

PULSED FIELD GRADIENT NMR INVESTIGATION OF MOLECULAR MOBILITY OF TRIMETHOXYMETHANE IN *NAFION* MEMBRANES

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ABSTRACT

Molecular mobility of water and trimethoxymethane (TMM) in *NAFION* membranes of two different equivalent weights (EW), 1100 and 1500, were investigated. Self-diffusion coefficients were determined by the NMR pulsed field gradient method, from the methyl proton NMR signal in saturated *NAFION* samples containing various concentrations of TMM in water, from 0.5 to 14 M, and at temperatures varying from 30°C to 80°C. Diffusion of molecular species containing methyl protons is more than a factor of two slower in the 1500 EW membrane than the 1100 EW membrane at 30°C and 1 M concentration; the difference rises to about a factor of four at 80°C and 14 M concentration. These differences are attributed mainly to the greater effective distance between acid functional groups in the higher ew material. *NAFION* samples containing methanol/water mixtures were also investigated. Comparison with the methanol results and the permeation behavior, as characterized by gas chromatographic methods, show that in fact, more than half of the TMM is hydrolyzed to methanol as it passes through the acidic membrane. The implications of these findings for alternative fuels in direct oxidation fuel cells are discussed.

INTRODUCTION

Direct methanol oxidation fuel cells are hampered by high methanol crossover rates. This has led to consideration of alternative fuels, one of which is trimethoxymethane (TMM - $[\text{CH}_3\text{O}]_3\text{CH}$). TMM is similar to methanol in terms of overall electrochemical activity but is a volumetrically efficient fuel. Other advantages that TMM has as a fuel include a substantially higher boiling point and lower vapor pressure than methanol. TMM is a considerably larger molecule than methanol, and previous studies have suggested reduced molecular crossover compared to methanol.¹ However, TMM is a rich fuel, yielding 20 electrons per complete oxidation reaction compared to six electrons for methanol. Therefore, the crossover "penalty" for TMM is higher than for methanol, on a per mole basis.

Another strategy for reducing cross-over which has been described is the use of higher equivalent weight membranes. In that case, the rationale has been the lower uptake of methanol (and water), which leads to lower permeability. Furthermore, the lower uptake is thought to help decrease the overall molecular mobility of fuel in the polymer.

Since the conductivity of the membrane also drops as EW is increased, there is a trade-off associated with increased EW membranes-- increased resistive loss in the cell versus decreased fuel permeation rates.

In this investigation, we studied the mobility of water, methanol and TMM in *NAFION* membranes. We also assessed the effect of changing the equivalent weight of the proton exchange membrane on molecular crossover for both methanol and TMM. We carried out permeation and self diffusion measurements, by gas chromatography and pulsed field gradient (PFG) NMR techniques respectively, in *NAFION* membranes equilibrated in various solutions of water/TMM and water/methanol. The PFG NMR method is a powerful technique which yields directly the self-diffusion coefficient, D^* , of a particular nucleus (e.g. ^1H) associated with a diffusing molecule.² In certain favorable cases, as in the present investigation, it is possible to distinguish between several species (e.g. water and methanol) containing the same NMR nucleus, and thus determine their D^* values separately. Inspection of the NMR results in light of known electrochemical crossover measurements led us to the chromatographic studies.

EXPERIMENTAL

NAFION membranes were obtained from E.I. DuPont de Nemours, Inc. in two ew forms, EW = 1100, which is commercially available as *NAFION-117*, and EW = 1500. The membranes were pre-treated in aqueous solutions of H_2O_2 , and then H_2SO_4 , and washed with deionized water, as described previously.^{2,3} The PFG NMR measurements were performed on a Bruker AMX-400 NMR spectrometer equipped with a microimaging probe with gradient coils which can sustain a maximum gradient strength of 4.0 mT/cm. Gradients were calibrated with a water standard and temperatures were controlled to $\pm 1\text{K}$ with a Bruker VT1000 temperature controller. For the NMR measurements, slivers of membrane of dimensions 8 mm X 15 mm were immersed for several days in aqueous solutions of TMM (obtained from Aldrich), with the TMM concentration varying from 0.5 to 14 M. The membranes were then removed from solution and quickly blotted dry to remove surface liquid, loaded into 10 mm OD glass NMR tubes and sealed with parafilm. The self diffusion coefficients, D^* were determined by the pulsed gradient, stimulated spin echo sequence (PGSSE),² utilizing the proton NMR signals originating from both water and methyl protons.

The determination of methanol permeability in polymer electrolyte membranes was accomplished by measuring the change in concentration as a function of time, by gas chromatographic methods, of two vessels separated by membrane samples. The procedure involved preparing a solution of the permeate and placing it in one vessel, typically 3.0M solutions, while the other vessel (B) contained de-ionized water. Samples were taken from the vessel B at specified times and analyzed with a Varian 3400 gas chromatograph equipped with a Carbowax column. An internal standard, such as a higher molecular weight alcohol, was added to the samples to determine the concentration.

The direct electrochemical oxidation of methanol and trimethoxymethane was investigated in liquid feed fuel/oxygen cells (25 cm² electrode area) which contained membrane electrode assemblies (MEAs) utilizing Nafion 1100 e.w. (7 mil.) and Nafion 1500 e.w. (5 mil.) membranes as the solid polymer electrolytes (MEAs were supplied by Giner, Inc., Watham, Mass.). In this design, an aqueous solution of the organic fuel is fed to an unsupported Pt/Ru anode, whereas oxygen is supplied to an unsupported Pt cathode containing $\sim 4.0\text{ mg cm}^{-2}$ Pt electrocatalyst. The cell was operated at temperatures ranging

from 20°C to 90°C, oxygen pressures of 20-30 psig, oxygen flow rates ranging between 1.0L/min. to 5.0L/min., and fuel concentrations of 0.5 to 2.0M. The cells were operated at current densities in the range of 1-400 mA cm⁻².

The methanol crossover rates present in operating fuel cells ^{were} ~~was~~ measured by analyzing the CO₂ content present in the cathode exit stream. This was accomplished by utilizing an on-line analyzer, purchased from Horiba Co., which measures the CO₂ volume percent in the cathode stream by passing the sample through an infra-red detector. Before each measurement, the instrument was calibrated with gases of known CO₂ content. X

RESULTS

To assess the overall permeation rate from individual measurements, we must know both the TMM uptake and the diffusion rate. The former could also yield some information concerning any selective partitioning of TMM into or out of the membrane. The ¹H NMR spectrum of solutions of TMM in water and in the membrane consisted primarily of two lines, from methyl protons and water protons. To determine the partitioning of TMM into the membrane, the water to methyl group peak intensity ratio was determined from the NMR spectrum. Intensity ratios were essentially identical inside the membrane to that observed in the immersion solution. Thus, no selective partitioning occurs.

Self-diffusion coefficients extracted from the PGSSE signal intensities for methanol and water in both *NAFION* 117 (N117) and the 1500 ew membrane (N1500) are plotted in Fig. 1a and 1b, respectively, under conditions of varying temperature and methanol concentration. The methanol diffusion results for N117 are essentially the same as previously reported. At similar methanol concentrations and temperatures, both water and methanol D* values drop by a factor of two to three in the higher EW material relative to those in N117. The lower water and methanol diffusion rates in N1500 are attributed to the lower overall \hat{O} plasticization \hat{O} of the N1500 membrane (i.e. lower solvent uptake) as well as the greater average spacing between SO₃⁻ functional groups, as compared to the N117. Although this result has important implications concerning methanol crossover, the proton conductivity is also lower in the higher EW material, most likely due to the same factor that limits the methanol and, more importantly, the water diffusivity. As noted previously for N117, there is a weak dependence of the diffusion coefficient on concentration in both membranes.

NMR diffusion coefficients of water and TMM in both membranes, equilibrated in water/TMM solutions, are plotted as a function of concentration for several temperatures in Figure 2a and 2b, respectively. The close similarity in TMM and methanol behavior is immediately apparent, and a more detailed comparison between the methanol and TMM data shows that the D* values are also quite similar. It should be emphasized that the NMR spectroscopic method cannot easily distinguish between CH₃ protons in CH₃OH and TMM since they have very similar electronic environments (both are in O CH₃ moieties). The diffusion results are apparently at odds with electrochemical permeation results. With similar diffusion coefficients and partitioning for methanol and TMM, we would expect a factor of >3 (the ratio of number of electrons harvested from TMM to that from methanol) increase in TMM electrochemical cross-over current. This led us to hypothesize that TMM can hydrolyze into methanol and other products within the highly acidic Nafion medium. Thus, gas chromatographic permeation measurements, presented below, were performed in order to test this hypothesis.

Methanol permeation data obtained by GC for both membranes are shown in Figure 3. Even though TMM is being studied as the permeant, the clear detection of methanol demonstrates that, indeed, the TMM hydrolyzes by the time the molecules reach the other side of the membrane. There is also evidence for the presence of about 5% of an unidentified secondary product, most likely methyl formate. Thus it appears that the NMR diffusion measurements reflect methanol rather than TMM diffusion in the equilibrated membranes. Comparison between the two membranes shows that the higher EW material is less permeable to the TMM hydrolysis product (mostly methanol). The membrane sample used was thinner than the N117 sample. For direct comparison in which membrane thickness is not a variable (Figure 3 indicates two different thicknesses), it should be noted that for identical thicknesses of 5 mil, a 1500 ew membrane has nearly a factor of three lower TMM permeability than a 1100 ew sample.

Crossover measurements in liquid feed fuel/oxygen cells at 60°C are displayed in Figure 4. Figure 4 shows a comparison of crossover molar flux, derived from current density measurements. The N1500 material exhibits significantly lower crossover than for N117^{1,4}, which is consistent with the NMR diffusion results. The relevant point of comparison to the NMR results is the open circuit value. Figure 4 suggests that TMM has a somewhat lower molar flux than methanol. In this case, it may be that the hydrolysis reaction is incomplete on the time scale of the permeation experiment.

The hydrolysis reaction is disappointing relative to the use of TMM as an alternative fuel based on the expected lower permeation rate of TMM. However it should be pointed out that the equilibration of the membrane in water/TMM solution represents a "worst case scenario". That is, it is expected that some of the fuel will be electro-oxidized at the anode before hydrolysis can occur within the bulk of the membrane in an operating fuel cell. The experiments reported here represent the long time limit behavior. The observable extent of hydrolysis will depend on the relative rates of cross-over and hydrolysis, which in turn will depend on temperature and membrane EW. Furthermore, the volumetric or specific energy benefit of using a rich fuel such as TMM still accrues.

CONCLUSIONS

Self-diffusion of water and methanol is substantially slower for high EW Nafion membranes than for low EW membranes. TMM diffusion measurements indicate a similar diffusion rate to that of methanol in any given Nafion membrane. This is probably a reflection of hydrolysis of TMM occurring in the highly acidic membrane microenvironment, as demonstrated via GC measurements. NMR results are generally consistent with findings from electrochemical permeation measurements.

ACKNOWLEDGMENTS

We gratefully acknowledge ONR and the DOE Office of Transportation Technology for support of this work. The part of the research described in this paper that was performed by the Jet Propulsion Laboratory, California Institute of Technology, was sponsored by DARPA, through an agreement with the National Aeronautics and Space Administration. One of the authors (S.G.) acknowledges the NASA/JOVE program and the National Research Council for sabbatical leave support.

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FIGURES

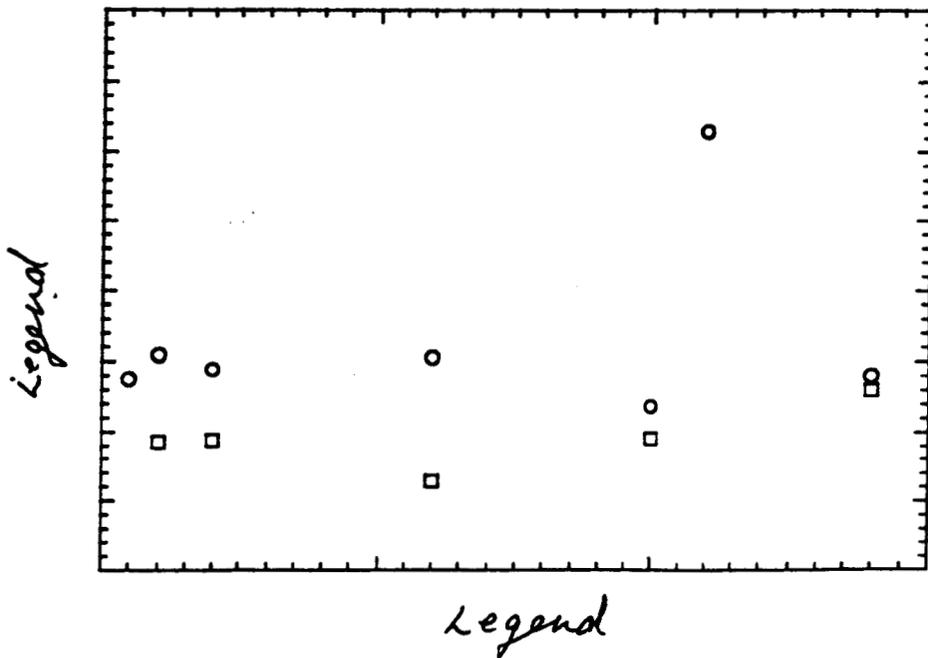
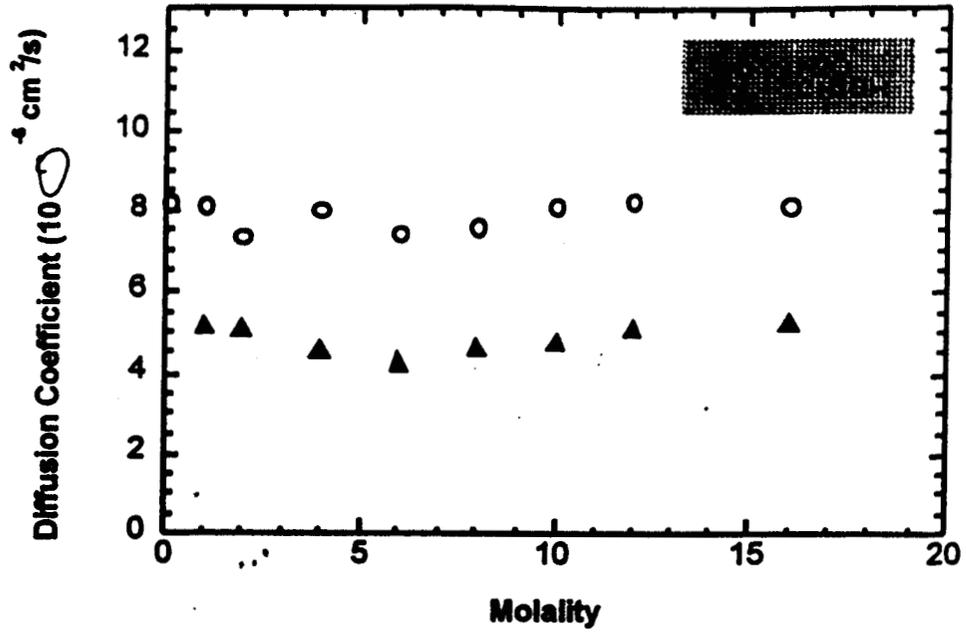
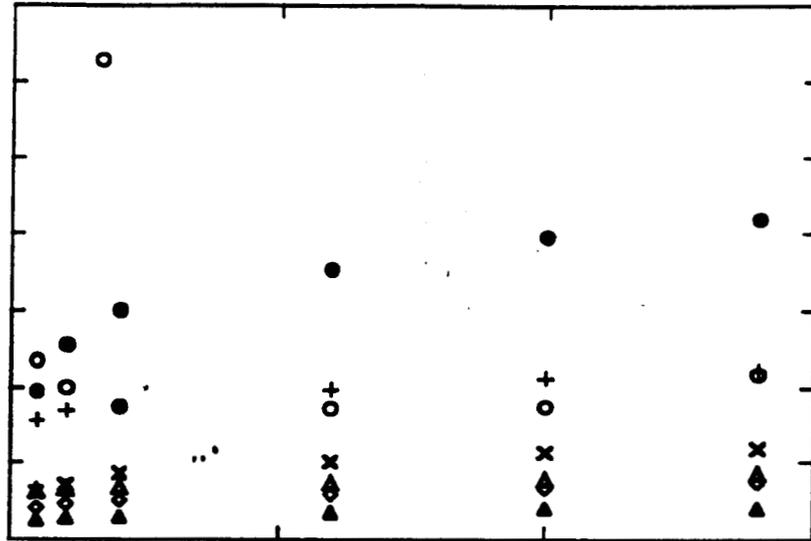
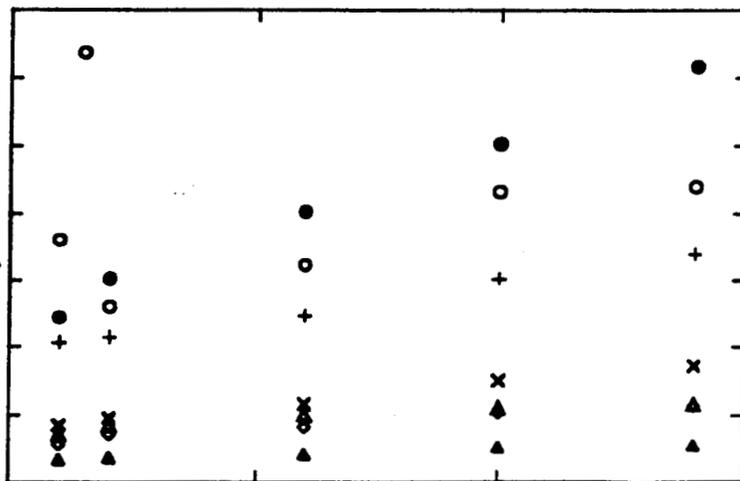


Figure 1a (top): Diffusion coefficients of water and methanol in a N117 membrane at 30°C; 1b (bottom): Diffusion coefficients of water and methanol in a N1500 membrane at 30°C



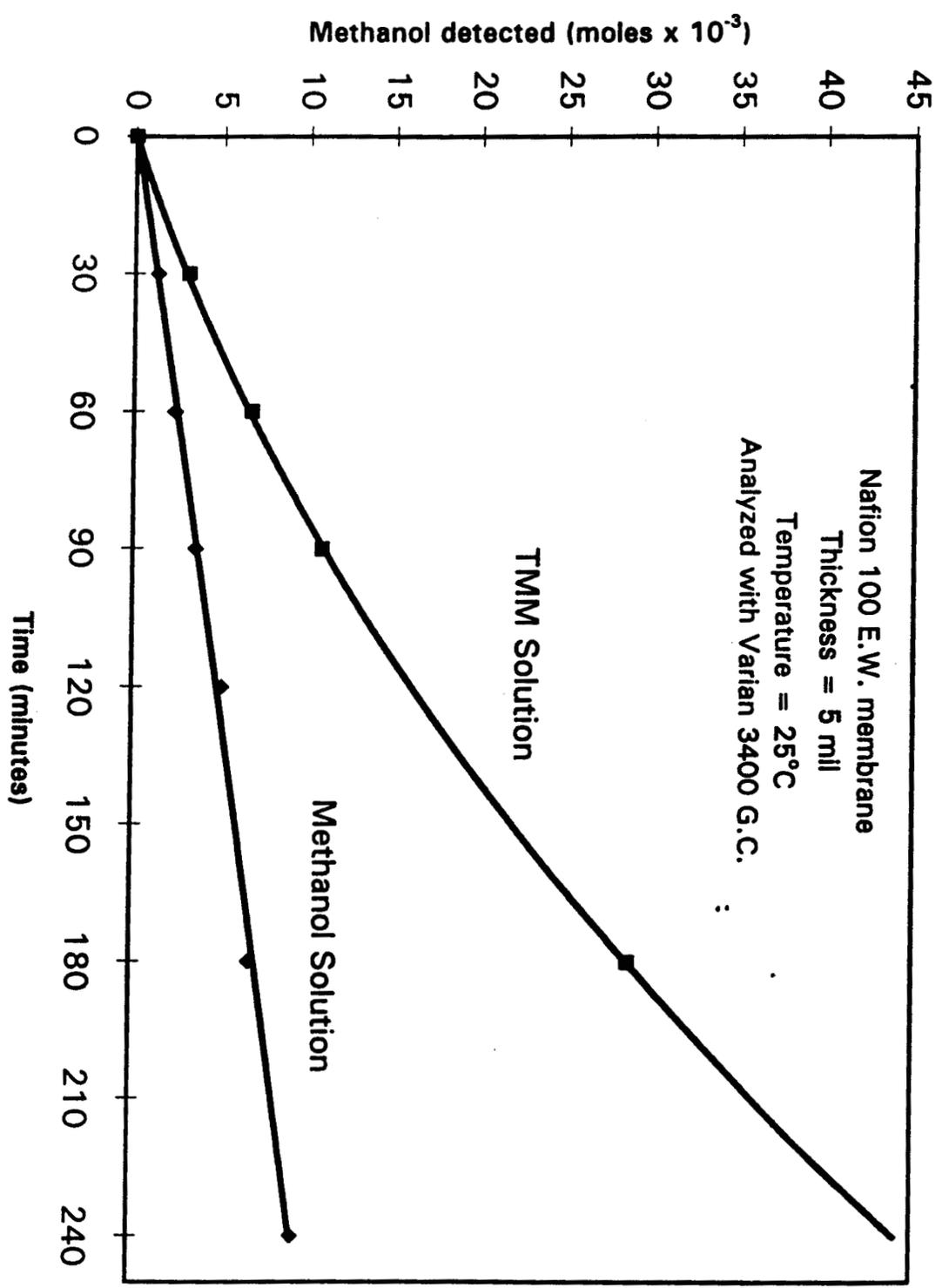
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Figure 2a (top) Diffusion coefficients of water in N117 and N1500 membranes at various temperatures; 2b (bottom): Diffusion coefficients of TMM in N117 and N1500 membranes at various temperatures.

**Methanol and Trimethoxymethane Permeability Measurements:
Nation 1500 E.W. Membrane**



**Crossover Rates in Fuel Cell with Nafion 1500 E.W. Membrane:
Methanol vs. Trimethyl orthoformate**

