# Chemical Polymerization of Aniline on a Poly(styrene sulfonic acid) Membrane: Controlling the Polymerization Site Using Different Oxidants

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Poly(styrene sulfonic acid) membranes (Neosepta CMX, Tokuyama Corp.) have been modified by in situ polymerization of aniline. $(NH_4)_2S_2O_8$, $FeCl_3$, $H_2O_2$, and $KIO_3$ were used as oxidizing agents, and two different modification methods (single-step versus two-step) were studied. The composite membranes were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, elemental analysis, electrodialysis, ion-exchange capacity, and conductivity measurements. Our results demonstrate that it is possible to control the polymerization site of aniline which in turn affects the membrane selectivity properties. Hence, composite membranes having a very thin and homogeneous surface polyaniline layer lead to a very low transport of $Zn^{2+}$ without increasing significantly the resistance to $H^+$ conductivity. On the other hand, membranes containing about the same quantity of PANI but inside the membrane do not block the transport of $Zn^{2+}$.

## Introduction

Conducting polymers such as polypyrrole (PPy) and polyaniline (PANI) are a class of material used for numerous applications because of their ease of preparation and stability. In fact, polyaniline and polypyrrole can be easily synthesized chemically by adding an oxidant to the monomer or electrochemically by applying an oxidative potential. Aniline and pyrrole have been polymerized on different substrates such as polymers, textile fibers, metal, silicon, and nanoparticles. Also, both polyaniline and polypyrrole have been used to prepare membrane composites used in several applications[1] including gas permeation,[2,3] pervaporation,[4] fuel cells,[5−7] and selective ion transport.[8−13]

Cation exchange membranes are used in different electrochemical techniques such as fuel cells, electrolyses, and electrodialysis. However, one challenge that still needs to be overcome is the selectivity of the membrane for specific ions or species used in these processes. For example, direct methanol fuel cells require membranes possessing good stability and proton conductivity while inhibiting methanol crossover. Pickup et al. have shown that the polymerization of pyrrole within a Nafion membrane can lower the methanol crossover in fuel cells.[6] Polyaniline has been used to selectively transport monovalent cations in the presence of bivalent cations during electrodialysis in neutral media ($Na^+$ vs $Ca^{2+}$)[11] and in acidic media ($H^+$ vs $Zn^{2+}$).[12,13]

Although Sata et al.[9] were able to obtain surface layers of PANI and PPy, to our knowledge, there were no studies comparing the permselectivity behavior of membranes with a PANI layer within the membrane versus a PANI layer at the surface of the membrane. Controlling the polymerization site of aniline within a poly(styrene sulfonic acid) membrane (Neosepta CMX) will be useful not only in understanding the permselectivity behavior in function of the PANI layer location but could also be useful for applications which require the

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**TABLE 1: Characteristics of the Membrane Given by the Manufacturer[14]**

| properties | Neosepta CMX |
|---|---|
| composition | poly(styrene-*co*-divinylbenzene) |
| supporting material | poly(vinyl chloride) |
| thickness | 170−190 $\mu$m |
| exchange capacity | 1.5−1.8 meq/g Na-form dry membrane |
| water content | 0.25−0.30 g $H_2O$/g Na-form dry membrane (equilibrated in 0.5 M NaCl) |
| electric resistance | 2.5−3.5 $\Omega cm^2$ (equilibrated in 0.5 M NaCl, at 25 °C) |

absence of conducting polymer at the surface, such as in fuel cells, to avoid short-circuiting the cell.

In this paper, we will present the results obtained in the characterization of the composite membranes prepared using different oxidants in the polymerization of aniline. The ultimate goal is to control the polymerization site and to obtain a very thin and homogeneous layer of PANI and then, to evaluate the effect of the position of the polyaniline layer within the membrane on the permselectivity of the CMX-PANI composite membrane.

## Experimental Section

*Materials.* $FeCl_3$·6 $H_2O$ (Aldrich), $KIO_3$ (EMD), HCl (EMD), $H_2O_2$ (EMD), $H_2SO_4$ (EMD), NaCl (BDH), $(NH_4)_2S_2O_8$ (BDH), and $ZnSO_4$·7 $H_2O$ (Anachemia) were of A.C.S. reagent grade and were used as received. Aniline (Acros) was distilled twice prior to use. Millipore water (18 M$\Omega$ obtained from a Sybron/Barnstead Nanopure system) was used for the preparation of all solutions. The poly(styrene sulfonic acid) cation exchange membrane used in this study was the Neosepta CMX membrane (Tokuyama Corp.); its characteristics are listed in Table 1.[14] The membrane was stored in 0.5 M NaCl prior to its use.

*Membrane Modification.* The CMX membranes were conditioned in 1 M HCl for more than 24 h prior to modification. The single-face modification was carried out at room temperature in a two-compartment cell made of Teflon containing 40 mL of reagents or water (surface modified: 9.6 $cm^2$). The

polymerization of aniline was done under stirring either in one step or in two steps (details are given below) with a reaction time of 1 h for each step unless otherwise specified. The solutions used for the modification are 1 M aniline diluted in 1 M HCl solution and 0.3 M oxidant diluted in water or in 0.01 M HCl for $FeCl_3$ solutions. The modified membranes were stored either in 1 M HCl or in 1 M $H_2SO_4$ solutions. The membrane identification is as follows: PXS-Y where P stands for polyaniline, X, the number of steps (S), and Y, the oxidant.

*Scanning Electron Microscopy (SEM).* Membranes were conditioned in 1 M HCl and were dried under vacuum overnight at room temperature in the presence of $P_2O_5$. The membranes were sputtered with gold to ensure good electronic conductivity of the samples. Surface micrographs were taken using a Hitachi model S-2300 scanning electron microscope at an angle of 60° to the surface.

*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 ($K_\alpha$ 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 $10^{-6}$ Pa. To compensate for charging effects, binding energies were corrected for covalent C1s at 284.6 eV after curve-fitting. Curve fitting and peak integration were carried out using the CasaXPS (version 2.1.25) software. After a Shirley background correction, all peaks were fitted by assuming a Gaussian−Lorentzian line shape. For the curve-fitting of the Cl2p and S2p peaks, the full width at half-maximum (fwhm) was fixed as constant and the peak area ratio was fixed at 1:2 for each pair of $Cl2p_{1/2}$−$Cl2p_{3/2}$ and $S2p_{1/2}$−$S2p_{3/2}$ peaks. The surface atomic composition was calculated using the high-resolution spectra and the appropriate relative sensitivity factors: C1s (1.00), N1s (1.80), O1s (2.93), $Cl2p_{1/2}$ (0.775), $Cl2p_{3/2}$ (1.51), $S2p_{1/2}$ (0.567), and $S2p_{3/2}$ (1.11).

*Elemental Analysis.* After being conditioned in 1 M HCl, samples were rinsed with water and dried under vacuum at room temperature for at least 36 h in the presence of $P_2O_5$. Sample analysis was performed on a Fisons Instruments SPA, model EA1108.

*Ion-Exchange Capacity (IEC).* All membranes were washed and stabilized in 1 M HCl, $H_2O$, and 1 M NaCl alternatively for 1 h in each solution during three cycles. The membranes are 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 under vacuum at room temperature for at least 36 h over $P_2O_5$ before being weighed. The $Na^+$ ions were ion-exchanged with $H^+$ by immersion in a 1 M HCl solution for 24 h. The sodium concentration in the latter solution was determined by atomic absorption spectroscopy (Varian SpectrAA 220FS).

*Water Content.* The membranes were washed, stabilized, and conditioned in 1 M NaCl as for IEC measurements. After removing excess chloride by immersion in water and rinsing with water, the membranes were blotted dry with a filter paper and were weighed immediately. Then, the membranes were dried and weighed again. The % $H_2O$ and $\lambda$, the number of moles of $H_2O$ per moles of sulfonic acid groups ($SO_3^-$), were determined according to the following equations:

$$\%H_2O = \frac{m_{\text{wetmembrane}} - m_{\text{drymembrane}}}{m_{\text{drymembrane}}} \times 100 \quad (1)$$

$$\lambda = \frac{\dfrac{m_{\text{wetmembrane}} - m_{\text{drymembrane}}}{m_{\text{drymembrane}}}/18\text{g H}_2\text{O/mol}}{\text{IEC}} \quad (2)$$

where $m$ is the mass (g) and IEC is the ion-exchange capacity (moles $SO_3^-$ per g of dry membrane).

*Electrodialysis.* Electrodialyses were performed in a two-compartment cell containing in the anodic compartment 150 mL of 1.5 g/L Zn in 0.5 M $H_2SO_4$ and in the cathodic compartment 33 mL of 0.5 M $H_2SO_4$. The modified surface, that is, the surface exposed to the oxidant, (surface area: 5.1 $cm^2$) was placed facing the anolyte unless otherwise specified. A current density of 50 mA/$cm^2$ was applied between two platinum plates for 3 h using an M273 Potentiostat/Galvanostat (EG & G Princeton Applied Research). The electrodialysis was carried under a nitrogen flow. The metal concentration in both compartments was determined by atomic absorption spectroscopy (Varian SpectrAA 220FS). From these concentrations, the % $Zn^{2+}$ leakage is calculated according to the following equation:

$$\% \text{ Zn}^{2+} \text{ leakage} = \frac{\text{mass of Zn}^{2+} \text{ in catholyte}}{\text{mass of Zn}^{2+} \text{ in catholyte and anolyte}} \times 100 \quad (3)$$

*Conductivity Measurements.* Measurements were carried out at room temperature ($23 \pm 1$) °C in 0.5 M $H_2SO_4$ using a two-compartment cell containing 150 mL of solution each and separated by the cation-exchange membrane (effective area: 0.44 $cm^2$) with the modified surface (exposed to the oxidant) facing the anodic compartment. Membranes were conditioned in 0.5 M $H_2SO_4$ for at least 24 h prior to measurements. The electrical current was applied between two platinum electrodes using the galvanodynamic mode at 1 $\mu$A/s, and the open-circuit voltage was measured between two Ag/AgCl (3 M KCl) reference electrodes placed on each side of the membrane at 4 mm from its surface. The instrument used to apply the current and to measure the open-circuit voltage was a Solartron 1470 battery test unit. The conductivity values were calculated from the slope of the current−voltage curves and from using a membrane thickness of 170 $\mu$m. The solution conductivity was measured using the same setup, and its value was subtracted from the conductivity values reported here.

## Results

*Chemical Polymerization of Aniline.* The chemical polymerization of aniline is performed in a two-compartment cell allowing partial modification of the membranes. Two different approaches were used to modify the membranes: the one-step and two-step methods, described in Figure 1. In the one-step method, the anilinium (or positively charged aniline) solution is added in one compartment and the oxidant in the second compartment allowing both reagents to diffuse through the membrane from its two faces. In the two-step method, the anilinium solution is first added in one compartment and water in the second compartment. Then, the aniline solution is replaced by the oxidant solution after rinsing the compartment with water. This two-step modification is intended to favor the modification on only one side of the membrane.

After modification, a green-blue layer appears on the membrane which indicates the presence of polyaniline. After dipping the membrane into an acidic solution (HCl or $H_2SO_4$) for several hours, the PANI layer is in its emeraldine salt form,

Chemical Polymerization of Aniline

*J. Phys. Chem. B, Vol. 109, No. 29, 2005* **14087**
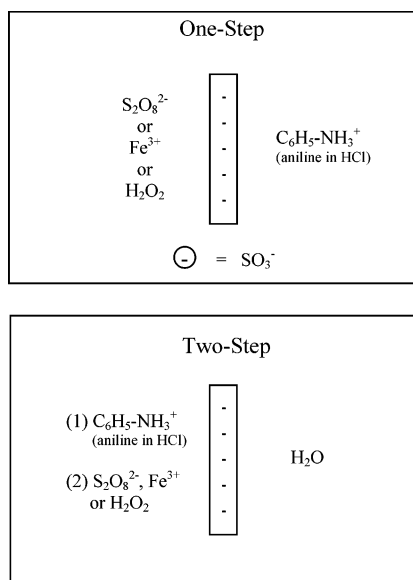


Figure 1. Membrane modification methods using a two-compartment Teflon cell: one-step versus two-step procedures.



Figure 2. Scanning electron microscopy (SEM) micrographs of the bare and modified CMX membranes. The surface shown is the side that was exposed to the oxidant during the modification procedures. The bar scale represents 5 $\mu$m.

the doped and conductive form of polyaniline.[15] The appearance of the green-blue layer was observed for all the membranes prepared using $(NH_4)_2S_2O_8$ and $FeCl_3$ as oxidants. When using $H_2O_2$, a brownish layer, a little darker than the bare CMX membrane, was obtained. This suggests that either polymerization did not take place or that degradation of the polyaniline occurred as soon as it was formed leaving only aniline oligomers or degradation products within the membrane. Indeed, during the formation of PANI, there is a competition between the polymerization reaction and the degradation of PANI.[13,16]

*Surface Characterization by SEM and XPS.* Since an objective of this work is to demonstrate the possibility of polymerizing aniline either on the surface, within, or both at the surface and within the membrane, both surface and bulk techniques are needed to characterize the modified membranes. We have previously demonstrated that the presence of PANI at the surface of the CMX membrane can be detected using SEM.[12] Figure 2 illustrates the SEM images of the bare and modified membranes using both the one-step and two-step methods. The bare membrane (Figure 2a) shows a rather smooth surface when compared to the membrane modified using $(NH_4)_2S_2O_8$ (Figure 2b). The latter has a coating layer with a rougher surface which can be associated to the presence of PANI. In the case of the membranes prepared using $FeCl_3$ (Figure 2c) and $H_2O_2$ (Figure 2d), no coating appears at the surface, although the morphology of the former membrane was slightly different from the bare membrane. The exact reason for this phenomenon is unclear at the moment, but it could be explained by the presence of polyaniline or aniline oligomers inside the membrane which can affect the surface morphology of the membrane. With the two-step modification method, the use of $(NH_4)_2S_2O_8$ (Figure 2e) and $FeCl_3$ (Figure 2f) both result in a PANI coating, and no change in morphology was observed with $H_2O_2$ treatment (Figure 2g).

The presence of PANI can also be detected by monitoring the chemical composition of the membrane surface by X-ray photoelectron spectroscopy (XPS). According to previous studies,[17-20] the N1s core level spectra of polyaniline can be defined by at least three peaks centered at 398.2 eV, 399.4 eV, and >400 eV attributed to quinoid imine ($-N=$), benzenoid amine ($-N-$), and positively charged nitrogen ($N^+$), respectively. For the CMX membrane, Figure 3 shows that the
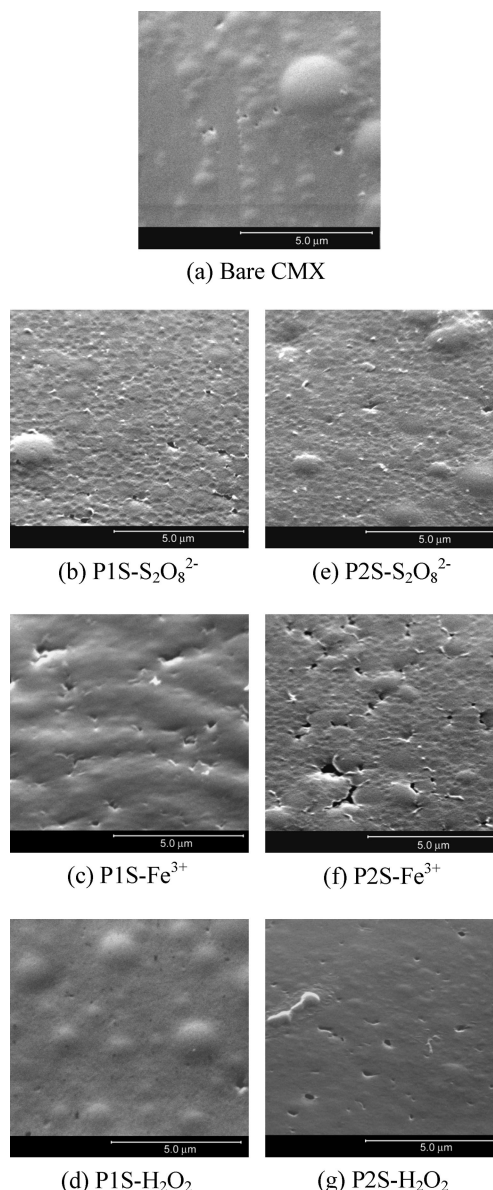
unmodified membrane exhibits a broad peak which can be fitted with at least two nitrogen peaks at 400.1 and 401.7 eV (Supporting Information, Figure S1). These peaks may be attributed to nitrogen compounds used in the fabrication of the commercial CMX membranes and for which their exact composition is unknown.[21] The comparison of the N1s spectra of the unmodified CMX and the $P1S-S_2O_8^{2-}$ membranes denotes the presence of additional components, evidenced by a broader peak envelope, which could imply the presence of PANI at the surface of the membrane. Although there are distinguishable peaks between the nitrogen arising from the commercial membrane and the nitrogen arising from PANI, the curve fitting of the N1s spectrum can only be taken as indicative since the amount of CMX nitrogen compounds decreases not only because of the coverage of these species as more PANI is coating the surface but also because of the oxidant (see below). For this reason, it is difficult to include the CMX nitrogen peaks in the curve fitting, and this does not allow us to calculate with very good precision the atomic % N ascribed only to PANI.
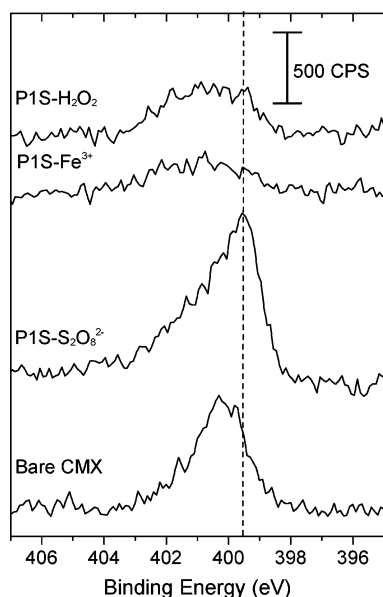
**Figure 3.** N1s core level spectra of the bare and modified CMX membranes using the one-step method. The surface shown is the side that was exposed to the oxidant during the modification procedures.

Nonetheless, the P1S$-$S$_2$O$_8^{2-}$ N1s spectra was fitted with three peaks at around 399.7 eV attributed to neutral amine groups and at 401.4 and 403.5 eV attributed to cationic nitrogen groups found in the polyaniline chains (Supporting Information, Figure S1). The unprotonated imine component of PANI (at 398.2 eV) is not present, only the protonated form of the imine groups is found at the membrane surface because these imine groups ($-$NH$^+$=, p$K_a$ = 5.5) are more easily protonated than the amine groups ($-$NH$_2^+-$, p$K_a$ = 2.5) and the membranes were conditioned in 1 M HCl.[20,22] Consequently, it is plausible to assume that all membranes with a N1s spectra which can be fitted into three components at 399.7, 401.4, and above 403 eV have a PANI layer at their surface. Hence, in addition to P1S$-$S$_2$O$_8^{2-}$, PANI characteristic peaks were also found on P2S$-$S$_2$O$_8^{2-}$ and P2S$-$Fe$^{3+}$ (Figure S1), which is consistent with the results obtained by SEM. The P1S$-$H$_2$O$_2$ N1s spectrum (Figure 3) was similar to the P1S$-$Fe$^{3+}$ (Figure 3) and the P2S$-$H$_2$O$_2$ spectra (Figure S1) showing no PANI peaks and a lower amount of nitrogen than the CMX membrane. These CMX nitrogen compounds seem to be partially lost after the membranes have been treated with an oxidant, and this change in nitrogen content is observed on the P1S$-$Fe$^{3+}$ and P1S$-$H$_2$O$_2$ N1s spectra. The degradation in nitrogen was also observed by XPS with membranes solely treated with the oxidants (Supporting Information, Table S1).

In an attempt to estimate the relative amount of PANI found at the surface of the membranes, the total atomic % N can be used. According to Table 2, the % N increases in the following order: P1S$-$S$_2$O$_8^{2-}$ ≤ P2S$-$Fe$^{3+}$ < P2S$-$S$_2$O$_8^{2-}$. Even if the % N are only estimated values, they are sufficiently reliable for the purpose of our study.

The fitted S2p core level spectra for the membranes studied are presented in Figure 4. The unmodified CMX membrane shows the presence of a doublet at 168.2 eV (S2p$_{3/2}$) and at 169.4 eV (S2p$_{1/2}$) attributed to the sulfonic acid ($-$SO$_3^-$H$^+$) groups on the poly(styrene sulfonic acid) backbone.[23] In the presence of PANI at the surface of the membrane, as for the N1s (CMX), the S2p peak signal decreases as the PANI layer gets thicker since XPS only probes the first 5$-$10 nm of the sample surface.[13] Moreover, two additional peaks are observed

**TABLE 2: XPS Analysis of the Surface of the Unmodified and Modified CMX Membranes**

| | % N[a] | % S | N$^+$/N$_{total}$ | S$_{PANI+}$/S$_{total}$ | Cl$^-$/N$^+$ |
|---|---|---|---|---|---|
| bare CMX | 3.4 | 5.0 | | | |
| P1S$-$S$_2$O$_8^{2-}$ | 4.6 | 3.9 | 0.35 | 0.49 | 0.22 |
| P1S$-$Fe$^{3+}$ | 1.7 | 4.9 | | | |
| P1S$-$H$_2$O$_2$ | 1.9 | 5.1 | | | |
| P2S$-$S$_2$O$_8^{2-}$ | 5.4 | 3.5 | 0.23 | 0.57 | 0.13 |
| P2S$-$Fe$^{3+}$ | 4.8 | 3.5 | 0.31 | 0.62 | 0.05 |
| P2S$-$H$_2$O$_2$ | 1.3 | 5.1 | | | |

[a] The CMX nitrogen contribution was not subtracted from the nitrogen values used in the data reported in this table.
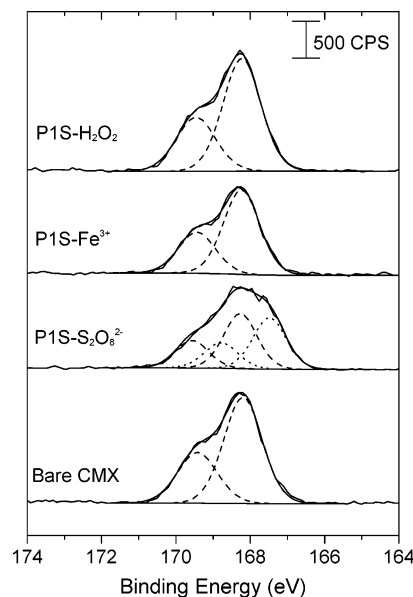


**Figure 4.** Deconvoluted S2p core level spectra of the bare and modified CMX membranes using the one-step method where (...) represents the SO$_3^-$ groups interacting with PANI$^+$ and (---) represents the SO$_3^-$ with an H$^+$ counterion. The surface shown is the side that was exposed to the oxidant during the modification procedures.

at lower binding energies, that is, at 167.4 and 168.7 eV for the S2p$_{3/2}$ and S2p$_{1/2}$ components, respectively. These peaks can be ascribed to the $-$SO$_3^-$ groups compensated by the charged imine or amine groups. The presence of a positively charged nitrogen atom of PANI near the sulfonate groups appears to lead to an increase in electron density of the sulfur atom and consequently to a decrease in binding energy.[13,19,23] Wei et al. have also observed the presence of a low binding energy doublet with self-doped sulfonated PANI where the sulfonate groups attached to the PANI backbone can be compensated by the positively charged imines or amines.[19] The P2S$-$S$_2$O$_8^{2-}$ and P2S$-$Fe$^{3+}$ (Supporting Information, Figure S2) S2p spectra also show the presence of the two S2p doublets as for the P1S$-$S$_2$O$_8^{2-}$ (Figure 4). On the other hand, the P2S$-$H$_2$O$_2$ (Figure S2) spectra is similar to the P1S$-$H$_2$O$_2$ and P1S$-$Fe$^{3+}$ spectra (Figure 4), that is, displaying a single doublet indicating the absence of PANI. The data obtained with the S2p spectra are consistent with the N1s spectra and the SEM images.

From the S2p spectra displaying two doublets, the proportion of the negatively charged sulfonate groups interacting with the positively charged PANI was calculated using the peak area ratio, S$_{PANI+}$/S$_{total}$. For the membranes covered with a PANI layer, these ratios were 0.49, 0.57, and 0.62 for the P1S$-$S$_2$O$_8^{2-}$, P2S$-$S$_2$O$_8^{2-}$, and P2S$-$Fe$^{3+}$ samples, respectively. These values can be correlated to the amount of PANI found at the surface of the membranes if we assume that the amount of PANI

Chemical Polymerization of Aniline

*J. Phys. Chem. B, Vol. 109, No. 29, 2005* **14089**

**TABLE 3: Elemental Analysis and Physical Properties of the Bulk Membranes**

| | elemental analysis[a] | | IEC (mmol/g) | $H_2O$ (wt %) | $\lambda$ (mol$_{H_2O}$/mol$_{SO_3^-}$) | $Zn^{2+}$ leakage (%) | $R$ ($\Omega cm^2$) | $\sigma$ (mS/cm) |
|---|---|---|---|---|---|---|---|---|
| | wt % N | wt % S | | | | | | |
| bare CMX | $0.61 \pm 0.07$ | $5.1 \pm 0.6$ | 1.61 | 29.0 | 10 | 7.9 | 0.226 | 75 |
| P1S$-$S$_2$O$_8{}^{2-}$ | $0.72 \pm 0.04$ | $5.1 \pm 0.1$ | 1.60 | 28.4 | 9.9 | 0.1 | 0.370 | 46 |
| P1S$-$Fe$^{3+}$ | $0.77 \pm 0.02$ | $5.0 \pm 0.1$ | 1.59 | 27.8 | 9.7 | 7.4 | 0.246 | 69 |
| P1S$-$H$_2$O$_2$ | $0.78 \pm 0.04$ | $5.1 \pm 0.1$ | 1.62 | 28.8 | 9.9 | 7.5 | | |
| P2S$-$S$_2$O$_8{}^{2-}$ | $0.76 \pm 0.03$ | $5.0 \pm 0.2$ | 1.57 | 27.8 | 9.8 | <0.1 | 0.359 | 47 |
| P2S$-$Fe$^{3+}$ | $0.87 \pm 0.04$ | $4.8 \pm 0.4$ | 1.53 | 27.5 | 10.0 | 0.1 | 0.447 | 38 |
| P2S$-$H$_2$O$_2$ | $0.76 \pm 0.06$ | $5.1 \pm 0.4$ | 1.63 | 28.7 | 9.8 | 7.8 | | |

[a] The values given are an average of five replicas.

compensated by the sulfonate groups is proportional to the total amount of PANI covering the surface of the membrane. Moreover, Table 2 shows that the $S_{PANI+}/S_{total}$ ratio is inversely related to the $Cl^-/N^+$ ratio, as expected when PANI$^+$ is primarily charge-compensated by the sulfonate groups of the membrane instead of by chloride anions from the solution. The XPS data confirm the presence of PANI chains (compensated by $Cl^-$) spread over the surface of the CMX matrix and partially interpenetrated within the surface of the CMX membrane for which the positively charged groups are compensated by the $SO_3^-$ groups. This is in agreement with the three-layer model previously reported which describes the interface between the PANI chains and the CMX membrane.[13]

*Bulk Membrane Characterization.* Determining the quantity of PANI found within the membrane is not straightforward since PANI is not very soluble. PANI is known to be partly soluble only in concentrated sulfuric acid and in a few polar solvents such as NMP, DMF, THF, DMSO, chloroform, and methanol.[24] However, partial solubilization of polyaniline is not sufficient to quantify the amount of PANI found within the membrane, and most of these solvents will also dissolve the whole membrane. We have also tried to determine the amount of PANI by weight difference, but the amount of PANI adsorbed within the membrane is so small that the weight differences are smaller than the experimental error. In fact, Sata et al. have determined the weight of PANI polymerized within a Neosepta membrane to be around 2% when using 1 M ammonium peroxodisulfate as the oxidant and modifying not only one side but the entire membrane.[11] The weight of PANI polymerized under the experimental conditions used in this study is expected to be below 2% since milder conditions were used and the membranes were only partially modified. An alternative way to determine the relative amount of PANI within the membrane is by elemental analysis. The weight % nitrogen (wt % N) given in Table 3 indicates that all modified membranes contained a small quantity of nitrogen originating either from PANI, its oligomers, or aniline. From the wt % N obtained by elemental analysis, it is possible to estimate the weight change due to the polyaniline adsorbed to the membrane. Hence, a 0.15% N is equivalent to approximately 1% in weight of PANI. This value is consistent with the value obtained by Sata et al. given above, knowing that there is less PANI in our membranes.[11] In addition, although it was shown by XPS that the amount of nitrogen originating from the CMX membrane decreases after contact with the oxidant, the total wt % N does not seem to vary after this same treatment (Supporting Information, Table S1). This suggests that only the surface nitrogen is partially degraded by the oxidant and thus allows the comparison of the wt % N values between the different samples.

Elemental analysis of sulfur was also used to ensure that no degradation of the sulfonic acid groups occurred during the oxidation. Strong oxidants can actually attack the hydrogen at the α-carbon of the poly(styrene sulfonic acid) chain, cleaving

an aromatic ring with its sulfonic acid group.[25] Our results (Table 3 and Table S1) do not indicate any degradation of the sulfonic acid groups in the CMX membrane.

Another possible technique used to determine the relative quantity of polyaniline found within the membrane is to measure the ion-exchange capacity (IEC) of the membrane with Na$^+$. The exchange of Na$^+$ with the $SO_3^-$ groups was used instead of H$^+$, the counterion commonly used for IEC measurements, to avoid the error generated from the protonation of imine and amine groups found on the polyaniline chains. The IEC found for the CMX membrane is 1.61 meq/g which is in accordance with the value given by the manufacturer (Table 1). This value is expected to decrease with the increase in the number of PANI chains interacting with the $SO_3^-$ groups of the CMX membrane. The positively charged imine and amine groups entrapped within the membrane and acting as a counterion to the $SO_3^-$ groups cannot be exchanged as opposed to the H$^+$ for the bare membrane. Hence, only the remaining $SO_3^-$ not interacting with the PANI chains will be quantified by IEC measurements. Table 3 shows that although very little changes in IEC are observed, their values are consistent with the data obtained by elemental analysis given in Table 3. For instance, the lowest IEC value was obtained with the P2S$-$Fe$^{3+}$ membrane, which corresponds to the membrane containing the highest wt % N. The small decrease in IEC values obtained for all modified membranes indicates that very little polyaniline is present within the membrane, and this can be confirmed by the light color of the PANI layer and by the very small weight gain following PANI formation. These data can be compared to the larger decrease in IEC previously reported where more PANI was adsorbed on the membrane (with 8.8% nitrogen detected by XPS at the surface of the membrane).[13] The larger quantity of nitrogen was obtained by using the two-step method and 1 M (NH$_4$)$_2$S$_2$O$_8$ instead of 0.3 M. The PANI layer was visually much darker than the PANI layers obtained here. Table 3 also shows that no significant variation in the quantity of water absorbed is observed suggesting that no swelling or shrinking occurs after modification.

*Transport Properties of the Membranes.* To evaluate the influence of the PANI layer on the permselectivity properties of the modified membranes, electrodialysis of an acidic solution containing a relatively high concentration of zinc ions (1.5 g/mL) was performed in a two-compartment cell. The modified surface was placed facing the anodic compartment containing the zinc ions. When comparing the zinc leakage obtained with the bare CMX membrane (7.9%) to the values obtained with the modified membranes given in Table 3, it appears that the following membranes block the transport of bivalent cations: P1S$-$S$_2$O$_8{}^{2-}$ (0.1%), P2S$-$S$_2$O$_8{}^{2-}$ (<0.1%), and P2S$-$Fe$^{3+}$ (0.1%). Moreover, it seems that no correlation can be made between the blocking properties of the membranes and the total amount of PANI found within the membrane since P1S$-$Fe$^{3+}$ contains about the same amount of PANI as P1S$-$S$_2$O$_8{}^{2-}$ (Table 3) but

**14090** *J. Phys. Chem. B, Vol. 109, No. 29, 2005*

Tan et al.

**TABLE 4: Standard Reduction Potential for Various Oxidants Used in the Chemical Polymerization of Aniline**

| half-reaction | $E°$ (V/NHE) |
| --- | --- |
| $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ | 2.01 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | 1.78 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.77 |

leads to a high metal leakage (Table 3). This confirms the hypotheses proposed in a previous work.[13]

For the membranes with a PANI layer blocking the transport of $Zn^{2+}$ ions, it is important to ensure that these membranes do not lead to a significant increase in resistance during electrodialysis which would lead to a loss in ionic conductivity. Therefore, conductivity measurements were performed in 0.5 M $H_2SO_4$. Table 3 indicates that a very small decrease in ionic conductivity ($\sigma$) is observed when membranes contain a PANI layer but $\sigma$ still remains in the same order of magnitude. Although imine and amine groups from the PANI chains can conduct protons,[26] the decrease in $\sigma$ could be because these functional groups are not as good proton conductor as sulfonic acid, the latter being a strong acid. Another factor to be considered in explaining the small loss in ionic conductivity is the small decrease in the number of sulfonic acid groups transporting the protons at the interface of the CMX membrane and the PANI layer. However, the very little changes in IEC values, given in Table 3, imply that the number of free $SO_3^-$, that is, not neutralized by positively charged groups on the PANI chains, is not affected significantly over the whole membrane.

The small decrease in IEC and $\sigma$ values can be contrasted with the S2p XPS data (Table 2) suggesting that around 50−60% of the sulfonic acid groups present at the surface of the membrane are compensated by $N^+$ species. The correlation between the S2p XPS data and the IEC data suggests that there is actually only a very small amount of PANI present in the composite membranes. Indeed, it should be recalled that XPS only allows the detection of elements present at the surface of the membrane (sample depth analysis about 10 nm) whereas IEC is related to the amount of free $-SO_3^-$ of the whole membrane. If 50−60% of the sulfonate groups are interacting with positively charged groups of PANI without affecting significantly the IEC value, it implies that most of the PANI is present at the surface of the membrane and in small quantity.

**Discussion**

*Redox Potential Effect on the Polymerization of Aniline.* Different oxidants were used in order to evaluate their efficiency in the polymerization of aniline on cation-exchange membranes. Oxidants possessing various redox potential and bearing either neutral ($H_2O_2$), positively ($Fe^{3+}$), or negatively charged ions ($S_2O_8^{2-}$) were chosen. The standard reduction potential for these oxidants, given in Table 4, can be compared to the relative quantity of polyaniline found at the surface and within the membrane (Tables 2 and 3). First, XPS data indicate that the strongest oxidant, ammonium peroxodisulfate ($E° = 2.01$ V), leads to the largest quantity of nitrogen at the surface of the modified membranes using both the one-step and two-step procedures. However, when using the second strongest oxidant, $H_2O_2$ ($E° = 1.78$ V), no polyaniline was observed at the surface of the membrane with both modification methods. The nitrogen detected by elemental analysis might be explained by the presence of oligomers or unpolymerized aniline trapped inside the membrane. Indeed, Pron et al.[27] reported earlier that a very acidic media (4 M HCl) is required to polymerize aniline with $H_2O_2$. The polymerization of aniline was not studied in such a acidic media in our study since degradation of the polyaniline chains occurs rapidly upon hydrolysis in very acidic solutions.[13,28] For membranes prepared with $Fe^{3+}$, the weakest oxidant used ($E° = 0.77$ V), a PANI layer was found only for the membrane prepared in two steps and the amount of nitrogen at the surface of P2S−$Fe^{3+}$ is slightly smaller than that for the P2S−$S_2O_8^{2-}$.

Now, when comparing the bulk content of nitrogen, a different tendency is observed. For the one-step method, the amount of nitrogen detected by elemental analysis increases in the following order: P1S−$S_2O_8^{2-}$ < P1S−$Fe^{3+}$ ≅ P1S−$H_2O_2$, whereas for the membranes prepared using the two-step method, we have P2S−$S_2O_8^{2-}$ ≅ P2S−$H_2O_2$ < P2S−$Fe^{3+}$. In addition, because no polymerization was achieved with $H_2O_2$, a fourth oxidant was also studied in the modification of the CMX membranes with polyaniline: $KIO_3$ ($E° = 1.09$ V). From a thermodynamic point of view, this latter oxidant should lead to a membrane having a PANI content lying between the membranes prepared with $S_2O_8^{2-}$ and $Fe^{3+}$. Actually, after 1 h oxidation with $IO_3^-$, no polymerization occurred with both methods, and 24 h was required to obtain a uniform PANI coloration on the membrane. Therefore, from these results, we believe that there is no relationship between the yield of reaction on the CMX membrane and the redox potential. Similar conclusions were previously reported by Cao et al.[29] for the polymerization of aniline in solution.

*Positively versus Negatively Charged Oxidants.* The charge found on the oxidative ions will most likely have an important effect in the PANI formation since the CMX membranes bear negatively charged groups ($-SO_3^-$). In fact, XPS results given in Figures 3 and 4 reveal that in the case of the one-step modification method, only membranes prepared with a negatively charged oxidant, $S_2O_8^{2-}$, have a PANI coating. The negatively charged sulfonic acid groups present within the membrane inhibits the transport of negatively charged ions through the membrane by Donnan exclusion. Therefore, the positively charged anilinium species, $C_6H_5-NH_3^+$, will diffuse through the membrane and reach the surface of the membrane in the second compartment containing the oxidant and then will polymerize at the surface facing this second compartment. In the case of the membranes prepared with $Fe^{3+}$, XPS data (Figures 3 and 4) do not show the presence of PANI at their surface. Also, no PANI was detected by XPS (and SEM) on the opposite face (facing the anilinium solution). Nevertheless, the green color of the membrane and the nitrogen content determined by elemental analysis (Table 3) confirm the presence of PANI within the membrane. Actually, $Fe^{3+}$ can be transported by ion-exchange through the cation-exchange membrane toward the anilinium compartment and the anilinium ions can also be ion-exchanged through the membrane in the opposite direction. When the anilinium ions come into contact with the oxidant, polymerization occurs inside the CMX membrane (see Figure 1).

Similar results were obtained with the different oxidants when using the two-step modification method. However, a PANI layer was found at the surface of the membranes prepared with ferric ions. The main difference here is that both the aniline and oxidant solutions were placed in the same compartment with a rinsing step between the two steps. Rinsing might not be sufficient to remove all the anilinium species adsorbed at the surface of the membrane because of the electrostatic interactions between the bare membrane $-SO_3^-$ groups and the $C_6H_5-NH_3^+$ ions. Therefore, polymerization of aniline can occur both at the surface and within the bulk of the membrane and in fact elemental analysis (Table 3) shows that $Fe^{3+}$ leads to a larger

Chemical Polymerization of Aniline

*J. Phys. Chem. B, Vol. 109, No. 29, 2005* **14091**
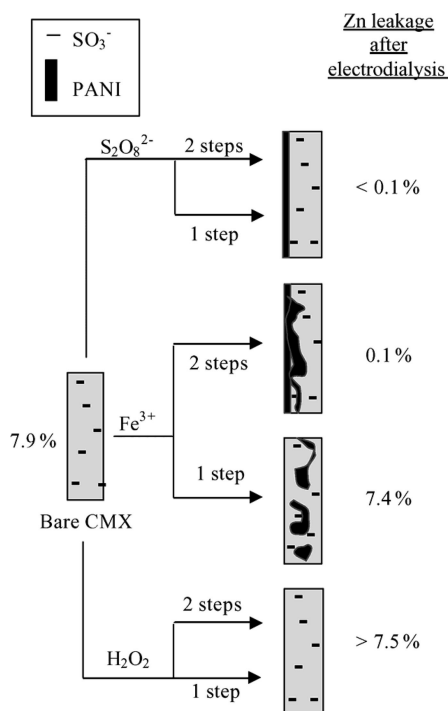


**Figure 5.** Schematic representing different polymerization sites of aniline obtained with the different oxidants studied in relation with the $Zn^{2+}$ leakage obtained after electrodialysis in 0.5 M $H_2SO_4$.



**Figure 6.** Potential drop versus time curves obtained during electrodialysis of 1500 ppm $Zn^{2+}$ in 0.5 M $H_2SO_4$ using the $P1S-S_2O_8^{2-}$ membrane with the surface exposed to the oxidant facing the anolyte (a) and facing the catholyte (b).

quantity of PANI polymerized within the membrane than for any other oxidants when using the two-step method. The reason explaining why more PANI is formed at the surface of $P2S-Fe^{3+}$ and $P2S-S_2O_8^{2-}$ relative to their one-step counterparts could be the fact that anilinium cations are readily available for polymerization to occur when the CMX is fully exchanged by these species in the two-step procedure.

With the results discussed above, it seems that the charge present on the oxidative ions plays an important role in the polymerization of aniline within a charged matrix. The polymerization site and the type of PANI layer can then be controlled by using either positively or negatively charged oxidants. In addition, the type of coating obtained will most likely have an impact on the transport properties and more specifically on the blocking behavior of the membrane toward bivalent cations.

*PANI Layer Effect on the Membrane Permselectivity Behavior.* Using SEM, XPS, elemental analysis, and IEC results, it is possible to determine where the PANI layer is found in the CMX membrane. Hence, Figure 5 shows that both $P1S-S_2O_8^{2-}$ and $P2S-S_2O_8^{2-}$ only have a thin surface layer of PANI on the basis of SEM, XPS results, and the light color of the PANI layer. On the other hand, $P1S-Fe^{3+}$ only has a PANI layer inside the membrane since SEM and XPS do not indicate the presence of PANI at the surface of the membrane. $P2S-Fe^{3+}$ seems to have a surface PANI layer extending inside the membrane since its total quantity of PANI (given by elemental analysis and IEC values in Table 3) is higher than for $P2S-S_2O_8^{2-}$ which, in turn, has a larger amount of PANI at the surface of the membrane (Table 2 and Figure S1). When comparing the electrodialysis results to the characterization results, a correlation can be established between the blocking efficiency of the membrane and the site where the PANI layer is found. Figure 5 shows that only the membranes having a PANI coating at the surface of the membrane, that is, membranes prepared using ammonium peroxodisulfate with the one-step and two-step methods and membranes prepared with ferric chloride using the two-step method, result in a good blocking
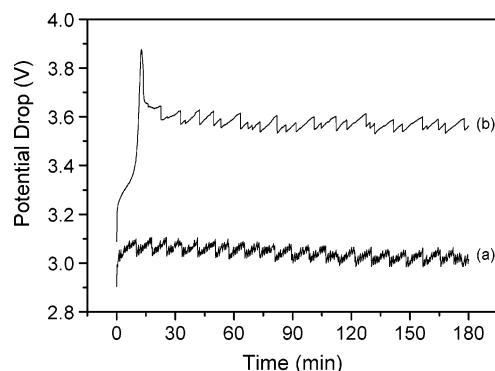
behavior toward $Zn^{2+}$ during electrodialysis in acidic media. Moreover, the membranes prepared with $KIO_3$ (24 h reaction time) (not shown) led to a $Zn^{2+}$ leakage value above 2.4% although it had a PANI coating at the surface. However, this higher metal leakage is probably explained by the fact that the PANI layer was not homogeneous and, indeed, SEM images (not shown) showed a PANI layer only in some areas of the composite membrane. Therefore, low zinc leakage can be obtained only when a homogeneous PANI layer is found at the surface. In addition, the light color of the PANI layer, the low % N obtained by element analysis, and the high IEC results obtained for the membranes let us believe that a very thin layer is sufficient to block the transport of bivalent cations.

The membrane with PANI found only within the membrane, that is, prepared with $FeCl_3$ using the one-step method, does not block efficiently the transport of bivalent cations. The reason might be related to the homogeneity of the PANI layer polymerized inside the membrane. Since polyaniline is polymerized within a rigid polymer matrix, the PANI chains formed might be shorter with a lower molecular weight than when it is polymerized at the surface of the membrane.

To get more information on the blocking mechanism of the CMX-PANI composite membranes, electrodialyses were carried out for the $P1S-S_2O_8^{2-}$ and $P1S-Fe^{3+}$ membranes with the surface exposed to the oxidant facing the catholyte. For the $P1S-Fe^{3+}$ membrane, no change in $Zn^{2+}$ leakage (7.6% vs 7.4%) was observed when placing the membrane on the reverse side, which confirms that the PANI is located solely inside the CMX matrix. In the case of the $P1S-S_2O_8^{2-}$ membrane, a higher $Zn^{2+}$ leakage (5.3% vs 0.1%) was obtained when placing the PANI layer facing the catholyte. The variation of potential during electrodialysis (Figure 6) was also different. Figure 6b shows that during the first 15 min of electrodialysis a rise in potential occurs indicating the increase in membrane resistance and then the potential drops sharply to reach a stable value. When reaching the interface near the PANI layer, the transport of $Zn^{2+}$ is stopped by the presence of positively charged groups. Following this, zinc ions are accumulated within the membrane, leading to an increase in membrane ionic resistance. The sharp drop in ionic resistance suggests a release of the accumulated $Zn^{2+}$ ions leading to the higher metal leakage obtained. Indeed, the total amount of PANI is small, which implies the presence of a small number of positively charged groups. These groups are either compensated by anions in solution or compensated by $SO_3^-$ groups from the CMX membrane when closer to the surface of the CMX membranes. In fact, as mentioned earlier, XPS shows that around 50% of these groups are neutralized by

the $SO_3^-$ groups of the membrane. Hence, when the $Zn^{2+}$ concentration within the membrane is high enough, transport of $Zn^{2+}$ will no longer be blocked as efficiently by the positively charged groups from PANI. On the other hand, when the PANI layer is facing the anolyte, the electrostatic repulsion is more important since there are more "free" (not compensated by the sulfonate groups) positively charged imine or amine groups available to block the transport of $Zn^{2+}$. Thus, the electrodialysis results for the membranes placed on the reverse side (surface exposed to the oxidant facing the catholyte) seem to suggest that the blocking mechanism in the transport of $Zn^{2+}$ is more of an electrostatic nature than physical. In addition, if this hypothesis is true, it could also explain why the presence of the PANI layer inside the membrane does not block the transport of $Zn^{2+}$. Inside the membrane, the positively charged imine and amine groups are most likely all compensated by the $SO_3^-$ groups of the CMX membrane resulting in the absence of electrostatic repulsion and no blocking behavior toward $Zn^{2+}$.

## Conclusion

In this study, we have demonstrated that it was possible to determine whether a PANI layer was found solely at the surface, within, or both at the surface and within the membrane. The control of the polymerization site of aniline was achieved by using different oxidants of opposite charges and a single-step reaction where both the monomer and the oxidant diffuse through the membrane at the same time from each side of the membrane. Indeed, a negatively charged oxidant, $S_2O_8^{2-}$, led to a very thin but homogeneous layer at the surface of the CMX membrane, whereas a positively charged oxidant, $Fe^{3+}$, led to the formation of PANI within the CMX membrane. Moreover, it was demonstrated that to block the transport of $Zn^{2+}$ while maintaining the transport of $H^+$ through the membrane during electrodialysis, only a very thin but homogeneous layer of PANI at the surface of the CMX membrane was required. The presence of PANI solely within the membrane does not seem to block the transport of $Zn^{2+}$. Finally, the blocking action of the PANI layer seems to be more related to the presence of electrostatic repulsion than to the presence of a physical barrier.

**Supporting Information Available:** N1s and S2p core level XPS spectra for the membranes modified using the two-step method as well as a table giving the XPS and elemental analysis results obtained with the membranes treated solely with the oxidants are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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