

Partitioning and Polymerization of Pyrrole into Perfluorosulfonate (Nafion) Membranes under Neutral Conditions

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The partitioning of pyrrole into Nafion membranes in their Na⁺, Me₄N⁺, and Et₄N⁺ forms has been investigated by electronic absorption spectroscopy and the results are compared with those previously obtained with membranes in the acid form (H-Nafion). In the absence of the acid-catalyzed reactions observed for H-Nafion, pyrrole partitioning into neutral Nafion is weak and follows a simple equilibrium model. The partition coefficients are 1.5 for Na-Nafion, 3.1 for Me₄N-Nafion, and 4.0 for Et₄N-Nafion. The use of neutral Nafion for the preparation of polypyrrole-modified membranes for direct methanol fuel cells has been shown to have significant advantages over the use of H-Nafion.

Introduction

Polypyrrole/Nafion composites have been the subject of numerous fundamental studies and have been investigated for a wide range of applications.¹ The combination of the electronic conductivity and electroactivity of polypyrrole with the high ionic conductivity and ion-exchange capacity of Nafion provides much scope for the design of materials with novel properties and applications. The use of Nafion, and other polyanions, to modify ion transport during the electrochemistry of polypyrrole to favor cation transport is a recurring theme.^{2–4} This provides potential applications for polypyrrole-rich composites in batteries^{5,6} and supercapacitors,⁷ sensors,^{8,9} and fuel cells.^{7,10} On the other hand, polypyrrole and other conjugated polymers can be used to modify the transport properties of Nafion and other cation-exchange membranes. Polypyrrole has been reported to markedly increase the permselectivity of Nafion and Neosepta membranes for Na⁺ relative to divalent cations and to decrease their permeability to neutral molecules.¹¹ Applications in electrodialysis^{11,12} and fuel cells^{13,14} are being developed.

We have recently reported a study of the partitioning of pyrrole into Nafion membranes and its subsequent polymerization with various oxidizing agents.¹⁵ Polypyrrole/Nafion composites containing 1–2% polypyrrole by mass, prepared in this way, have shown excellent performances as membranes for direct methanol fuel cells (DMFC),¹⁴ exhibiting decreased methanol crossover to the anode by 30–80% and thereby decreased poisoning of the cathode and loss of fuel.

Our initial mechanistic study¹⁵ of the formation of these polypyrrole/Nafion composites focused on membranes in the acid form (H-Nafion) that allow the pyrrole to be polymerized with noncontaminating oxidizing agents such as O₂ and H₂O₂. However, the partitioning of pyrrole into H-Nafion is complicated by its protonation, trimerization, and oxygen-driven polymerization.¹⁵ As these processes prevent a quantitative analysis of the partitioning kinetics and equilibria, neutral Nafion salts (Na-Nafion, Me₄N-Nafion, and Et₄N-Nafion) have been used in the work reported here. The goals of this work were to quantify the partitioning of pyrrole into these forms of Nafion

TABLE 1: Pyrrole Loading Conditions, Methanol Crossover Currents, and Specific Resistances for Nafion 115 Membranes^a

membrane	[pyrrole], M	time, h	<i>I</i> _{lim} , mA cm ^{−2}	<i>R</i> , Ω cm ²
Nafion 115			136	0.16
Na-Nafion 1	0.2	1	119	0.22
Na-Nafion 2	0.5	2	101	0.40
H-Nafion	0.2	1	38	1.8

^a Pyrrole loaded membranes were treated with 0.08 M Fe³⁺ solution for 10 h, washed repeatedly with 1 M H₂SO₄(aq) until the wash solution was colorless, and washed with water.

and to investigate the effect of the Nafion counterion on the properties of the polypyrrole/Nafion composites formed by subsequent polymerization of the pyrrole with Fe(III).

Experimental Section

Materials. Nafion 115 (DuPont; donated by H Power Corp) was cleaned following a standard literature protocol.¹⁶ Membranes were converted to the salt forms by equilibration with 1 M aqueous solutions of NaOH, Me₄NBr, or Et₄NCl. The procedure was repeated for Me₄NBr and Et₄NCl to ensure a high degree of ion exchange. The final pH values of the second Me₄NBr and Et₄NCl solutions were 5.4 and 3.4, respectively. Pyrrole (Aldrich) was purified by filtration through a plug of silica immediately prior to use. Nanopure water was used to prepare all aqueous solutions and for washing membranes. All other chemicals were used as received.

Polymerization of Pyrrole in Nafion 115. Nafion 115 membranes were immersed in 0.2 or 0.5 M pyrrole for 1 or 2 h and then immersed in 0.08 M Fe(NO₃)₃(aq) for 10 h to polymerize the pyrrole. They were then washed repeatedly with 1 M H₂SO₄(aq) until the wash solution was colorless and finally washed well with water.

Fuel Cell Experiments. Membranes were evaluated at 60 °C in a commercial 5 cm² active area fuel cell (ElectroChem. Inc.) as previously described.¹⁴ The high-frequency resistance of the fuel cell (at 60 °C) multiplied by the active area is reported in Table 1. Methanol crossover (at 60 °C) was measured and is reported as the limiting current for oxidation of methanol reaching the cathode, with N₂ being passed through the cathode

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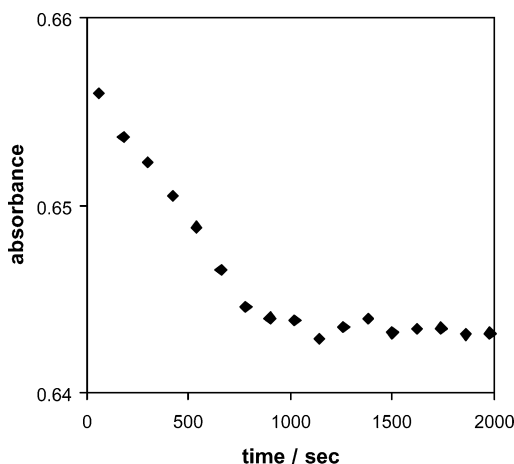


Figure 1. Absorbance at 206 nm (λ_{\max} for pyrrole) for a 0.094 mM pyrrole solution (3 mL) following immersion of a 72 mg piece of Na-Nafion 115.

compartment and 1 M aqueous methanol passing through the anode compartment.

Results and Discussion

Partitioning of Pyrrole into Nafion Membranes. The uptake of pyrrole into Nafion membranes was monitored by electronic absorption spectroscopy.¹⁵ Pieces of Nafion (ca. 100 mg) were immersed in aqueous pyrrole solutions (3 or 5 mL) for various times. In one type of experiment the membrane was immersed in a cuvette containing aqueous pyrrole such that the absorbance of the solution at λ_{\max} for pyrrole (206 nm) could be continuously monitored without removing the membrane. Figure 1 shows a representative result for a Na-Nafion membrane in ca. 0.1 mM pyrrole solution. As expected for a simple partitioning equilibrium, the concentration of pyrrole in the solution fell for a period of time and then became constant after 15 min. From the limiting loss of pyrrole from the solution, the equilibrium concentration of pyrrole in the membrane can be estimated to be 0.14 mM, yielding a partition coefficient of 1.5. These results are in stark contrast to those obtained with H-Nafion, in which the concentration of pyrrole in the solution was found to decrease indefinitely (>4 days) due to reactions occurring within the membrane.¹⁵

The uptake of pyrrole has also been monitored by measuring the absorption spectrum of the Nafion membrane (supported between two quartz disks) following its removal from the pyrrole solution. Figure 2 shows spectra of films that had been immersed in 3.2, 6.3, and 9.6 mM pyrrole (aq) for 2 days. The partition coefficient in these experiments (1.5 ± 0.1) was independent of concentration and the same as the value obtained at ca. 0.1 mM. The spectra show that the pyrrole in the Na-Nafion membrane is almost exclusively in the form of free pyrrole ($\lambda_{\max} = 206$ nm). However, there are also small absorbance peaks that can be assigned to bipyrrrole ($\lambda_{\max} = 276$ nm)¹⁷ and polypyrrole ($\lambda_{\max} = 435$ nm).¹⁷

Also shown in Figure 2 is the result of a similar experiment conducted with H-Nafion. Despite the shorter time (1 day) used for this experiment, and the exclusion of air, the amount of pyrrole extracted into the H-Nafion membrane was more than an order of magnitude higher and the formation of pyrrole derivatives¹⁵ was enhanced by an even larger factor. When the same experiment was performed in the presence of air, the absorbance due to polypyrrole in the membrane was another order of magnitude higher (>5).¹⁵ These results clearly confirm that the partitioning of pyrrole into H-Nafion is driven by

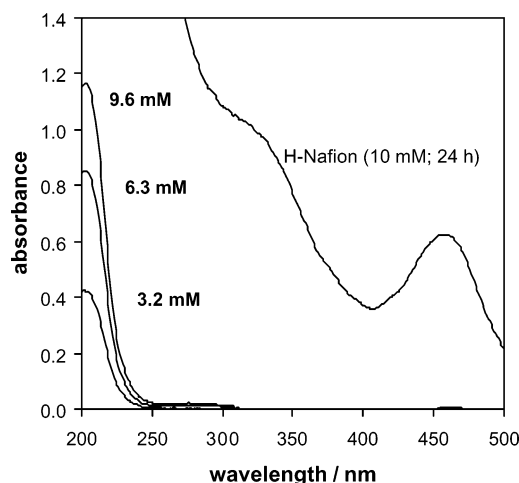


Figure 2. Electronic absorption spectra of Na-Nafion 115 membranes following 2 days of immersion in aqueous pyrrole at the indicated concentrations. Data for a H-Nafion membrane¹⁵ are also shown.

reactions promoted by its high acidity. The details of these reactions have been previously discussed.¹⁵

Similar partitioning experiments were performed with Me₄N-Nafion and Et₄N-Nafion using 10 mM pyrrole solutions. The results were similar to those reported above for Na-Nafion, with the films rapidly equilibrating with the solution in a simple partitioning process with no significant side reactions. However, the partition coefficients were slightly larger at 3.1 for Me₄N-Nafion and 4.0 for Et₄N-Nafion. These results suggest that hydrophobic interactions enhance the partitioning of pyrrole into Nafion and that it becomes concentrated in the interfacial regions of the membrane (between the fluorocarbon regions and water filled pores) when hydrophobic cations are present in these regions. It is possible, but unlikely, that the very small residual amount of H⁺ in these membranes is responsible for the higher partition coefficients.

Extraction of Pyrrole from Nafion Membranes. When pyrrole is partitioned into H-Nafion, much of it cannot be removed by washing with water and other solvents.¹⁵ This was attributed primarily to the formation of a protonated trimeric species. It was therefore of interest to determine whether pyrrole could be extracted from Na-Nafion membranes, which do not appear to promote the formation of the trimeric species

Figure 3 shows spectra of a pyrrole loaded Na-Nafion membrane (117 mg), the same membrane following immersion in water (5 mL) for 1 h, and a clean Nafion membrane. The lack of an absorbance peak at 206 nm indicates that all of the pyrrole was extracted from the membrane by the water, as would be expected based on the low partition coefficient (1.5). However, the light scattering of the washed membrane was somewhat higher than that of a clean Nafion membrane. This cannot be due to any residual conjugated materials (e.g., polypyrrole or pyrrole oligomers), since there are no absorption peaks due to such species. It may be due to structural changes in the membrane.

The pyrrole extracted from the film in Figure 3, and a second film extracted for 2 h, was also quantified from the spectrum of the extract. In each of these experiments the extraction was quantitative, within experimental error ($\pm 10\%$). The significance of these results, which appear to be quite mundane and predictable, is that they are in stark contrast to those obtained with H-Nafion,¹⁵ in which >50% of the pyrrole in the membrane remained after repetitive washing with water, methanol, acetonitrile, or toluene.

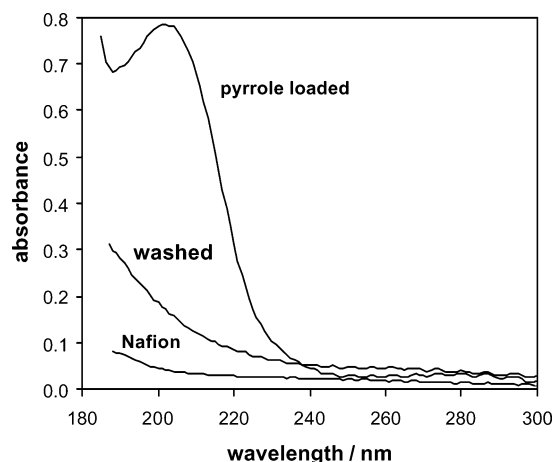


Figure 3. Electronic absorption spectra of a pyrrole-loaded (25 h in 10 mM pyrrole) Na-Nafion 115 membrane initially and following immersion in water (5 mL) for 1 h. A spectrum of an untreated Na-Nafion 115 membrane is also shown.

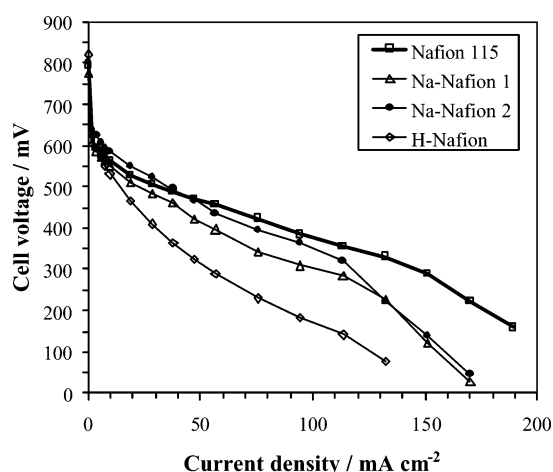


Figure 4. Polarization curves for 5 cm² active area DMFCs (60 °C, 1 M MeOH, 3.7 × air stoichiometry at 200 mA cm⁻²) with Nafion 115 and modified Nafion 115 membranes.

Evaluation of Polypyrrole/Nafion Composite Membranes in Direct Methanol Fuel Cells (DMFC). Polypyrrole/Nafion composite membranes were prepared using pyrrole-loaded Na-Nafion, and H-Nafion, with Fe(III) as the oxidizing agent for polymerization of the pyrrole. The conditions used for pyrrole loading are listed in Table 1, together with methanol crossover currents and cell resistances measured in a direct methanol fuel cell. Fuel cell performances are shown in Figure 4. Under the same conditions (1 h in 0.2 M pyrrole + 10 h in 0.08 M Fe³⁺), H-Nafion becomes much more heavily modified than Na-Nafion. This is reflected in its much lower methanol crossover (72% vs 13% decrease relative to unmodified Nafion) and much higher specific resistance (11 vs 1.4 times relative to unmodified Nafion).

In the DMFC, the benefits of the very low methanol crossover for the modified H-Nafion membrane are offset by the increased resistance and other factors, so that its performance is much worse than for unmodified Nafion. In contrast, the benefits of the small reduction in crossover with the Na-Nafion 1 modified membrane are seen at low current densities where it outperforms the unmodified membrane. The reason for the better performance of the unmodified membrane at high current densities is unclear, since the slightly lower resistance would only result in a 9 mV increase in cell voltage at 150 mA cm⁻². Increasing the concentration of the pyrrole solution used to modify

Na-Nafion (Na-Nafion 2 in Table 1) effectively further reduces methanol crossover, but leads to increased resistance and inferior DMFC performance (Figure 4).

Conclusions

The partitioning of pyrrole into neutral Nafion from water is very weak, indicating that there are not strong interactions between pyrrole and Nafion. The higher concentrations observed in the membrane relative to the contacting solution indicate a slight driving force for partitioning, and the effects of changing the Nafion counterion indicate that this is due to hydrophobicity. The pyrrole is therefore presumably concentrated in the interfacial regions between the PTFE network and water-filled pores. If pyrrole were solely in the aqueous phase of the pores, the partition coefficient would be only ca. 0.4, as observed for methanol.¹⁸ If it were in the PTFE network, a dependence on the counterion would not be expected.

These results support the assertion that the large apparent partition coefficients observed for H-Nafion¹⁵ are due to acid-driven reactions (protonation, coupling, and polymerization) of the pyrrole within the membrane. The facile extraction of pyrrole from neutral membranes confirms that the pyrrole-like species that cannot be extracted from H-Nafion¹⁵ is indeed a reaction product and not free pyrrole that is immobilized in some way. The assignment as a protonated tetrahydroterpyrrole¹⁵ appears to be justified.

The disappointing DMFC performances seen in this work with modified membranes appear to be due to poor bonding with the electrodes. As previously discussed,¹⁴ use of Fe³⁺ as the oxidizing agent leads to the deposition of polypyrrole on the surface of the membrane and this interferes with bonding of the electrodes. Bonding issues aside, the modification of neutral Nafion membranes with polypyrrole offers significant potential for improving DMFC performance. The use of nonacidic Nafion salts in the production of composite membranes will permit increased control of the initial pyrrole concentration in the membrane and the polymerization process and more effective removal of unreacted pyrrole and byproducts and will eliminate formation of the protonated pyrrole trimer.¹⁵ Each of these are factors that will aid the production of well-defined composite systems to enable the development of DMFC performance/composite structure relationships.

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