrogen and nitrogen on either side of the membrane in the cell. When a hydrogen molecule crosses the membrane from the anode to the cathode, it becomes oxidized, providing the current for measurement. More hydrogen molecules can be oxidized as the voltage is increased until a mass-transfer limiting current is reached. Table 3 tabulates the fuel crossover responses for the design-of-experiment. It seems the only factor at $\alpha = 0.4$ or a 60% confidence level (CL) that greatly influences the hydrogen crossover is the curing time. The α parameter is the probability of rejecting the null hypothesis when the null hypothesis is really true (Type 1 statistical error); that is to say, finding a significant association when one does not really exist. For example, a value of $\alpha = 0.4$ means that finding an effect that does not really exist is 40% likely, or if an effect is found to be significant, it would be 60% certain that it is true. Note that, in some cases throughout this paper, the interactions between three or four factors appear to influence the outcome. When dealing with such complex interactions, further statistical analysis is required to ensure they do in fact contribute significantly and are not artifacts of the original analysis. For this work, we are confident of and discuss only the two factor interactions, although, for the sake of completeness, the three- and four-factor interactions are reported.

The first step in the analysis is to determine which factors and interactions were significant. Figure 1 shows the Pareto chart generated by MINITAB for hydrogen crossover. Any bar that passes the vertical line is significant at the chosen confidence level. These charts were generated for each response (hydrogen and methanol crossover; in- and through-plane conductivity). The information obtained from these charts is summarized in Tables 3 and 4. A shorter curing time seems to be more effective at producing a membrane that reduces hydrogen crossover than a longer one, as illustrated in Figure 2. The charts in Figure 2 are interaction plots that show the effect of two factors together on the crossover current. For example, the first plot shows that, for both the mechanical and ultrasonic mixers, a curing time of 4 h produces membranes with better crossover reduction properties than those cured at 12 h. Each data point on the interaction plot corresponds to the average crossover current of

the membranes that were made using the specific level of two factors. The 4-h curing time is clearly favored over the 12 h in each interaction. This may be due to the changes in the organization of the Nafion and clay that occur when heated. It is hypothesized that the curing allows the molecules of the membrane to become more mobile and align into more of a crystalline structure, which decreases the severity of the tortuous path through which hydrogen must navigate to cross to the anode. Therefore, a longer curing time would produce a membrane less adept at reducing fuel crossover. The interactions between the curing time and temperature and curing time and clay percentage affect the results at just less than a 60% CL. These effects are mentioned because it is important to note that the curing time plays an important role in influencing the membrane's permeability. It is worth emphasizing that even though the percentage of clay is not itself a significant factor for reducing crossover at high CL, the addition of clay makes a significant difference in the crossover current, as seen in Figure 3. In all but one case (membrane 11), the clay nanocomposite membrane exhibited lower crossover current than the control. The interaction between the clay and curing time indeed makes a difference. The best curing time for 5 wt % was 4 h. With the addition of more clay, the curing time becomes more important, and a shorter time, by far, is preferable to a longer one. At both curing temperatures, the shorter curing time yields a membrane with better crossover reduction capabilities. The effect is more apparent at the lower temperature than the higher.

The effects of the factors on the methanol crossover differed from hydrogen crossover, suggesting that the two fuels travel through the membrane differently. The hydrogen molecules diffuse through the "interfacial area"; however, the diffusion of methanol could happen within the aqueous phase inside the pores of Nafion, although the blocking mechanism for the clay could be the same.⁴ None of the four factors individually influence the methanol crossover reduction; however, several important interactions are shown in Figure 4 and reported in Table 3. The first is the interaction between the clay percentage and the curing temperature. Membranes with lower clay percentage are best when cured at the lower temperature and vice versa. The second important interaction is that between the type of mixer and curing temperature. The mechanical mixer works best with the lower temperature and the ultrasonic mixer worked best with the higher temperature. The third interaction of significance is between the type of mixer and clay percentage, where the mechanical mixer works best with the lower clay percentage and vice versa. Lastly, the interaction between the curing temperature and time is significant. The membranes cured at the lower temperature are the best when cured at the longer curing time, while the opposite is true for membranes cured at the higher temperature. Again, the increasing crystallinity of the membrane at higher temperatures for a longer time may render the tortuous path less severe, making methanol crossover easier. Interestingly enough, not all the membranes doped with clay reduced methanol crossover when compared to the control membrane. This again shows the need further studies regarding how methanol traverses the membrane. The processing conditions seem to be of utmost importance for methanol crossover reduction, because choosing the wrong ones could lead to membranes that are no better than the control.

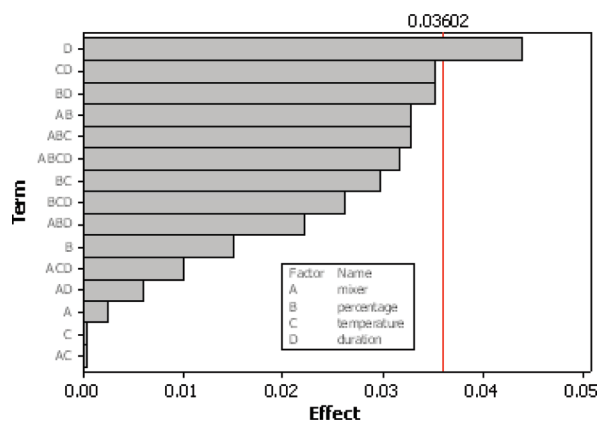
3.2. Conductivity. To determine how the four factors affect the through-plane and in-plane conductivities of the membranes, the AC impedance technique was used to measure the real impedance, which occurs when the imaginary component is equal to zero. Using this value, the ohmic conductivity was calculated.

Table 2. Matrix of 16 Designs and Their Responses

run order and ID	type of mixer ^a	clay percentage (%)	cure temperature (°C)	cure time (h)	Crossover		Conductivity	
					hydrogen (mA/cm ²)	MeOH (%)	through-plane (S/m)	in-plane (S/m)
control	M	0	120	6	0.51	8.8	2.41	11.24
1	M	5	110	4	0.37	4.5	1.49	9.41
2	M	5	110	12	0.35	4.0	1.53	10.58
3	M	5	140	12	0.43	9.2	2.05	6.72
4	U	5	140	12	0.42	8.8	1.87	7.04
5	U	10	110	4	0.34	9.3	1.04	6.98
6	M	10	110	4	0.34	9.6	1.41	6.12
7	M	5	140	4	0.42	9.6	1.28	8.08
8	U	10	110	12	0.41	8.1	1.04	7.55
9	U	5	110	12	0.46	7.5	1.10	8.97
10	M	10	140	12	0.38	7.1	1.26	4.63
11	M	10	110	12	0.55	9.6	1.26	4.43
12	U	10	140	12	0.40	4.5	0.90	4.57
13	M	10	140	4	0.38	7.1	0.97	4.57
14	U	5	110	4	0.40	7.8	0.99	9.67
15	U	5	140	4	0.43	6.5	1.41	6.99
16	U	10	140	4	0.37	5.3	0.99	5.10

^a M = mechanical; U = ultrasonic.**Table 3. Responses from the Factorial Design-of-Experiment to the Fuel Crossover^a**

factor	H Crossover		MeOH crossover	
type of mixer (A)	$\alpha = 0.4$	—	$\alpha = 0.3$	—
clay percentage (%) (B)	$\alpha = 0.4$	—	$\alpha = 0.3$	—
cure temperature (C)	$\alpha = 0.4$	—	$\alpha = 0.3$	—
cure time (D)	$\alpha = 0.4$	+	$\alpha = 0.3$	—
interaction	$\alpha = 0.45$	CD BD	$\alpha = 0.3$	BC AC ABC AB ABD CD

^a Note that “—” indicates no significant effect and “+” indicates a significant effect.**Figure 1.** Pareto chart generated by MINITAB, showing the significance of factors and interactions upon hydrogen crossover ($\alpha = 0.4$).

The in-plane technique is usually employed to avoid contact resistance, giving a value for only the membrane's in-plane impedance. However, in actual use in a fuel cell, the protons will be conducted through the plane of the membrane. The through-plane method closely resembles this and gives a better indication of which method will best improve conductivity for use in fuel cells. To minimize the impact of contact resistance, through-plane conductivities were measured under increasing pressures. The conductivity was determined to be when the measured values ceased reducing as the pressure increased, so the influence of contact resistance between the platinum current collectors and PEM can be minimized, the details of which have been discussed in ref

Table 4. Response of the Conductivity to the Factors^a

factor		Conductivity	
		in-plane	through-plane
type of mixer (A)	$\alpha = 0.3$	—	+
clay percentage (%) (B)	$\alpha = 0.3$	+	+
cure temperature (C)	$\alpha = 0.3$	+	—
cure time (D)	$\alpha = 0.3$	—	—
interaction	$\alpha = 0.3$	AB ABC ABCD	BC

^a Note that “—” indicates no significant effect and “+” indicates a significant effect.

4. Figure 5 shows a comparison of through-plane and in-plane conductivities for all the membranes made in the experiment, including the control membrane. It seems that the through-plane conductivity varies much less than the in-plane conductivity, which may be a result of the differing orientations in the bulk and at the surface of the membrane.

Table 4 tabulates the response of the conductivity to the factors. At a 70% CL, the type of mixer and clay percentage have significant impact on the through-plane conductivity. Figure 6 shows the main effects plots for these two factors. Unlike interaction plots, main effects plots only show the effect of one factor on the result. The interaction between clay percentage and the curing temperature is also significant. Figure 7 illustrates the clay percentage and curing temperature interaction. The most conductive membrane at either temperature was made with the lower clay percentage. The mechanical mixer is the better choice for improved through-plane conductivity. The lower percentage of clay is also preferable, which is expected because clay nanocomposites have a tendency to have lower conductivities than plain Nafion. When curing is performed at the lower temperature, it does not matter what the curing time is; however, when curing is performed at the higher temperature, the longer time produces a more conductive membrane. The lower temperature of 110 °C seemingly did not allow the membrane's morphology to change enough to significantly alter the conductivity after 4 or 12 h. The higher temperature of 140 °C obviously allows for more of a structural change to the membrane, likely producing a more crystalline nature where the sulfonic acid clusters are more aligned, enhancing the proton conduction network. With 5 wt % clay, the higher curing temperature yields a more-conductive membrane. The opposite is true for 10 wt %. Still, the conductivity for the

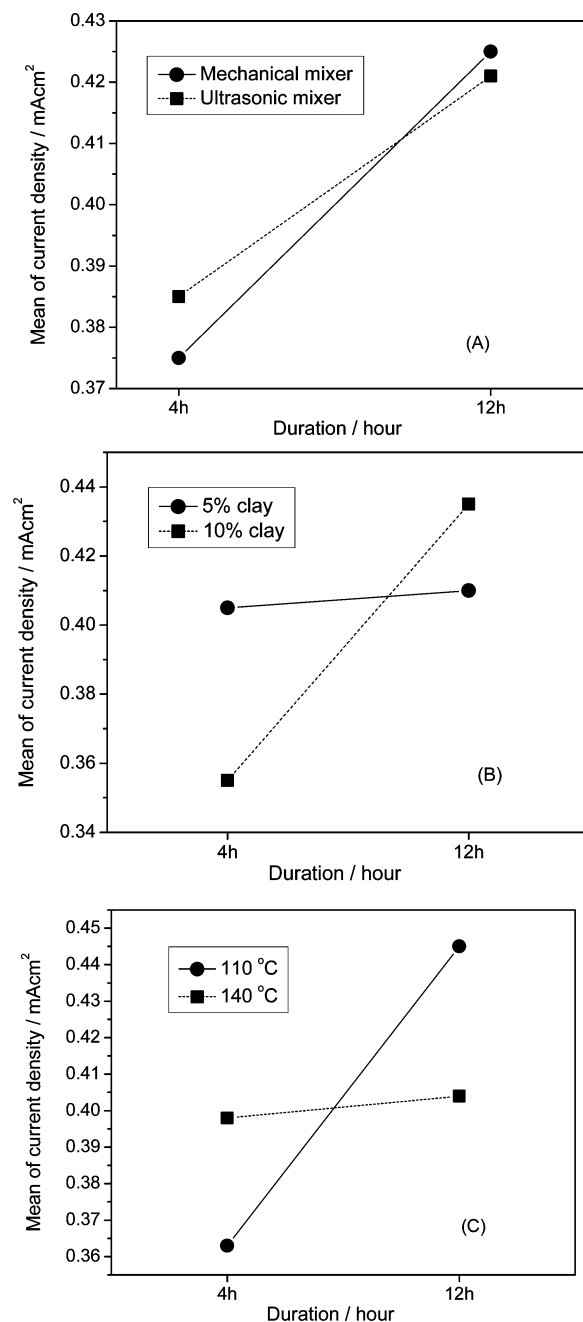


Figure 2. Interaction plots generated by MINITAB showing the effect on hydrogen crossover from the interactions between (a) type of mixer and curing time, (b) clay percentage (wt % MMT) and curing time, and (c) curing temperature and curing time.

membranes with more clay is, at best, still lower than the membranes with less clay.

As shown in Table 4, factors that affect the in-plane conductivity differ slightly from those that affect through-plane conductivity. The clay percentage and curing temperature have a significant effect by themselves, while the interactions between the type of mixer and clay percentage and all four factors also have significant effects. Again, as shown in Figure 8, an increase in clay percentage reduces the conductivity of the membrane, probably for the same reason that it reduced the through-plane conductivity. The curing temperature is a significant factor for the through-plane conductivity. The lower curing temperature yields membranes with a higher in-plane conductivity, also shown in Figure 8. This may result from the anisotropy of Nafion membranes, which may develop at higher curing temperatures. At a lower temperature, more of the proton

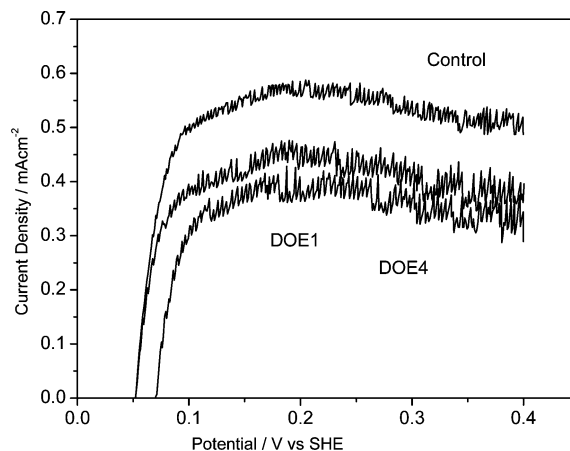


Figure 3. Linear voltammetry for control membrane and membranes 1 and 6 of the design-of-experiment.

conduction network may remain at the surface of the membrane. The differences between the two conductivities may be due to the varying orientations of the clay platelets and homogeneity of the membranes resulting from different processing methods and how that affects through-plane versus in-plane properties. As shown in Figure 9, which depicts the interaction plot between the type of mixer and clay percentage, the membranes with smaller amounts of clay have a much higher in-plane conductivity than those with larger amounts, regardless of the mixer used.

3.3. Process Optimization. When considering the ideal properties of a nanocomposite membrane for use in fuel cells, only the through-plane conductivity is important; therefore, the in-plane conductivity was not considered when choosing the best process. The mechanical mixer and a lower percentage of clay were clearly the best choices for optimal through-plane conductivity. The higher curing temperature is then preferred, according to the significant interaction between it and clay percentage. At a lower CL (50%), it is apparent that the longer curing time has a positive impact on through-plane conductivity in all cases. To reduce hydrogen crossover, it appears that the most important factor is a shorter curing time, as an independent factor, and also in conjunction with the curing temperature and time. The factors and interactions that affect the methanol crossover vary somewhat from those affecting hydrogen crossover. Again, through-plane conductivity must be maintained, so the use of the mechanical mixer and a lower clay percentage is vital. This means the lower curing temperature and longer curing time are the best choices for reducing methanol crossover.

In summary, the best method for fabricating Nafion nanocomposite membranes to reduce hydrogen crossover and maintain conductivity is to use a mechanical mixer, a lower percentage of clay, a lower curing temperature, and a medium curing time (8 h). Five more membranes were fabricated using this method, except for the clay percentage. One membrane was made with 2% clay and four membranes were made with 5%, 15%, 20%, and 25% clay. Membranes with higher and lower clay percentages than those in the design-of-experiment were made to determine the range of effective clay percentages. Table 5 tabulates the responses of these membranes against the control membrane. It is interesting to note that the membrane with only 2% clay yields a hydrogen crossover reduction comparable to that off the 5% and 10% clay membranes of the design-of-experiment. This is promising, because the less clay that is needed to hinder fuel crossover, the more conductive the membrane will be. Of course, the membranes with 15%, 20%, and 25% clay suffer lower conductivities. UMB-004 was made with Cloisite 10A clay that was run through a H⁺ ion-exchange resin, as described in section 2.3. This membrane shows

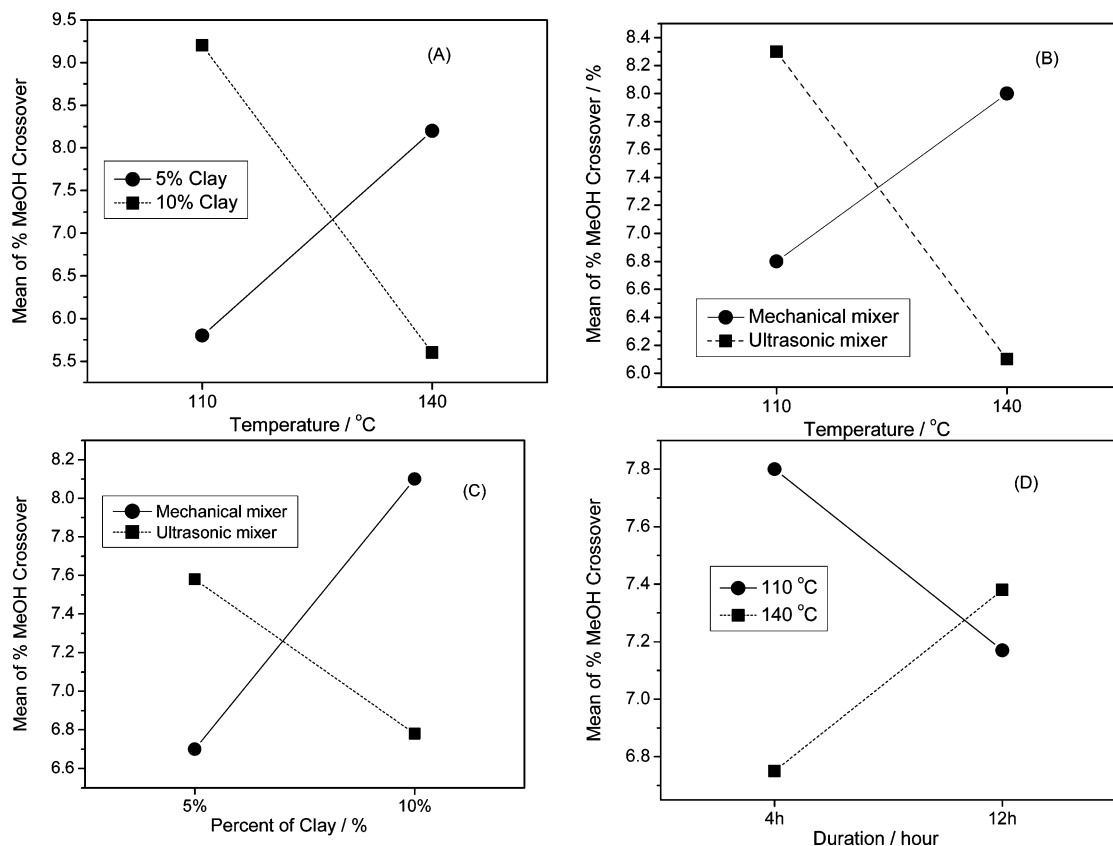


Figure 4. Interaction plots generated by MINITAB showing the effect on methanol crossover from the interactions between (a) type of mixer and curing temperature, (b) curing temperature and curing time, (c) clay percentage (wt % MMT) and curing temperature, and (d) type of mixer and clay percentage (wt % MMT).

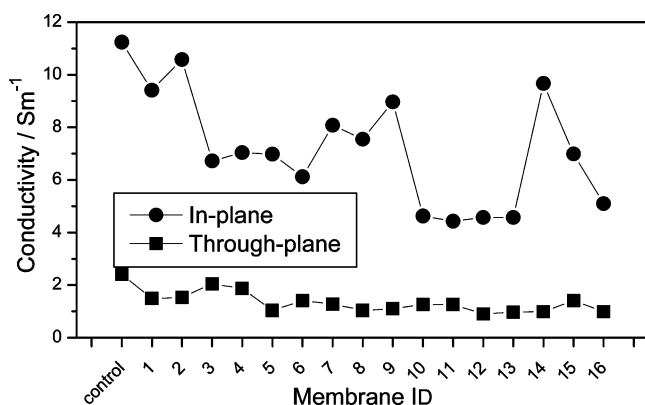


Figure 5. Comparison of in-plane and through-plane conductivities for the membranes made in the design-of-experiment and the control membrane.

increased conductivity when compared to the other 5% clay membranes. This has promising implications for nanocomposite membrane development, because the clay-doped membranes made with H⁺-exchanged clay may have improved conductivities, making the membranes more comparable to plain Nafion.

As stated earlier, the factors affect methanol crossover differently than they do hydrogen crossover. The best method for fabricating a membrane that best reduces methanol crossover while maintaining conductivity is to use a mechanical mixer, low clay percentage, low curing temperature, and long curing time. One may expect the membranes with 15%–25% clay would hinder methanol crossover more than those with 2% or 5% clay. However, the process used to make these membranes with high clay percentage was ideal for the reduction of hydrogen crossover, not methanol crossover. This may explain why the methanol crossover reported for membranes with

higher clay percentage does not differ much from the two with a lower clay percentage. In fact, it was not possible to get results for UMB-003. It appears the membrane immediately failed at blocking methanol.

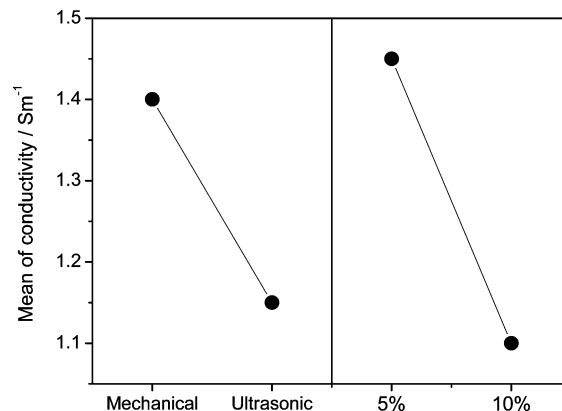


Figure 6. Main effects plots generated by MINITAB for the effect on through-plane conductivity of (a) both mixers and (b) both clay percentages (wt % MMT) studied.

Table 5. Summary of Data for Membranes Fabricated Using the Best Method for Hydrogen Crossover

ID	type of mixer	clay percentage (%)	cure temperature (°C)	cure time (h)	Crossover		Conductivity	
					hydrogen (mA/cm ²)	MeOH (%)	through-plane (S/m)	in-plane (S/m)
control	M	0	120	6	0.51	8.8	2.41	11.24
UMB-001	M	15	110	8	0.28	10.5	0.96	3.67
UMB-002	M	20	110	8	0.38	6.1	0.65	1.92
UMB-003	M	25	110	8	0.23	NA	0.37	1.01
UMB-004	M	5	110	8	0.35	10.9	1.82	9.52
UMB-005	M	2	110	8	0.35	9.7	1.18	11.25

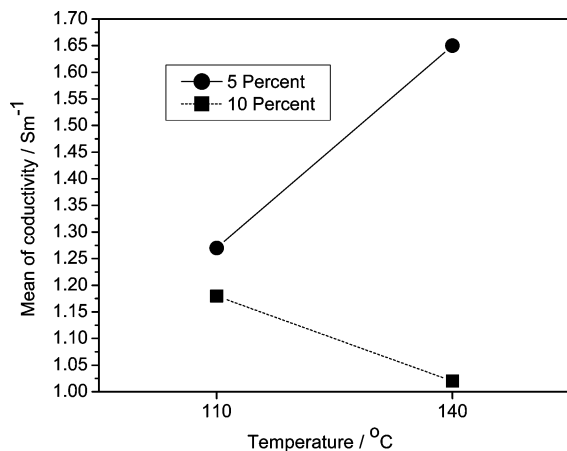


Figure 7. Interaction plot generated by MINITAB for the effect on through-plane conductivity of the interaction between clay percentage (wt % MMT) and curing temperature.

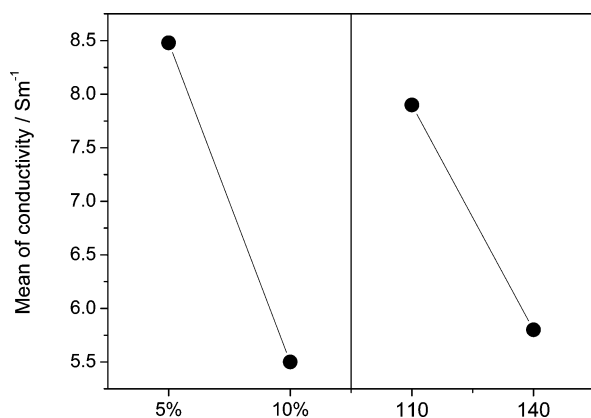


Figure 8. Main effects plot generated by MINITAB for the effect on in-plane conductivity of (a) both clay percentages (wt % MMT) and (b) both curing temperatures studied.

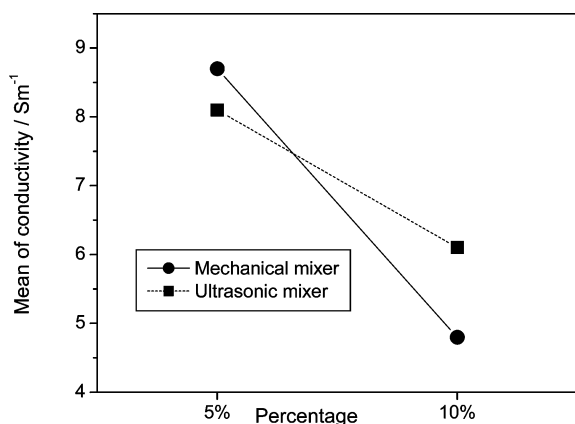


Figure 9. Interaction plot generated by MINITAB for the effect on in-plane conductivity of the interaction between the type of mixer and clay percentage (wt % MMT).

This test was performed for UMB-003 twice, each time using a different piece of membrane. It may be that the amount of clay (25%) added to this membrane altered its effectiveness in liquids or made it more brittle and likely to tear.

4. Conclusion

Four process variables are studied to determine their effects on Nafion–clay nanocomposite membranes: the type of mixer, the clay percentage, the curing time, and the curing temperature.

The best process to fabricate a membrane with good conductivity and hydrogen crossover reduction uses a mechanical homogenizer, a lower percentage of clay, and a lower curing temperature for a medium duration of time. The best process to fabricate a membrane with good conductivity and methanol crossover reduction uses a mechanical mixer, a lower percentage of clay, and a lower curing temperature for a long curing time.

These conclusions can be a “jumping-off point” to further studies in process development. There are many other factors to consider, such as the solvent, casting temperature, membrane thickness, and clay modification.

Acknowledgment

The work was partially supported by the National Aeronautics and Space Administration (NASA), through a subcontract, and was partially supported through the University of Massachusetts Boston (UMB) New Faculty Start-Up Grant. Both financial supports are gratefully acknowledged. The authors also wish to thank Professor Bela Torok, at UMB, and his graduate student, Mr. Dmitry Borkin, for their support.

Literature Cited

- (1) Kim, T. K.; Kang, M.; Choi, Y. S.; Kim, H. K.; Lee, W.; Chang, H.; Seung, D. Preparation of Nafion–sulfonated clay nanocomposite membrane for direct methanol fuel cells via a film coating process. *J. Power Sources* **2007**, *165*, 1.
- (2) Alonso, R. H.; Estevez, L.; Lian, H.; Kellarakis, A.; Giannelis, E. P. Nafion–clay nanocomposite membranes: Morphology and properties. *Polymer* **2009**, *50*, 2402.
- (3) Burgaz, E.; Lian, H.; Alonso, R. H.; Estevez, L.; Kellarakis, A.; Giannelis, E. P. Nafion–clay hybrids with a network structure. *Polymer* **2009**, *50*, 2384.
- (4) Felice, C.; Ye, S.; Qu, D. Nafion–montmorillonite nanocomposite membrane for the effective reduction of fuel crossover. *Ind. Eng. Chem. Res.* **2010**, *49*, 1514.
- (5) Chen, B.; Evans, J. R. G.; Greenwell, H. C.; Boulet, P.; Coveney, P. V.; Bowden, A. A.; Whiting, A. A critical appraisal of polymer–clay nanocomposites. *Chem. Soc. Rev.* **2008**, *37*, 568.
- (6) Choi, Y. S.; Kim, T. K.; Kim, E. A.; Joo, S. H.; Pak, C.; Lee, Y. H.; Chang, H.; Seung, D. Exfoliated Sulfonated Poly(arylene ether sulfone)–Clay Nanocomposites. *Adv. Mater.* **2008**, *20*, 2341.
- (7) Song, M. K.; Park, S. B.; Kim, Y. T.; Kim, K. H.; Min, S. K.; Rhee, H. W. Characterization of polymer–layered silicate nanocomposite membranes for direct methanol fuel cells. *Electrochim. Acta* **2004**, *50*, 639.
- (8) Kim, D. W.; Choi, H. S.; Lee, C.; Blumstein, A.; Kang, Y. Investigation on methanol permeability of Nafion modified by self-assembled clay–nanocomposite multilayers. *Electrochim. Acta* **2004**, *50*, 659.
- (9) Chen, B.; Evans, J. R. G. Poly(ϵ -caprolactone)–Clay Nanocomposites: Structure and Mechanical Properties. *Macromolecules* **2006**, *39*, 747.
- (10) Boo, W. J.; Sun, L.; Liu, J.; Moghbelli, E.; Clearfield, A.; Sue, H.; Pham, H.; Verghese, N. Effect of Nanoplatelet Dispersion on Mechanical Behavior of Polymer Nanocomposites. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 1459.
- (11) Guan, R.; Dai, H.; Li, C.; Liu, J.; Xu, J. Effect of casting solvent on the morphology and performance of sulfonated polyethersulfone membranes. *J. Membr. Sci.* **2006**, *277*, 148.
- (12) Kaliaguine, S.; Mikhailenko, S. D.; Wang, K.; Xing, P.; Roberson, G. P.; Guiver, M. D. Properties of SPEEK based PEMs for fuel cell application. *Catal. Today* **2003**, *82*, 213.
- (13) Vengatesan, S.; Cho, E.; Kim, H.; Lim, T. Effects of curing condition of solution cast Nafion membranes on PEMFC performance. *Korean J. Chem. Eng.* **2009**, *26*, 679.
- (14) Jung, H.; Cho, K.; Lee, Y. M.; Park, J.; Choi, J.; Sung, Y. Influence of annealing of membrane electrode assembly (MEA) on performance of direct methanol fuel cell (DMFC). *J. Power Sources* **2007**, *163*, 952.
- (15) Miller, J. N.; Miller, J. C. *Statistics and Chemometrics for Analytical Chemistry*; Pearson Education: Harlow, England, 2005.
- (16) Kocha, S. S.; Yang, J. D.; Yi, J. S. Characterization of gas crossover and its implications in PEM fuel cells. *AIChE J.* **2006**, *52*, 1916.

Received for review August 22, 2010
 Revised manuscript received November 8, 2010
 Accepted November 19, 2010