# Partitioning and Polymerization of Pyrrole into Perfluorosulfonic Acid (Nafion) Membranes

**Brandi L. Langsdorf, Brian J. MacLean, John E. Halfyard, Jeremy A. Hughes, and Peter G. Pickup***

*Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7 Canada*

*Received: August 26, 2002; In Final Form: December 3, 2002*

Details of Nafion/polypyrrole composite formation have been obtained using electronic absorption spectroscopy. Three distinct process—monomer loading, polymerization, and removal of unreacted monomer—have been studied. Pyrrole loading displays a square root dependence on time, indicative of a diffusion controlled partitioning process. Partitioning of pyrrole into Nafion, however, is complicated by protonation of pyrrole and acid-catalyzed oxidation to give oligomeric and polymeric species. These processes are affected by the presence of oxygen and are photosensitive. A variety of oxidizing agents have been used to effect polymerization including $Fe^{3+}$, $H_2O_2$, ammonium persulfate, and UV irradiation.

## Introduction

The polymerization of aromatic monomers within polymer membranes is an attractive method to produce hybrid materials or composites that take advantage of desirable properties of two widely different classes of polymer. For example, polypyrrole and polyaniline have been polymerized within poly(vinyl chloride)[1,2] and poly(vinyl alcohol)[3] membranes to produce flexible conducting materials and within cation exchange membranes to produce membranes whose ion exchange characterics can be controlled electrochemically.[4−6]

Recently, 1-methylpyrrole has been polymerized in situ in commercially available perfluorosulfonate membranes (Nafion) in order to produce proton exchange membrane (PEM) fuel cell electrolytes that are less permeable to methanol and other organic fuels.[7,8] The resulting poly(1-methylpyrrole) Nafion membrane composite displayed a 40% reduction in methanol crossover when evaluated as a proton exchange membrane for use in direct methanol fuel cells. In addition, the composite system displayed an increase in ionic resistance of less than 20%. The optimization of these preliminary results will be greatly aided by a more complete understanding of the factors that influence production of this type of composite material.

Perfluorosulfonate membranes are composed of perfluoroethylene chains with pendant sulfonate groups. The fluorinated backbone of the polymer imparts a high degree of chemical resistance and thermal stability making these materials attractive for a wide variety of industrial separation applications. The heterogeneity of the membranes is evident from the distinct regions of the polymer microstructure: (i) the hydrophillic anionic clusters, (ii) the hydrophobic terfluoroethylene backbone, and (iii) an interfacial region between the two.[9,10] The overall microstructure depends greatly on hydration level, with a fully hydrated material composed of ionic clusters consisting of ~70 anion exchange sites and 1000 water molecules, whereas in a completely dried perfluorosulfonate membrane, the ionic clusters are composed of only ~25 anionic sites. In the completely protonated form, the ionic clusters present an extremely acidic environment that has been exploited as "superacid" nano-reactors.[11]

Although the polymerization of an aromatic monomer, such as pyrrole, within ion-exchange membranes has been exploited in many studies and applications,[6] limited information is available concerning mechanistic details and the factors that influence the rate, extent, and location of the polymerization.[12] Previous studies have focused on the generation of composites with high conjugated polymer loadings, to produce systems with high electronic conductivity and electrochemical activity. In contrast, conjugated polymer|Nafion composites for use as PEMs in fuel cells should have relatively low conjugated polymer loadings (1−5% by mass), so that high proton conductivity is maintained and the cell is not shorted by electronic conduction through the membrane.[7]

In this paper, the steps that comprise the production of polypyrrole Nafion membrane composites with low polypyrrole loadings are examined in detail. The partitioning of pyrrole into Nafion from aqueous solutions, its spontaneous reactions within the Nafion structure, and its polymerization with added oxidizing agents have been followed by electronic absorption spectroscopy.

## Experimental Section

**Materials.** Nafion 115 (DuPont; donated by H Power Corp) was cleaned following a literature protocol.[13] Membranes were in the acid form for all experiments reported here. 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.

**Instrumentation.** Absorbance spectra were collected using a Varian Cary 5E spectrophotometer. Nafion membranes were supporting between two quartz disks during measurements.

**Partition Experiments.** In a typical partitioning experiment, Nafion 115 (ca. 100 mg) was immersed in 3.0 mL of aqueous pyrrole solution in a quartz cuvette. The change in concentration of the soaking solution was measured at regular time intervals with the film raised out of the beam. Between measurements, the film was submerged in the soaking solution and the cuvette was covered with a Teflon cap to prevent potential evaporation of pyrrole. The membrane was not rinsed at any time during these experiments.

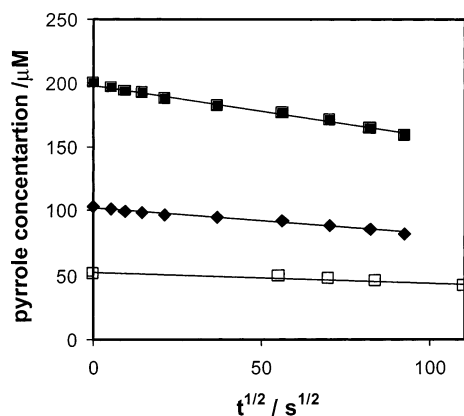* To whom correspondence should be addressed. E-mail: ppickup@mun.ca.

Partitioning and Polymerization of Pyrrole

*J. Phys. Chem. B, Vol. 107, No. 11, 2003* **2481**



**Figure 1.** Loading of pyrrole into Nafion 115 membranes plotted as the decrease in the concentration of pyrrole in the soaking solution as a function of time$^{1/2}$. Initial pyrrole concentrations were 200 (■), 100 (◆), 50 $\mu$M (□).

**Polymerization of Pyrrole in Nafion 115.** In a typical polymerization experiment, Nafion 115 (ca. 100 mg) was immersed in 20 mM pyrrole for 120 s. The initial loading of the film was then measured by absorption spectrometry and the loaded film was then immersed in the oxidizing medium. Its absorption spectrum was measured at various times following removal from the oxidizing medium and rinsing with water. In some cases, the film was returned to the oxidizing medium between measurements.

**Results**

**Partitioning of Pyrrole into Nafion Membranes.** The uptake of pyrrole into Nafion membranes was monitored by electronic absorption spectroscopy in various concentrations of aqueous pyrrole. Pieces of Nafion were immersed in aqueous pyrrole solutions, and the absorbance of the solution at $\lambda_{max}$ for pyrrole (206 nm) was monitored as a function of time. No oxidizing agent was used in these experiments, but air was not excluded unless specified.

Figure 1 shows representative results, plotted against the square root of time, for pyrrole concentrations ranging from 50 to 200 $\mu$M. The concentration of pyrrole was found to decrease linearly with $t^{1/2}$, as expected for a diffusion controlled process, and this decrease continued over the entire duration of these experiments. In separate experiments, the decrease in the pyrrole concentration in the solution was found to continue for at least 4 days. There is no indication that the uptake of pyrrole by the Nafion membranes approaches saturation over this time scale.

The uptake of pyrrole can also be monitored by observing changes in the absorption spectrum of the Nafion membrane as a function of time, as illustrated in Figure 2. Over relatively short time scales (<30 min), a single absorption at 206 nm with a lower energy shoulder is observed, and this can be attributed primarily to the pyrrole monomer in the film. Both the peak and shoulder increase in intensity with time in the pyrrole solution, with the shoulder becoming more pronounced and causing the peak to shift to slightly lower energy. New absorptions begin to appear at ca. 330 and 450 nm during the first 30 min, and these continue to grow over a period of days. The absorbance at ca. 450 nm is due to polypyrrole ($\lambda_{max} = 435$ nm)[14] formed in the membrane by air oxidation of pyrrole. The 15 nm red shift from the literature value can be attributed to partial protonation of the polypyrrole (see below) or possibly a solvent and/or environmental effect.

When the absorbance maximum at ca. 206 nm in the membrane is compared with the loss of pyrrole from the
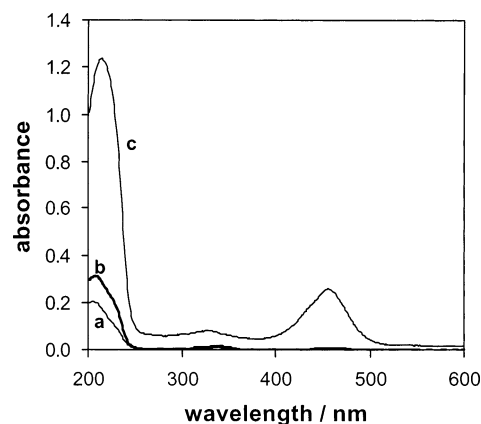


**Figure 2.** Electronic absorption spectra of Nafion 115 membranes (ca. 100 mg) following (a) 1, (b) 2, and (c) 22 h of immersion in 3 mL of an air saturated 0.93 mM aqueous pyrrole solution. A separate membrane and aliquot of solution was used for each experiment. Membranes were not rinsed before recording of their spectra.
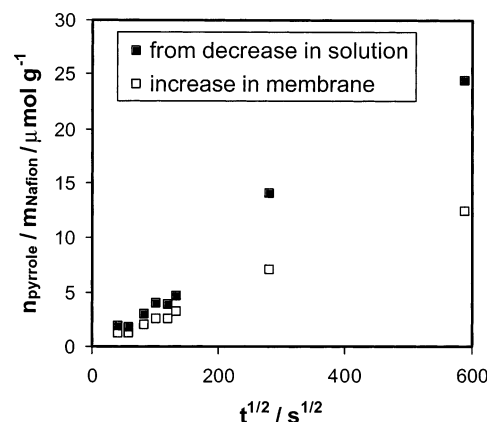


**Figure 3.** Moles of pyrrole per mass of Nafion 115 as a function of time$^{1/2}$ in a 0.93 mM pyrrole solution. (■) Calculated form the decrease in absorbance at 206 nm of the solution. (□) Calculated from the increase in absorbance at 206 nm of the membrane. Membranes were not rinsed before recording of their spectra.

solution, it is always lower than expected based on a simple partitioning model (i.e., that all of the pyrrole extracted from the solution is in the form of free pyrrole in the membrane). It will be assumed here that the absorbance maximum at 206 nm is due to free pyrrole in the membrane and that other absorbances are due to pyrrole in other forms (e.g., protonated pyrrole, oligomers, and polypyrrole).

Figure 3 shows both the loss of pyrrole from the solution and the amount estimated to be in the membrane from the absorbance at 206 nm (both normalized for the mass of membrane used) vs $t^{1/2}$ for a series of films that had been immersed in 1 mM pyrrole solutions for various times. The molar absorptivity of pyrrole has been assumed to be the same in the membrane as in the solution. The results shown in Figure 3 indicate that the amount of free pyrrole in the membrane is lower at all times than that extracted from the solution. The difference ranges from 30 to 50% for the data in Figure 3 and shows a significant increase with time. These observations are consistent with the spectra shown in Figure 2, which show that a portion of the pyrrole extracted into the membrane is converted to other forms with absorbances at ca. 220, 330, and 450 nm. The increasing amount of polypyrrole ($\lambda_{max} \sim 450$ nm) with time is primarily responsible for the decreasing proportion of extracted pyrrole that is observed as free pyrrole in the membrane.
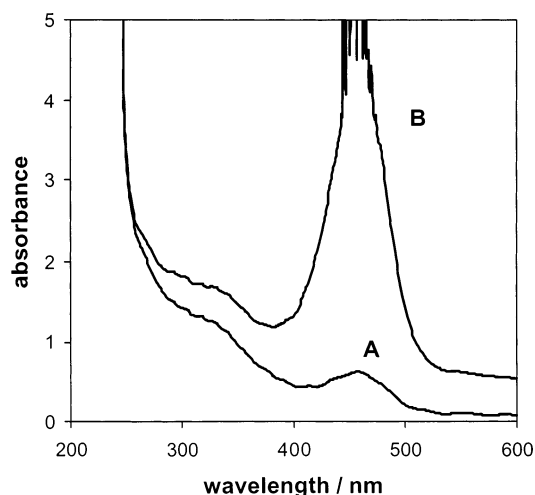
**Figure 4.** Electronic absorption spectra of Nafion 115 membranes following 24 h in 10 mM pyrrole in the absence (A) and presence (B) of air.
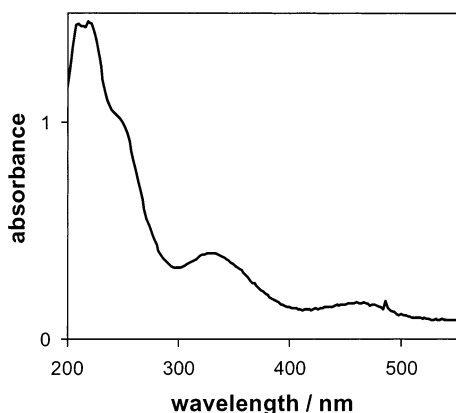


**Figure 5.** Electronic absorption spectrum of a Nafion 115 membrane following 19 h in 0.3 mM pyrrole in the absence of light.



**Figure 6.** Electronic absorption spectra of a pyrrole loaded (5 min in 20 mM pyrrole) Nafion 115 membrane initially (A), following immersion in water (5 mL) for 15 min (B), and following immersion in a second aliquot of water for 60 min (C).



**Figure 7.** Electronic absorption spectra of a pyrrole loaded (1 min in 20 mM pyrrole) Nafion 115 membrane following 0 (A), 5.7 (B), 25 (C), and 69 h (D) sandwiched between two quartz disks in air.

The assumption that the absorbance at 206 nm is solely due to free pyrrole is clearly only approximate, because the products of its reaction in the membrane will also have some absorbance at 206 nm. The amount of free pyrrole in the membrane indicated by the data in Figure 3 is therefore somewhat overestimated.

When the above partitioning experiments are performed in the absence of oxygen, to prevent polymerization of pyrrole in the membrane, the absorption peaks at 330 and 450 nm are still observed, although they are much smaller and do not increase with time after an initial period (Figure 4). We have not been able to exclude oxygen sufficiently (by purging with $N_2$) to completely prevent polymerization.

As well as being dependent upon the presence of oxygen, absorption spectra of pyrrole loaded Nafion membranes are also influenced by exposure to ambient light. No attempts were made to exclude light in the experiments represented by Figures 1-4, whereas the spectrum shown in Figure 5 was obtained for a film that had not been exposed to light during loading with pyrrole. An additional absorbance is observed at 250 nm in the spectrum of the film that was not exposed to light, and the absorbance peak at 330 nm is much larger relative to the monomer (206 nm) and polymer (450 nm) peaks.

**Extraction of Pyrrole from Nafion Membranes.** To further investigate the nature of the species formed when pyrrole partitions into Nafion, attempts were made to extract them together with unreacted pyrrole into a variety of solvents.
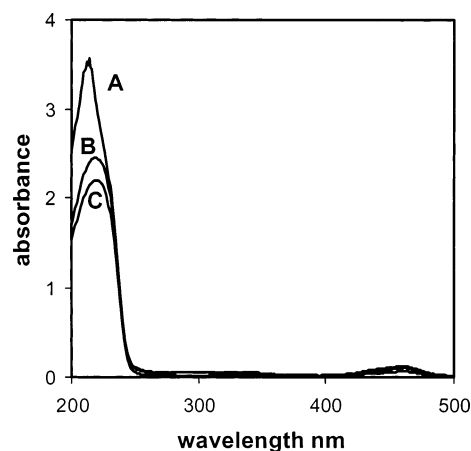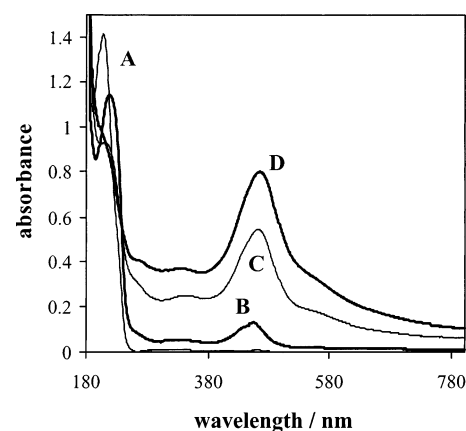
Washing of pyrrole loaded membranes with water resulted in an initial decrease in the absorbance at 206 nm by ca. 30%, but repetitive and extended washing failed to decrease the absorbance much further (Figure 6). Although washing decreases the absorbance maximum at 206 nm, it does not appear to influence the shoulder at ca. 220 nm, which becomes the main peak in washed membranes. Washing with methanol, acetonitrile, or toluene gave similar results, with 50−70% of the absorbance in the 220 nm region remaining after extended washing in each solvent.

**Polymerization of Pyrrole within Nafion Membranes.** Pyrrole partitioned into a Nafion membrane can be polymerized by a wide variety of oxidizing agents,[15] including oxygen in air as shown above. Figure 7 shows electronic absorption spectra of a pyrrole loaded membrane as a function of time spent in air. As the polypyrrole peak develops at ca. 460 nm, the monomer peak at ca. 206 nm decreases in intensity and shifts to slightly higher wavelength, before becoming a shoulder on a lower wavelength absorption that is below the range of the instrument used. Minor absorbance peaks or shoulders are observed at ca. 250, 320, and 550 nm as polypyrrole is formed in the membrane, and there is a broad envelope of absorption extending over the whole region of the spectrum.

More rapid pyrrole polymerization has been achieved by using $Fe^{3+}$, $(NH_4)_2S_2O_8$, or $H_2O_2$ as oxidizing agents or by using UV radiation (254 nm) to drive the polymerization in air. The evolution of the electronic absorption spectrum with $Fe^{3+}$ or
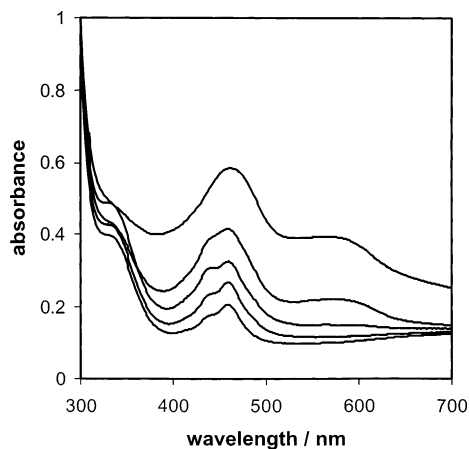
Partitioning and Polymerization of Pyrrole

*J. Phys. Chem. B, Vol. 107, No. 11, 2003* **2483**



**Figure 8.** Electronic absorption spectra of a pyrrole loaded (1 min in 20 mM pyrrole) Nafion 115 membrane following 5 min in 20 mM Fe(NO$_3$)$_3$(aq), and 0, 30, 90, 240, and 360 min sandwiched between two quartz disks in air. Absorbances above 400 nm increase with time.
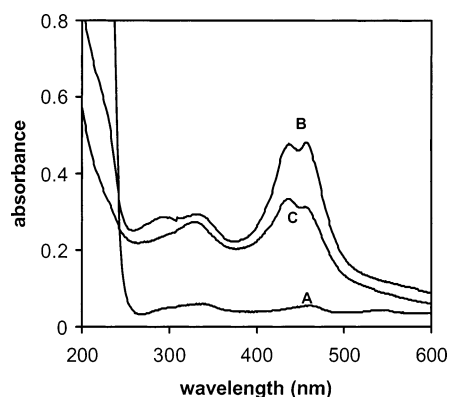


**Figure 9.** Electronic absorption spectra of a pyrrole loaded (2 min in 20 mM pyrrole) Nafion 115 membrane following 0 (A), 2 (B), and 8 h (C) in 20 mM ammonium persulfate in 1 M H$_2$SO$_4$(aq).

S$_2$O$_8$$^{2-}$ as the oxidant is shown in Figures 8 and 9, respectively. The spectra in Figure 8 are dominated by a strong Fe$^{3+}$ absorption at wavelengths below 350 nm, but this does not obscure the essential features of the developing polypyrrole sprectrum. Spectral changes with UV irradiation were very similar to those observed in air (Figure 7). Absorbances for polypyrrole at ca. 450−460 nm are plotted as a function of time in Figure 10. When S$_2$O$_8$$^{2-}$ (in 1 M H$_2$SO$_4$) or 30% H$_2$O$_2$ were used as oxidizing agents, the polypyrrole absorbance increased rapidly over the first hour and then began to decrease (e.g., Figure 9).

**Discussion**

Understanding and quantifying the partitioning of pyrrole into Nafion membranes is crucial to a proper understanding of the polymerization process and will lead to better control of the amount of polymer formed. This study of pyrrole polymerization in Nafion therefore began with an investigation of the partitioning of pyrrole into Nafion 115 membranes from dilute aqueous solutions. The partitioning process was monitored by UV absorption spectrometry of the monomer solution and/or the membrane.

Uptake of pyrrole by Nafion was found to follow a square root dependence on time, indicating that it is a diffusion controlled process. Diffusion of pyrrole into a Nafion membrane should therefore be described by Fick's laws. Under conditions where the decrease in pyrrole concentration in solution is small
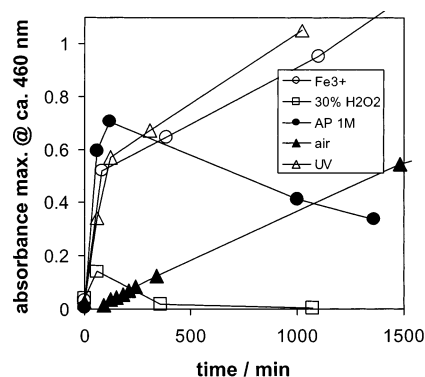


**Figure 10.** Absorbance at 460 nm (polypyrrole, $\pi-\pi^*$) as a function of time for pyrrole loaded Nafion 115 films immersed in 20 mM Fe(NO$_3$)$_3$ (aq) (○), 20 mM ammonium persulfate(aq) /1 M H$_2$SO$_4$ (●), 30% H$_2$O$_2$ (□), or air saturated water (▲), or exposed in air to 254 nm light (△).

(as for the data shown in Figure 1), the flux (mol cm$^{-2}$ s$^{-1}$) is given approximately by eq 1[16]

$$\text{flux} = D^{1/2}KC_s /\pi^{1/2}t^{1/2} \qquad (1)$$

$D$ is the diffusion coefficient of pyrrole in the membrane, $C_s$ is the concentration of pyrrole in the solution, and $K$ is the equilibrium constant for partitioning of pyrrole into the membrane. The change in concentration in the solution ($\Delta C_s$) is then given by eq 2

$$\Delta C_s V = 2AD^{1/2}KC_s t^{1/2}/\pi^{1/2} \qquad (2)$$

where $A$ is the surface area of the membrane (both sides) and $V$ is the volume of the solution. Use of this equation to estimate the diffusion coefficient of pyrrole in the membrane is complicated by the need to know the partition coefficient, $K$. The involvement of pyrrole in several different chemical reactions in the membrane (even in the absence of oxygen) makes it very difficult to even estimate $K$. However, based on the uptake of pyrrole at the longest times in Figure 1 ($\Delta C_s = 40$ $\mu$M for the 200 $\mu$M solution corresponds to a concentration of ca. 1.5 mM in the membrane) and the indication from the results in Figure 3 that approximately 50% of the pyrrole absorbed by the membrane remains as free pyrrole, $K$ would appear to be at least 4. The results shown in Figure 1 yield an average $DK^2$ value of 8.3 × 10$^{-7}$ cm$^2$ s$^{-1}$, which for $K > 4$ corresponds to a pyrrole diffusion coefficient in the membrane of <5 × 10$^{-8}$ cm$^2$ s$^{-1}$. This value is much lower than would be expected for diffusion of a small neutral molecule through the water filled pores of the membrane (the diffusion coefficient of methanol in Nafion is ca. 5 × 10$^{-6}$ cm$^2$ s$^{-1}$ at 30°C[17]). It suggests that the partition coefficient of pyrrole into the membrane may actually be closer to 1 and that pyrrole becomes concentrated in the membrane in various forms by reaction to from more strongly bound forms. Protonation, for example, would lead to enhanced partitioning and a low apparent diffusion coefficient.[16]

The nature of the species formed from pyrrole as it reacts within a Nafion membrane can be established from the positions of the peaks observed in the electronic absorption spectra shown in Figures 2 and 5. Protonation of pyrrole has been reported to produce a peak at $\lambda_{max} = 241$ nm in H$_2$SO$_4$(aq),[18] and this corresponds well to the shoulder observed at ca. 250 nm in Figure 5. The absence of this peak in spectra recorded for samples that had been exposed to light (e.g., Figure 2) suggests that light drives the reaction of protonated pyrrole to other products. The formation of 2,5-bis(2-pyrrolyl)-pyrrolidine (struc-

ture **1**) has been shown to occur in 20% hydrochloric acid[19] and therefore would be expected to occur within the highly acidic pores in Nafion. Compound **1** has a reported $\lambda_{max}$ of 219 nm, and this would appear to be a reasonable assignment for the shoulder observed in this region for pyrrole in Nafion (Figures 2 and 5). The results in Figure 6 show that this species cannot be removed from the membrane by washing.



**1**
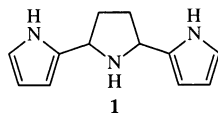
The fully conjugated pyrrole oligomers, 2,2′-bipyrrole, 2,2′,5′,2″-terpyrrole, and pentapyrrole, have $\lambda_{max}$ values (in $CH_3$-CN) of 276, 317, and 367 nm, respectively.[14] By extrapolation (assuming that $\lambda_{max} \propto$ number of rings),[14] $\lambda_{max}$ for quaterpyrrole should be 342 nm. On the basis of the spectra in Figures 2 and 5, none of these species appear to be present in the membranes in detectable concentrations. However, the absorbance seen at ca. 330 nm may be due to protonated terpyrrole.

The spectral changes accompanying polymerization of pyrrole in the membrane are similar for all oxidants (Figures 7−9), and are dominated by the growth of the polymer peak at ca. 460 nm. This peak exhibits a high energy shoulder at ca. 435 nm during the polymerization, and this could be due to segments of polymer that are not protonated. All spectra also show a small peak or shoulder at 330 nm due presumably to terpyrrole (probably protonated), which is one of the major expected intermediates in the polymerization. Substantial absorbance is also seen at higher wavelengths than the main polymer peak, either as a shoulder at ca. 550 nm for polymerization with air or $S_2O_8^{2-}$ or as a peak at ca. 570 nm for polymerization with $Fe^{3+}$. This can be attributed to partial oxidative doping of the polypyrrole.[14, 20]

From Figure 10, it can be seen that $S_2O_8^{2-}$ produces the most rapid polymerization of pyrrole in the Nafion membrane. However, under the conditions employed, it causes degradation of the polypyrrole before complete polymerization is achieved. The decay of the polypyrrole absorbance at long times is presumably a result of its overoxidation.[21] $Fe^{3+}$ and UV irradiation both produce rapid polymerization (given the need for diffusion of the oxidant into the membrane) without degradation of the resulting polypyrrole. The UV method is particularly attractive because it does not contaminate the membrane. Use of $Fe^{3+}$ leaves high concentrations of $Fe^{3+/2+}$ in the membrane, requiring washing with acid for removal. $H_2O_2$ is also effective for polymerization of pyrrole in Nafion over short time scales but, upon longer treatments, leads to rapid degradation of the polypyrrole.

## Conclusions

The multifaceted behavior of pyrrole in Nafion membranes arises as a direct consequence of the extremely acidic nature of the perfluorsulfonate polymer resulting in the production of protonated, oligomeric, and polymeric products. Although the continued uptake of pyrrole into the membrane is greatly influenced by the acidity of the ionic clusters, the overall contribution to the composite material of these small molecule species is negligible under the dilute conditions investigated here.

The surprising complexity of the partitioning of pyrrole into Nafion from aqueous solutions, resulting from its spontaneous reactions within the Nafion structure, makes it difficult to control the formation of polypyrrole/Nafion composites. In other work,[22] we have found that the water content and history of the membrane can greatly influence the course of composite formation and the properties of the resulting membrane and that variation of process parameters can have unpredictable effects. The origin of these complications is now clear, and steps can be taken to improve process control. One step that is proving to be effective is the use of nonacidic Nafion membranes, which take-up pyrrole in a simple diffusion controlled partitioning process.[23]

**References and Notes**

(1) Niwa, O.; Tamamura, T. *Chem. Commun.* **1984**, 817.
(2) De Paoli, M.-A.; Waltman, R. J.; Diaz, A. F.; Bargon, J. *Chem. Commun.* **1984**, 1015.
(3) Chen, S.-A.; Fang, W.-G. *Macromolecules* **1991**, *24*, 1242.
(4) Iyoda, T.; Ohtani, A.; Shimidzu, T.; Honda, K. *Chem. Lett.* **1986**, 687.
(5) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Electroanal. Chem.* **1987**, *224*, 123.
(6) Pickup, P. G. In *Handbook of Advanced Functional Molecules and Polymers*; Nalwa, H. S., Ed.; Gordon and Breach: Amsterdam, 2001; Vol. 3, pp 155−175.
(7) Jia, N.; Lefebvre, M. C.; Halfyard, J.; Qi, Z.; Pickup, P. G. *Electrochem. Solid. State. Lett.* **2000**, *3*, 529.
(8) Pickup, P. G.; Qi, Z. Canadian Patent Application No. 2,310,310, PCT/CA 01/00767, 2000.
(9) Gierke, T. D.; Hsu, W. S. In *Perfluorinated Ionomer Membranes. ACS Symp. Ser. 180*; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, DC, 1982.
(10) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.
(11) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S. *Synthesis* **1986**, 513.
(12) Sata, T.; Funakoshi, T.; Akai, K. *Macromolecules* **1996**, *29*, 4029.
(13) Ren, X.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **2000**, *147*, 92.
(14) Zotti, G.; Martina, S.; Wegner, G.; Schluter, A. D. *Adv. Mater.* **1992**, *4*, 798.
(15) Jia, N. M. Sc. Dissertation, Memorial University of Newfoundland, St. John's, Nwefoundland, Canada, 1999.
(16) Mohan, H.; Iyer, R. M. *J. Chem. Soc., Faraday. Trans.* **1992**, *88*, 41.
(17) Ren, X. M.; Springer, T. E.; Zawodzinski, T. A.; Gottesfeld, S. *J. Electrochem. Soc.* **2000**, *147*, 466.
(18) Chiang, Y.; Whipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763.
(19) Potts, H. A.; Smith, G. F. *J. Chem. Soc. (C)* **1957**, 4018.
(20) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(21) Pud, A. A. *Synthet. Metal.* **1994**, *66*, 1.
(22) Halfyard, J. E.; Pickup, P. G. Unpublished work, 2000.
(23) Langsdorf, B. L.; Pickup, P. G. Manuscript in preparation.