Characterization of a Cation-Exchange/Polyaniline Composite Membrane

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A composite membrane was prepared by chemical polymerization of a thin layer of polyaniline (PANI) in the presence of high oxidant concentration on a single face of a sulfonated cation-exchange membrane (Neosepta CMX from Tokuyama Soda Inc.). The CMX−PANI composite membrane was characterized as a function of the polymerization time by cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), and ion-exchange capacity (IEC) measurements. CV and XPS results demonstrate that, under our experimental conditions, the maximum PANI loading is attained after 1 h of polymerization. This is accompanied by a decrease in membrane ion-exchange capacity due to the presence of the cationic PANI acting as counterions for the sulfonate groups of the membrane. The optimal membrane permselectivity for protons against bivalent metallic cations (Zn^{2+} and Cu^{2+}) was also found at a polymerization time of 1 h. In fact, at longer polymerization times, XPS data indicate the occurrence of PANI degradation. UV− visible spectroscopy confirmed the presence of benzoquinone, the major degradation product of PANI, in the solution used for the oxidation of aniline into polyaniline. Correlating XPS and IEC results with permselectivity of the composite membrane let us believe that although some small amount of PANI is still present at the surface and within the membrane, it is not sufficient to maintain good permselectivity properties. To create an effective blocking barrier to the bivalent cations, the PANI layer formed at the surface of the CMX membrane needs to be sufficiently thick and uniform.

Introduction

Polyaniline (PANI) is a technologically important material due to its unique electrical, electrochemical, and optical properties which enable its use in energy storage systems,[1] electrochromic devices,[2] electronics,[3] electrochemical actuators,[4] sensors,[5] and separation science.[6,7] In the latter case, PANI was used as free-standing membranes, supported films, and surface layers for applications ranging from gas separation and pervaporation to electrodialysis.[8]

Interestingly, PANI separation properties can be tailored by the nature of the dopant as well as by the doping level of the polymer.[8] Typically, an undoped film is more permeable to gases than a doped film since undoping, which involves the removal of the dopant, leads to void space in the polymer. It was also reported that PANI can separate mixtures of liquids (pervaporation) owing to the hydrophobic and hydrophilic character of the undoped and doped films, respectively.[8] With PANI, separation is possible based on the size of the molecules, molecules larger than 4.5 Å being prevented from permeating.

In electrodialysis processes, the presence of a polyaniline layer at the surface of commercial sulfonated cation-exchange membranes (Neosepta) led to improved selectivity for specific ion transport.[6,7] The permselectivity of this composite membrane (Neosepta CM-1−PANI) for Na^+ in the presence of Ca^{2+} ions for electrodialysis in neutral solutions was reported by Sata et al.[6] We have recently demonstrated that the Zn^{2+} and Cu^{2+} leakage is reduced by a factor of at least 20 for electrodialysis with a PANI-modified CMX membrane relative to a bare Neosepta CMX membrane.[7] The results also showed that the time the H^+ ions within the membrane are allowed to exchange with the anilinium species in a 10% (v/v) aniline + 1 M HCl solution, prior to polymerization, does not have a significant effect on the metal leakage as well as on the ion-exchange capacity above 1 h.

Despite that permselectivity has been demonstrated for several divalent cations versus monovalent species for PANI-modified CMX membrane, very little is known of the composition of the PANI film that is present at the membrane surface or within the membrane when a high oxidant concentration is used for the chemical polymerization of PANI. This study will specifically address this point as the effect of polymerization time will be investigated. An extensive characterization of the CMX−PANI membrane by X-ray photoelectron spectroscopy, cyclic voltammetry, and ion-exchange capacity measurements is described below. In addition, UV−visible spectra of the oxidant solution, placed in contact with the sulfonated membrane loaded with anilinium cations, were also monitored to look for the presence of reaction intermediates that might diffuse out of the membrane.

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(1) (a) Novak, P.; Muller, K.; Santhanam, K. S. V.; Hass, O. *Chem. Rev.* **1997,** *97,* 207. (b) Naudin, E.; Gouérec, P.; Bélanger, D. *J. Electroanal. Chem.* **1998,** *459,* 1. (c) Bélanger, D.; Davey, J.; F. Uribe, F.; Gottesfeld, S. *J. Electrochem. Soc.* **2000,** *147,* 2923. (d) Fusalba, F.; Gouérec, P.; Villers, D.; Bélanger, D. *J. Electrochem. Soc.* **2001,** *148,* A1.

(2) Leventis, N.; Chung, Y. C. *J. Electrochem. Soc.* **1990,** *137,* 3321.

(3) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992,** *357,* 477.

(4) Wang, H.-L.; Gao, J.; Sansinena, J.-M.; McCarthy, P. *Chem. Mater.* **2002,** *14,* 2546.

(5) (a) Bartlett, P. N.; Birkin, P. R.; Wallace, E. N. K. *J. Chem. Soc., Faraday Trans.* **1997,** *93,* 1951. (b) Bélanger, D.; Nadreau, J.; Fortier, G. *J. Electroanal. Chem.* **1989,** *274,* 143.

(6) Sata, T.; Ishii, Y.; Kawamura, K.; Matsusaki, K. *J. Electrochem. Soc.* **1999,** *146,* 585.

(7) Tan, S.; Viau, V.; Cugnod, D.; Bélanger, D. *Electrochem. Solid-State Lett.* **2002,** *5,* E55−E58.

(8) Conklin, J. A.; Su, T. M.; Huang, S.-C.; Kaner, R. B. In *Handbook of Conducting Polymers,* 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, Jr., Eds.; Dekker: New York, 1998; Chapter 33, p 945 and references therein.

Experimental Section

Chemicals. $(NH_4)_2S_2O_8$ (EM Science), HCl (EM Science), HNO_3 (EM Science), NaCl (BDH), H_2SO_4 (EM Science), $ZnSO_4 \cdot 7H_2O$ (Anachemia), and $CuSO_4 \cdot 5H_2O$ (Anachemia) were of ACS reagent grade and used as received. Aniline (Aldrich) was distilled twice prior to use. Millipore water (18 MΩ) was used for the preparation of all solutions.

Modification of Cation-Exchange Membranes. The Neosepta CMX (Tokuyama Soda) membranes were stored in 0.5 M NaCl and conditioned in 1 M HCl for more than 24 h before modification. The protocol used for the preparation of CMX–PANI composite membranes is based on a published procedure.[6] The single face modification was carried out in a two-compartment cell made of Teflon containing 40 mL of reagents in one compartment and 40 mL of water in the other (surface modified: 9.6 cm^2). The first step consisted in exchanging the protons, initially present in the CMX membrane, with anilinium species using a 10% (v/v) aniline in 1 M HCl solution added in the reagent compartment while stirring for 1 h at room temperature. In the second step, the polymerization was induced by replacing the aniline solution with a 1 M $(NH_4)_2S_2O_8$ aqueous solution and stirring for various times at room temperature. The cell was rinsed with water between both steps. Before use, the composite membranes were conditioned in a 1 M HCl aqueous solution for 40 h or longer to ensure complete protonation of PANI. The modified membranes were identified as followed: PX-Y; P for PANI, X for the time (hours) of immersion in the 10% (v/v) aniline solution (1 h in most cases), and Y for the time (hours) of polymerization. It should be noted that the polymerization time is in fact the time for which the membrane is in contact with the oxidant and could also imply other side reactions such as degradation.

Electrodialysis (ED). Electrodialyses were performed in a two-compartment cell containing in the anodic compartment 150 mL of 15 000 ppm Zn or Cu in 0.5 M H_2SO_4 and in the cathodic compartment, 33 mL of 0.5 M H_2SO_4. The modified surface (surface: 5.1 cm^2) was placed facing the anolyte. A current density of 100 mA/cm^2 was applied between two platinum plates during 3 h using an M273 potentiostat/galvanostat (EG & G Princeton Applied Research). The metal concentration in both compartments was determined by atomic absorption spectroscopy (Instrumentation Laboratory AA/AE spectrophotometer Model 257).

Cyclic Voltammetry (CV). Prior to the preparation of electrodes, the CMX–PANI membranes were conditioned for at least 1 week in 0.5 M H_2SO_4. Samples of 16 mm^2 were then cut, slightly dried with a tissue, and pressed into stainless steel grids at 10 tons/cm^2 during 10 s. CV scans were carried out in a 0.5 M H_2SO_4 aqueous solution with a Solartron 1470 multipotentiostat using a three-electrode configuration at a scan rate of 50 mV/s between -0.1 and 0.8 V. The reference electrode was Ag/AgCl (saturated NaCl), and the counter electrode was a platinum grid. All potential values are reported versus Ag/AgCl.

X-ray Photoelectron Spectroscopy (XPS). After being conditioned in 1 M HCl, samples were rinsed with water and dried under vacuum at room temperature for 36 h in the presence of P_2O_5. XPS analyses were performed using a VG Escalab 220i-XL system equipped with a hemispherical analyzer and an Al anode (Kα X-rays at 1486.6 eV) used at 10 kV and 15 mA. The data were recorded at room temperature and at a pressure below 10^{-8} Torr. To compensate for charging effects, binding energies were corrected for covalent Cl $2p_{3/2}$ at 200.6 eV after deconvolution. Curve fitting for Cl 2p and S 2p, as well as peak integration, were carried out using Origin software (version 6.0). After a Shirley background correction, the Cl 2p and S 2p peaks were deconvoluted by assuming a Gaussian line shape. The full width at half-maximum (fwhm) was fixed as constant and the peak area ratio fixed at 1:2 for each pair of Cl $2p_{1/2}$–Cl $2p_{3/2}$ and S $2p_{1/2}$–S $2p_{3/2}$ peaks. In the case of chlorine, the peak separation between Cl $2p_{1/2}$ and Cl $2p_{3/2}$ was allowed to vary within (1.6 $\pm$ 0.1) eV. The elementary analysis was done using the appropriate sensitivity factors: C 1s (1.00), N 1s (1.80), O 1s (2.93), Cl $2p_{1/2}$ (0.775), Cl $2p_{3/2}$ (1.51), S $2p_{1/2}$ (0.567), and S $2p_{3/2}$ (1.11).

Scanning-Electron Microscopy (SEM). Samples were dried under vacuum overnight at room temperature in the presence
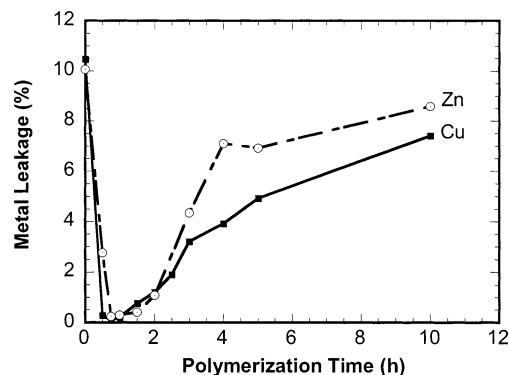
Figure 1. Percentage of zinc and copper leakage after electrodialysis of a 15 000 ppm Zn^{2+} or Cu^{2+} in 0.5 M H_2SO_4 solution with unmodified and CMX–PANI composite membranes as a function of polymerization time. $t = 0$ corresponds to the unmodified membrane. It should be noted that the polymerization time is in fact the time for which the membrane is in contact with the oxidant and could also imply other side reactions such as degradation.

of P_2O_5. Surface micrographs were taken using a Hitachi Model S-2300 scanning electron microscope.

UV–Visible Spectroscopy. An HP 8452A diode array spectrophotometer was used to analyze the 1 M $(NH_4)_2S_2O_8$ solution obtained after various polymerization times. Single scans were recorded between 190 and 820 nm. Water was used as a blank. Samples were diluted 250 times in water.

Ion-Exchange Capacity (IEC). All membranes were washed and stabilized several times in 1 M HCl, H_2O, and 1 M NaCl alternatively for 1 h in each solution during three cycles. The membranes were then soaked for 24 h in a 1 M NaCl solution to ion exchange H$^+$ with Na$^+$. After removing excess sodium chloride (by immersion in water for 30 min and rinsing with water), the membranes were dried for 1 h at 65 °C in order to measure their weight in the Na$^+$ form. The Na$^+$ ions were ion exchanged with H$^+$ by immersion in a 1 M HCl solution during 24 h. The sodium concentration in the latter solution was determined by atomic emission spectroscopy (Instrumentation Laboratory AA/AE spectrophotometer Model 257).

Results

Electrodialysis–Metal Leakage vs Polymerization Time. Figure 1 illustrates how the percent metal leakage of Zn and Cu changes with polymerization time after electrodialysis. The metal leakage found for the bare CMX membrane is given at time zero (10.1 and 10.5% for Zn^{2+} and Cu^{2+}, respectively). As PANI formation takes place, the permselectivity for bivalent cations decreases to reach a minimum value (about 0.3% for Zn and 0.2% for Cu) after approximately 45–60 min of polymerization. Above 1 h of polymerization, the percent metal leakage increases to values reaching 8% for 10 h of polymerization.

Cyclic Voltammetry. Figure 2a contrasts the cyclic voltammograms obtained in 0.5 M H_2SO_4 for bare and modified CMX membranes as a function of the polymerization time. As expected, the bare CMX ion-exchange membrane cyclic voltammogram is featureless. As PANI is formed at the surface of the membrane, oxidation peaks are detected. Hence, after 20 min of polymerization, which is the minimal time at which a PANI layer is visible on the membrane, two oxidation peaks are detected. The peak at 0.3 V represents the first oxidative doping peak of PANI. The second peak located at 0.6 V can be attributed to the hydroquinone/benzoquinone (HQ/BQ) redox couple.[9–12] On the reverse scan, the corresponding reduction peaks can

(9) Stilwell, D. E.; Park, S.-M. *J. Electrochem. Soc.* **1988**, *135*, 2254.
(10) Stilwell, D. E.; Park, S.-M. *J. Electrochem. Soc.* **1988**, *135*, 2497.
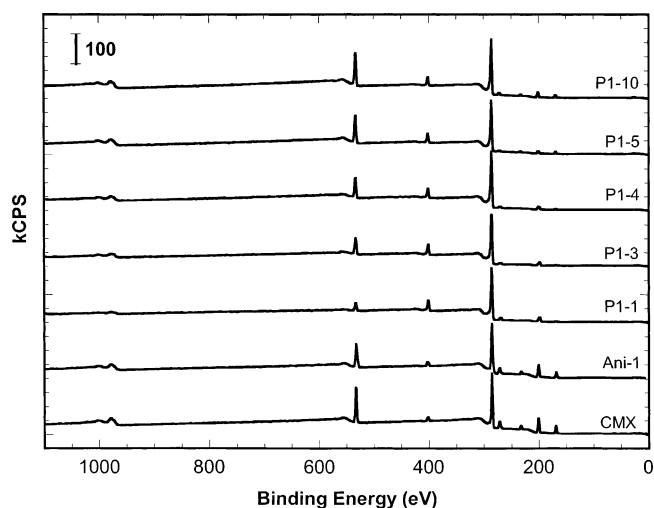(11) Büttner, E.; Holze, R. *J. Electroanal. Chem.* **2001**, *508*, 150.
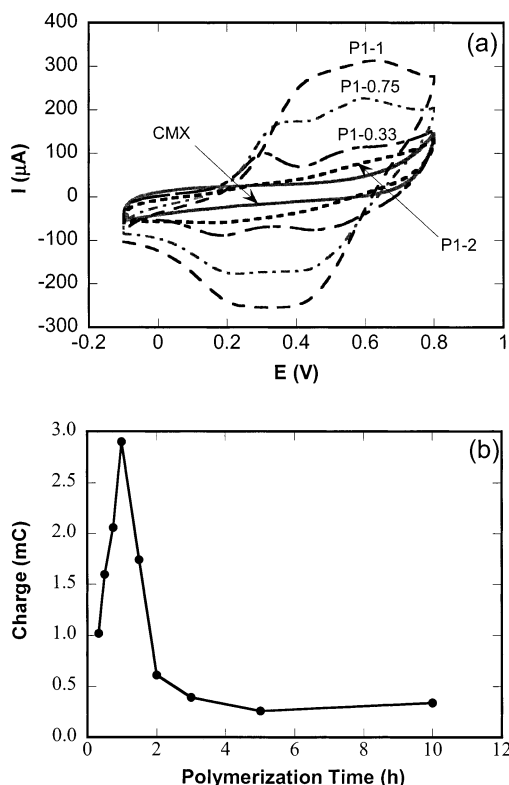
Figure 2. (a) Cyclic voltammograms in 0.5 M H_2SO_4 at 50 mV/s of CMX and CMX−PANI membranes prepared with different polymerization times. Time of immersion in 10% (v/v) aniline/1 M HCl solution was 1 h. (b) Corresponding charges integrated from the oxidation peaks as a function of polymerization time.

Figure 3. XPS survey spectra of the unmodified CMX, Ani-1 (membrane ion-exchanged with anilinium ions for 1 h using a 10% (v/v) aniline in 1 M HCl solution), and CMX−PANI membranes prepared with different polymerization times.

be observed at 0.18 and 0.45 V. When increasing the polymerization time up to 1 h, both PANI and HQ/BQ peak intensity are enhanced and the PANI oxidation peak is shifted to a more positive potential, indicating an increase in resistivity. Also, the peaks tend to merge and are more difficult to distinguish. Over 1 h of polymerization, the signal of both redox couples nearly disappears. Figure 2b represents the relative Coulombic charge calculated from the cyclic voltammograms. It can be observed that the electroactivity of PANI increases from 20 min to 1 h of polymerization, after which the doping charge decreases significantly.

X-ray Photoelectron Spectroscopy. Survey Spectra. XPS has been extensively used to study the different oxidation states of PANI.[13−15] Figure 3 illustrates the XPS survey spectra for the unmodified membrane (CMX), the membrane exchanged with anilinium ions (Ani-1), and the composite CMX−PANI membranes prepared at various polymerization times. The bare CMX membrane spectrum exhibits peaks at 978 eV (O(KL$_{2,3}$L$_{2,3}$) Auger peak), 531 eV (O 1s), 228 eV (S 2s), and 169 eV (S 2p) characteristic of the sulfonate (SO_3^-) groups; 271 eV (Cl 2s) and 200 eV (Cl 2p) were attributed to the poly(vinyl chloride) support. A small N 1s peak is also detected at 400 eV on the unmodified CMX membrane due to the

presence of nitrogen-based compounds used for the fabrication of CMX membranes.[16]

After anilinium ions are incorporated within the membrane by an ion-exchange process with the protons, very little variation in peak intensity is observed for the different elements. The formation of PANI on the membrane is confirmed by the significant changes observed in the survey spectra. For instance, the peaks associated with the sulfonate groups as well as with PVC have a reduced signal whereas the nitrogen peak appears to be more intense. As the polymerization time is increased, the relative signal intensities of all elements of interest fluctuate significantly, particularly when comparing the samples polymerized at 1 and 10 h.

Core Level Spectra. The Cl 2p, S 2p, and N 1s core level spectra are described below. Table 1 gives the elemental composition and the relevant ratio values determined with the core level spectra. The evolution of these atomic concentrations will be discussed below.

Cl 2p. The Cl 2p spectra for the CMX and CMX−PANI membranes are depicted in Figure 4. The doublet observed on the CMX spectra corresponds to the Cl 2p$_{3/2}$ (200.6 eV) and Cl 2p$_{1/2}$ of PVC.[17] Once a PANI layer is formed, the gradual decrease of the PVC doublet is first observed and replaced by a peak envelope that was deconvoluted in two doublets at 197.8 and 199.4 eV (Cl 2p$_{3/2}$) attributed to ionic chloride dopants.[18] Then, the process is reversed and the well-defined PVC peaks slowly reappear. The covalent and ionic chlorine contents are presented in Table 1. It should be noted here that, in order to separate the contributions of each type of chlorine, the spectra were deconvoluted into three doublets (one for PVC and two for PANI) (Supporting Information, Figure 1S).

S 2p. The large peak observed at 169 eV (Figure 5) on the CMX membrane is characteristic of the sulfonate groups.[17,19,20] When deconvoluted, the peak can be separated into a doublet for which the peak centers are found at 168.9 and 170.1 eV corresponding to the 2p$_{3/2}$ and 2p$_{1/2}$

(12) Trivedi, D. C. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2, Chapter 12, p 505 and references therein.

(13) (a) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci.* **1993**, *106*, 135. (b) Neoh, K. G.; Kang, E. T.; Tan, K. L. *J. Phys. Chem. B* **1997**, *101*, 726.

(14) Snauwaert, P.; Lazzaroni, R.; Riga, J.; Verbist, J. J.; Gonbeau, D. *J. Chem. Phys.* **1990**, *92*, 2187.

(15) Monkman, A. P.; Stevens, G. C.; Bloor, D. *J. Phys. D.: Appl. Phys.* **1991**, *24*, 738.

(16) Mizutani, Y.; Tesima, W.; Akiyama, S.; Yamane, R.; Ihara, H. United States Patent 3,451,951, 1969.

(17) Beamson, G.; Briggs, D. In *High-Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*; John Wiley & Sons: New York, 1992; pp 240−241 and 266−267.

(18) (a) Tan, K. L.; Tan, B. T. G.; Kang, E. T.; Neoh, K. G. *Phys. Rev. B* **1989**, *39*, 8070. (b) Neoh, K. G.; Kang, E. T.; Tan, K. L. *J. Phys. Chem.* **1991**, *95*, 10151.

Table 1. Elemental Composition of Unmodified CMX, CMX Ion Exchanged with Anilinium Species, and CMX−PANI Composite Membranes Determined by XPS

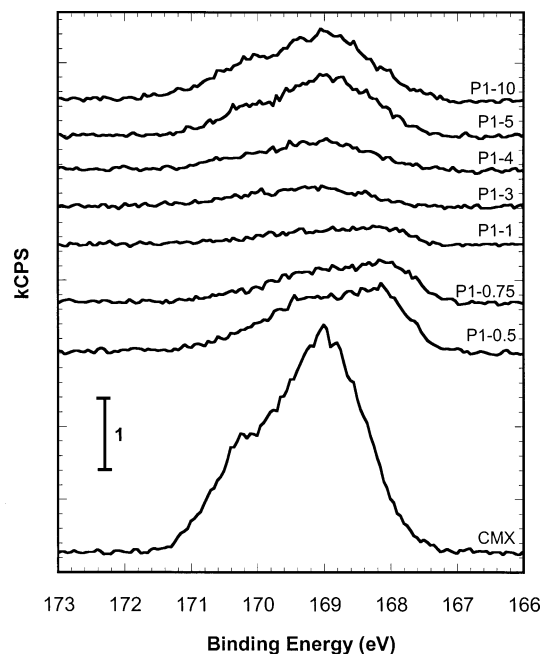|	CMX	Ani-1	P1-0.5	P1-0.75	P1-1	P1-3	P1-4	P1-5	P1-10
element (%)									
Cl (PVC)	8.8	6.6	1.8	0.92	0.47	0.59	0.87	1.4	2.6
Cl (ionic)[a]	0	0	1.6	2.2	3.4	2.1	1.6	0.44	0.45
C 1s	62.9	69.0	78.0	79.1	81.7	76.9	77.8	71.8	70.4
O 1s	18.7	15.3	9.1	7.7	5.0	11.8	10.9	17.0	18.2
N 1s (total)	3.9	4.5	7.4	8.6	8.8	8.0	8.0	7.6	6.4
N 1s (PANI)[b]	0.00	1.3	5.9	7.6	8.4	7.5	7.3	6.4	5.0
S 2p	5.7	4.6	2.1	1.5	0.63	0.66	0.91	1.8	2.0
ratio									
Cl$^-$/N[c]		0	0.27	0.29	0.40	0.28	0.22	0.07	0.09
N/S[c]	0	0.29	2.81	5.02	13.30	11.36	8.02	3.64	2.57

[a] PVC contribution removed and both ionic doublet included (Cl $2p_{3/2}$ centered at 197.8 and 199.4 eV). [b] Nitrogen contribution from CMX removed. The value removed was calculated based on the proportion of S 2p detected for the sample against the value detected for the bare membrane: $\%N(CMX)_{sample} = (\%S_{sample}/\%S_{CMX}) \times \%N(total)_{sample}$. [c] Nitrogen from PANI only.
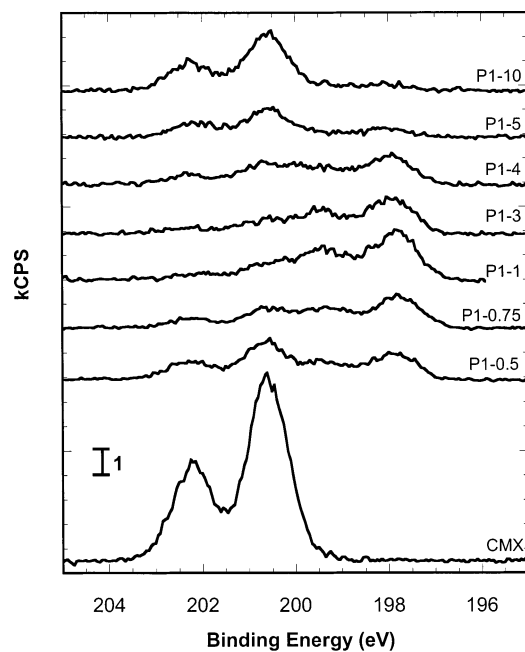
Figure 4. Cl 2p core level spectra of unmodified CMX and CMX−PANI membranes prepared with different polymerization times.

Figure 5. S 2p core level spectra of unmodified CMX and CMX−PANI membranes prepared with different polymerization times.

contributions (Supporting Information, Figure 2S). Figure 5 and Table 1 demonstrate that the S 2p peak intensity variation follows the same trend as for the covalent chlorine. Upon polymerization, the characteristic groups associated with the unmodified membrane, sulfonate in this case, are hidden, and as polymerization time is increased, there is a reappearance of this latter group.

N 1s. The N 1s spectra for the different membranes are represented in Figure 6. As specified above, unmodified CMX reveals the presence of nitrogen compounds. After membrane modification, a more intense peak appears at a lower binding energy (400 eV), and as the polymerization time is increased, the peak maximum is displaced toward higher binding energy. For the membranes prepared at longer polymerization times, the spectra resemble that of the bare CMX membrane.

Ion-Exchange Capacity (IEC). To determine the variation in the amount of amine/imine groups compensated by sulfonate groups, ion-exchange capacity measurements were performed with the CMX and CMX−PANI

(19) Wei, X.-L.; Fahlman, M.; Epstein, A. J. *Macromolecules* **1999**, *32*, 3114.

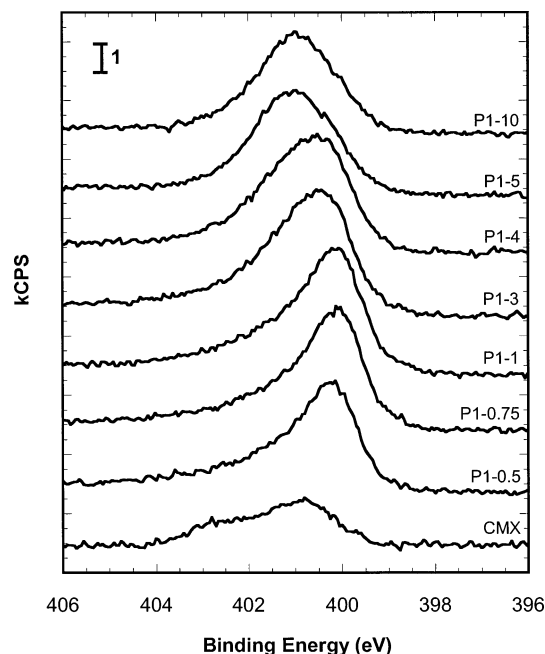(20) Goh, S. H.; Lee, S. Y.; Zhou, X.; Tan, K. L. *Macromolecules* **1998**, *31*, 4260.

membranes prepared at various polymerization times (Figure 7). An IEC value of 1.48 meq/g dry membrane was obtained for the unmodified CMX membrane. This value indicates that the sulfonate groups constitute 5 wt % of the membrane, whereas a value of 12% is calculated from the XPS spectra (see Table 1). Since XPS is a surface technique and IEC measurements involve the whole membrane, the 2-fold difference is an evidence that a higher sulfonate concentration is found on the surface than within the bulk of the membrane. The IEC values decrease with polymerization time. This is to be contrasted with the evolution of the metal leakage which shows a minimum at a polymerization time of about 1 h.

Discussion

The chemical composition of the surface of the membrane is clearly changing as the polymerization time increases. One consequence of the change is that a minimum metal cation leakage is obtained after 45−60 min of polymerization. With a polymerization time shorter than 1 h, the decrease in metal leakage would presumably be explained by the need to achieve a sufficiently high and homogeneous PANI content before the adsorbed layer becomes efficient in blocking the transport of bivalent cations. On the other hand, explaining why a loss in

Figure 6. N 1s core level spectra of unmodified CMX and CMX−PANI membranes prepared with different polymerization times.

Figure 7. Ion-exchange capacity of unmodified (at $t = 0$) and CMX−PANI composite membranes as a function of polymerization time. Time of immersion in 10% (v/v) aniline/1 M HCl solution was 1 h.

blocking efficiency is observed over 1 h of polymerization is not as obvious. Interestingly, an optimal polymerization time of 1 h was also obtained when a CM-1−PANI membrane was used for the separation of Ca^{2+} from Na^+ by electrodialysis in a neutral solution.[6] The blocking behavior of the PANI layer was thought to be due to the positively charged and conductive state of PANI in its emeraldine form. Electrostatic repulsions between the protonated amine/imine groups on the PANI chains and the multivalent cations would hamper the transport of multivalent cations through the membrane. It was also suggested that a polymerization time longer than 1 h leads to the formation of the insulating form of PANI, pernigraniline, which would explain the loss in permselectivity of the composite membrane.
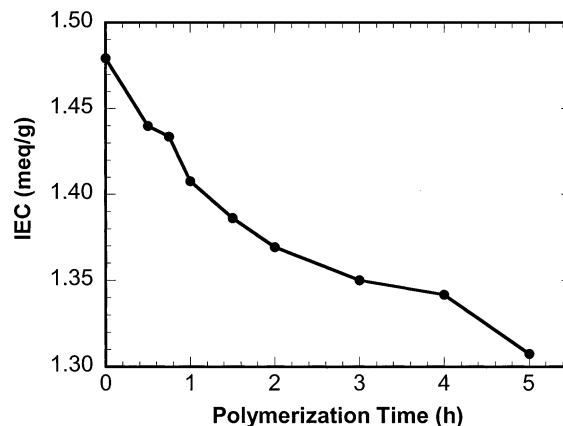
PANI is known to exist in different oxidation states going from the most reduced amine form (leucoemeraldine) to the mixed amine−imine form (emeraldine) and the quinoid form (pernigraniline):[21]
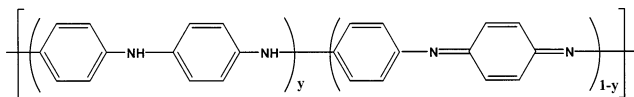
where y = 1, 0.5, and 0 for leucoemeraldine, emeraldine base, and pernigraniline, respectively. Among all these oxidation states, only the emeraldine form can be doped to form the emeraldine salt, the conducting form of PANI:[22]
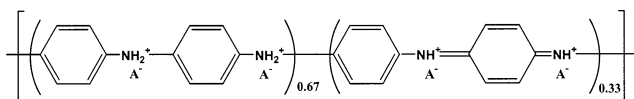
where A^- is, under our experimental conditions, either Cl^-, $(1/2)SO_4^{2-}$, or $CMX−SO_3^-$. Under our polymerization

conditions, we would expect to obtain any form or intermediates between the emeraldine base or salt and pernigraniline.[21,22]

To confirm the formation of pernigraniline, Sata et al. have evaluated the electronic conductivity and the doping level of PANI as a function of polymerization time.[6] They have demonstrated an optimal conductivity at 1 h, and over 10 h, PANI can no longer be doped with bromide indicating that the insulating form was obtained. However, the gradual loss in permselectivity of the composite membrane between 1 and 10 h of polymerization time by using a high oxidant concentration was not extensively discussed. In the present study, cyclic voltammetry, XPS, SEM, UV−visible spectroscopy, and exchange capacity measurements were performed in order to investigate the decrease in permselectivity with polymerization time and the relationship between the PANI surface layer chemical composition and the permselectivity of the modified membrane.

Very important information can be retrieved from the XPS spectra. First, when comparing the Ani-1 and P1-1 survey spectra (Figure 3), significant differences in peak intensity for N 1s are noticeable, even though the immersion time in the aniline solution is the same (1 h). It should be recalled here that XPS measurements only allow surface characterization of 5−10 nm depth. Accordingly, the increase in nitrogen content for P1-1 suggests that, upon polymerization on the membrane, anilinium ions diffuse toward the surface of the membrane where they are consumed at the membrane/oxidant solution interface in the early stages of the polymerization process. We believe that sulfonate groups fixed on the membrane inhibit the diffusion of oxidant anions, $S_2O_8^{2-}$, toward the bulk of the membrane. These phenomena favor polymerization at the surface of the membrane.

Second, the Cl 2p (Figure 4), S 2p (Figure 5), and N 1s (Figure 6) core level spectra demonstrate that, upon polymerization, the peaks associated with the bare CMX membrane, i.e., those corresponding to covalent chlorine from PVC, sulfonate groups, and high binding energy nitrogen, are progressively hidden and replaced by the peaks pertaining to PANI. A similar behavior was recently reported for the adsorption of cationic polyacrylamide onto the surface of a Nafion cation-exchange membrane.[23] Table 1 shows that the maximum nitrogen concentration and the lowest chlorine (from PVC) and sulfur (sulfonate)

(21) (a) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317. (b) Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998**, *23*, 1443.
(22) Hatchett, D. W.; Josowicz, M.; Janata, J. *J. Phys. Chem. B* **1999**, *103*, 10992.

(23) Kim, Y.-H.; Oblas, D.; Angelopoulos, A. P.; Fossey, S. A.; Matienzo, L. J. *Macromolecules* **2001**, *34*, 7489.
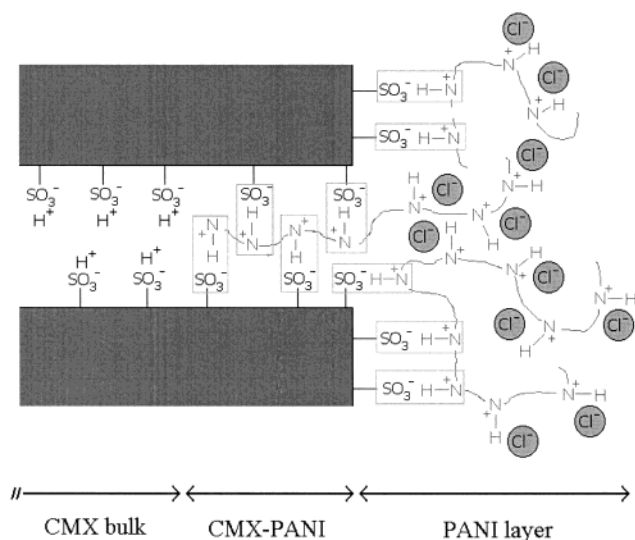
Figure 8. Idealized schematic representing the three different layers found on a CMX−PANI composite membrane. This is a representation for the membrane showing the best permselectivity for our experimental conditions.

Figure 9. (a) UV−vis spectra of 1 M $(NH_4)_2S_2O_8$ solution taken in the reagent compartment after various polymerization times. Time of immersion in 10% (v/v) aniline/1 M HCl solution was 1 h. (b) Corresponding absorbance recorded at 244 nm as a function of polymerization time.

concentration are reached after 1 h of polymerization. The presence of PANI yielding to an improved permselectivity of the CMX membrane could also be demonstrated by cyclic voltammetry. Indeed, the Coulombic charge, associated with the PANI doping process, rises with increasing polymerization time to reach a maximum at 1 h (Figure 2). The latter observation can be associated with the growth of the electroactive PANI layer. Interestingly, the optimal polymerization time for electrochemical activity is obtained at 1 h and matches the polymerization time at which optimal permselectivity is achieved in electrodialysis.

Using the above data and knowing that the PANI chains are found both on and within the surface of the membrane,[6,7] a three-layer model is proposed for the CMX−PANI composite membrane. As illustrated in Figure 8, the outer surface would be composed of a PANI layer for which the positive charges are compensated by chloride anions introduced after conditioning in an aqueous HCl solution. The intermediate layer would be constituted of positively charged PANI chains interacting with the fixed sulfonate groups found on the CMX membrane. The last layer would be the bulk of the unmodified CMX membrane.

The interactions between the positively charged PANI chains and the sulfonate groups found in the intermediate layer were actually demonstrated by the S 2p core level spectra. Figure 5 shows that the S 2p peak is displaced toward lower binding energy after 1 h of polymerization (168.3 and 169.6 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively) in comparison to the bare CMX (168.9 and 170.1 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively) (Supporting Information, Figure 2S and Table 2S). Interactions between the positively charged imine/amine groups from PANI and the sulfonate groups could explain this displacement. In fact, neutral sulfonate groups (SO_3H) have a lower electron density, and consequently a higher binding energy, than the SO_3^- interacting with $=NH^+-$ and/or $-NH_2^+-$ groups.[19,20]

When the polymerization time is extended over 1 h, a drop in CMX−PANI permselectivity (Figure 1) and electroactivity (Figure 2) occurs. Possible explanations for these data could be either the overoxidation of PANI
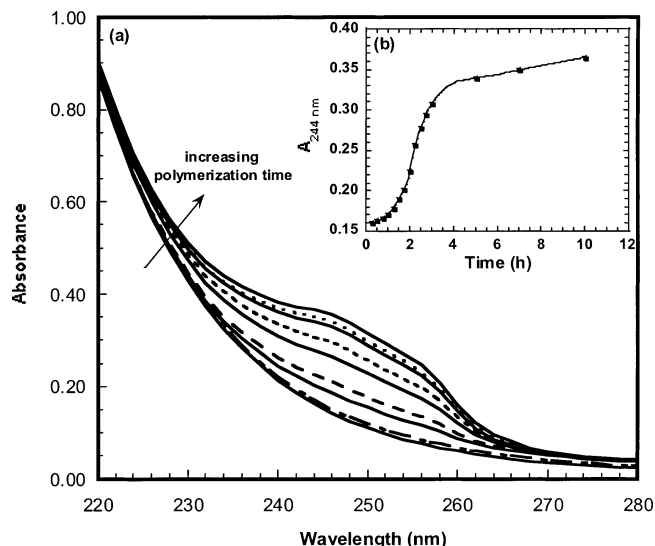
into its nonconductive form, pernigraniline, as suggested by Sata et al.,[6] or the loss in PANI content due to its degradation. It has been reported in the literature that PANI can be degraded into benzoquinone after hydrolysis of the imine groups: [9−12]
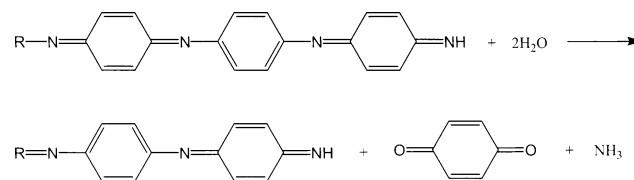
The same authors have confirmed the presence of BQ by UV−vis spectroscopy and CV. Thus, the same techniques were used in this study to detect BQ. The cyclic voltammograms represented in Figure 2a show the presence of peaks at 0.6 and 0.45 V attributed to the BQ/HQ redox couple. However, it should be pointed out that the enhancement of these peaks should not be directly interpreted as an increase in PANI degradation product concentration with polymerization time since the characterization method used here involves the electrochemical oxidation and the degradation of PANI taking place as the measurements are recorded.

For this reason, the kinetics of BQ formation was monitored by UV−visible spectroscopy. UV−vis spectra of the oxidant solution used in the polymerization step were recorded at various reaction times. Figure 9a reveals the appearance of a band located at 244 nm which can be attributed to BQ.[10,24] The BQ formation seems to start between 1 and 2 h of polymerization since the absorbance at 244 nm increases significantly (see Figure 9b). Afterward, the absorbance nearly stabilizes at around 4 h. These CV and UV data demonstrate the presence of BQ, the degradation product of PANI, but do not explain how and where the degradation occurs. Moreover, the CV results are not in total agreement with those obtained by ED (Figure 1), since the PANI layer still possesses a blocking behavior toward bivalent cations at polymeri-

(24) Chung, Y. H.; Park, S.-M. *J. Appl. Electrochem.* **2000**, *30*, 685.

zation times over 1 h while no more electrochemical activity is found by CV. It should be noted that the electrode preparation technique used for the CV experiments only allows the detection of the fraction of PANI in direct and close contact with the stainless steel grid, as it is believed that, at long polymerization times, the PANI chains no longer form a continuous network at the surface of the membrane.

The XPS study allows a better understanding of the phenomenon occurring above 1 h of polymerization. Beyond this oxidation time, the Cl 2p (Figure 4), S 2p (Figure 5), and N 1s (Figure 6) spectra exhibit a gradual return to the spectra corresponding to the unmodified membrane (see also Table 1). Subsequently, the decrease in electrochemical activity as well as the permselectivity properties seem to be explained by the progressive loss of the PANI layer due to its degradation into BQ. These data are confirmed by SEM (Supporting Information, Figure 3S). The photomicrograph of the P1-1 membrane shows a rough surface previously ascribed to the presence of PANI, whereas the P1-10 membrane shows a smoother surface which is almost identical to the micrograph taken for the bare CMX surface.[7]

Apparently, XPS and SEM data suggest that the outermost PANI layer illustrated in Figure 8 would be almost completely degraded. The fact that some nitrogen is still detected (Table 1) and that the Cl 2p (Figure 4), S 2p (Figure 5), and N 1s (Figure 6) spectra of the CMX membrane are not totally recovered after 10 h of polymerization indicates that a very thin or nonuniform PANI layer remains present. The PANI left on or within the membrane might contribute to partially block the bivalent cation transport since the metal leakage for P1-10 is not as high as for the bare CMX. Also, the removal of most of the first PANI layer (Figure 8) might also justify the lowering of the Cl⁻/N ratio observed in Table 1. As more and more PANI is removed from the surface of the membrane, a higher proportion of the remaining charged amine/imine groups detected by XPS are compensated by sulfonate groups. Conversely, the progressive shift of the S 2p peaks toward higher binding energies (Figure 5) with increasing polymerization time seems to imply that sulfonate groups are less and less involved in interactions with cationic PANI chains. These apparent contradictions can be reconciled by considering that the polymerization of PANI extends within the membrane, leaving free sulfonated groups at the surface (not compensated by PANI).

The ongoing PANI degradation explains the increase in resistivity found by cyclic voltammetry. The degradation of the conductive polymer would lead to loss in electronic contact between the PANI adsorbed on the composite membrane surface and the stainless steel grid used as a current collector. The variation in surface electronic conductivity noted by Sata would also be explained by this gradual degradation of PANI.[6] Nevertheless, our results do not seem to indicate whether there is progression in oxidation states prior to degradation. Given that the components of the PANI N 1s peaks associated with its different oxidation states have been well identified,[13−15] a more detailed interpretation of the N 1s spectra might eventually allow us to characterize the oxidation states obtained on the membrane as a function of the polymerization time. Due to the presence of nitrogen on the unmodified CMX membrane and for which the exact nature is not identified, the deconvolution was not attempted. A complete study of the N 1s spectra will instead be performed on a Nafion 117 membrane, which

does not contain nitrogen in its unmodified form.[25] The N 1s peak displacement toward higher binding energy (Figure 6) can solely be attributed to the presence of a more important contribution of the nitrogen originating from the bare CMX.

The CV, XPS, and SEM results characterize solely the PANI found on the surface of the membrane. Although important degradation occurs at the surface, the modified membranes still show a dark coloration at long polymerization times, suggesting the presence of a significant amount of PANI. To determine whether the degradation observed at the surface can be extended to the PANI located inside the membrane, ion-exchange capacity measurements were performed. Upon degradation, less PANI should be found in the membrane and it should normally lead to a rise in exchange capacity after a polymerization time longer than 1 h, in the same manner as the rise in metal leakage observed in Figure 1. However, Figure 7, illustrating the IEC of the composite membrane at various polymerization times, demonstrates a decrease in IEC even after 1 h. The data could be explained by the presence of more and more positively charged PANI oligomers inside the membrane as polymerization time increases. The oligomers could be produced during polymerization either after a sufficient time is reached to allow the penetration of $S_2O_8^{2-}$ through the first formed PANI layer, or following the degradation of PANI chains. These oligomers would lower the exchange capacity since they might be trapped within the CMX membrane or diffuse out very slowly. For instance, it was observed that, after more than 36 h of membrane immersion, a pink or light purple solution is recuperated for P1-5 and P1-10 membranes, indicating the release of oligomers in solution. Another possible explanation would be based on the consideration that continuous polymerization takes place with time, leading to PANI fibers extending into the CMX bulk. Actually, this phenomenon was proposed previously to explain the evolution of the S 2p spectra with polymerization time. Considering the polymerization model presented earlier (Figure 8), the thin surface layer is degraded into BQ as the oxidation time is increased. In the meantime, longer fibers are formed inside the CMX which would result in decreasing the IEC values. The formation of oligomers and/or PANI fibers toward the bulk of the membrane cannot be detected by CV or XPS since they are located too far from the surface. Only the ends of the chains of these oligomers and/or fibers located near the surface would be detected. Moreover, these oligomers and/or fibers do not provide an efficient blocking barrier for bivalent cations, as demonstrated by the ED results (Figure 1), despite the fact that IEC values seem to indicate their presence in large quantity. Thus, having a sufficiently uniform and thick PANI layer at the CMX surface seems to be necessary to achieve good permselectivity properties.

Conclusion

Commercial sulfonated cation-exchange membranes were modified on a single side by chemical polymerization of aniline into polyaniline. A dramatic effect of the polymerization time was noticed. XPS and CV data confirmed the formation of an electroactive polyaniline layer at the surface of the membrane when the polymerization time was kept below 1 h. For longer polymerization times, the degradation of the polyaniline layer at the surface was demonstrated. These results enable the understanding of the variation of the CMX−PANI mem-

(25) Tan, S.; Bélanger, D. Work in progress.

branes permselectivity with polymerization time. A three-layer model for the most permselective CMX−PANI composite membrane was also proposed based on XPS and IEC data: the outer layer would be constituted of positively charged PANI doped with chloride ions, the intermediate layer of positively charged PANI compensated by the fixed sulfonate groups of the CMX, and the last layer of the CMX bulk membrane. To better control the polymerization/degradation kinetics, we are currently studying several parameters including the choice of oxidant, its concentration, and the pH of the reaction medium. Finally, our results suggest that composite membranes having most of the conducting polymer either at the surface or within the membrane can be produced. Despite that the former appears to be more useful for the specific application described in this study, the latter might eventually prove useful, as well, for other technological applications such as other separation processes.[8]

Supporting Information Available: Examples of Cl 2p and S 2p deconvoluted XPS spectra as well as SEM micrographs of the membrane surface for CMX, CMX−P1-1, and CMX−P1-10. This material is available free of charge via the Internet at http://pubs.acs.org.

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